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COMMISSION ON PHYSICAL ORGANIC CHEMISTRY*

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

(IUPAC Recommendations 1994)

Prepared for publication by

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List of General Symbols

- A** pre-exponential factor in Arrhenius equation (see *energy of activation*).
- α** order of reaction with respect to reactant A, or Brønsted coefficient (see *order of reaction*, *Brønsted relation*).
- β** order of reaction with respect to reactant B or Brønsted coefficient (see *order of reaction*, *Brønsted relation*).
- C_p** heat capacity (at constant pressure).
- e** base of natural logarithms ($e = 2.718$).
- E_a** energy of activation (see *energy of activation*).
- G** Gibbs energy.
- H** enthalpy.
- \hbar** Planck constant.
- K** Kelvin (unit of thermodynamic temperature).
- K^\ominus** equilibrium constant.
- k** rate constant (see *order of reaction*).
- k_B** Boltzmann constant.
- ln** natural logarithm.
- lg** decadic logarithm.
- λ** wavelength.
- v** frequency.
- °** (superscript) relating to thermodynamic standard state.
- p** pressure.
- R** gas constant.
- S** entropy.
- s** second (unit of time).
- Σ** summation.
- T** thermodynamic temperature.
- t** time.
- v** rate of reaction (see *rate of reaction*).
- ‡** (superscript) relating to transition state.
- ↔** See *delocalization*.
- [X]** amount concentration of X.

See also IUPAC QUANTITIES (1988).

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY**2nd Edition, 1994**

Synopsis. This glossary contains definitions and explanatory notes for terms used in the context of research and publications in physical organic chemistry. Its aim is to provide guidance on physical organic chemical terminology with a view to achieve a far-reaching consensus on the definitions of useful terms and on the abandonment of unsatisfactory ones. As a consequence of the development of physical organic chemistry, and of the increasing use of physical organic terminology in other fields of chemistry, the 1994 revision of the Glossary is much expanded in comparison to the previous edition, and it also includes terms from cognate fields. A few definitions have been refined, some others totally revised in the light of comments received from the scientific community.

INTRODUCTION TO THE 1994 REVISION**General Remarks**

The "Glossary of Terms Used In Physical Organic Chemistry" was published in provisional form in 1979 (IUPAC PHYSICAL ORGANIC GLOSSARY (1979)) and in revised form in 1983. A historical account of procedure and progress up to that stage was outlined in the provisional publication. The 1983 revision incorporated modifications agreed by the IUPAC Commission III.2 (Physical Organic Chemistry), partly in response to comments received since the provisional publication. The terms defined in the 1983 Glossary are incorporated in the IUPAC "COMPENDIUM OF CHEMICAL TERMINOLOGY" (1987) (Victor Gold Book).

The present revision was undertaken with the long-term objective of compiling a compendium of organic chemical terminology. For this reason the criteria for inclusion of terms were much expanded. The criteria for the 1983 edition were that the meaning of a term was either not given in non-scientific dictionaries or standard textbooks or differed significantly from the definition in such reference works, or that the term was associated with some ambiguity or uncertainty with respect to its meaning. The present compendium tries to be comprehensive, but without including trivial terms and without redefining IUPAC approved terms. In particular, terms from cognate fields which are used by physical organic chemists, are included. The terminology for the various spectroscopic methods of interest to organic chemists is not treated in the present document, except for some terms from NMR spectroscopy, but may be the subject of a separate study. As a matter of policy, named reactions (such as Diels-Alder) and symbolic representation of reaction mechanisms (S_N1 , etc.) have been excluded with a few exceptions. These topics have been treated in separate reports of this Commission (IUPAC REACTION MECHANISMS (1989), IUPAC TERMINOLOGY FOR TRANSFORMATIONS (1989)).

The work has been coordinated with that of other Commissions within the Division of Organic Chemistry, which deal with terminology, (e.g., IUPAC PHOTOCHEMICAL GLOSSARY (1988), and its revision (1992), Commission III.3; IUPAC TERMINOLOGY OF STEREOCHEMISTRY (1993), joint project of Commissions III.1 and III.2, and IUPAC CLASS NAMES (1993), joint project of Commissions III.1 and III.2), and with that of Commission I.5. Discrepancies in the views between the Commissions have been eliminated. Whenever there was overlap or disagreement between the 1983 glossary and one of the more recent ones, the best available definitions were incorporated in the present text with a reference to their origin. Otherwise this glossary was not expanded into areas where other Commissions or working parties are already active. It is hoped that a merged compendium will be published after approval of the various glossaries.

The aim of the Glossary is to provide guidance on physical-organic chemical terminology with a view to achieving a far-reaching consensus on the definitions of useful terms and the abandonment of unsatisfactory ones. The Commission is anxious to emphasize that it cannot (and would not wish to) impose rules or restrictions which might hinder rather than help the precise formulation of new ideas.

Generally speaking, operational definitions were preferred to definitions couched in terms of theoretical models. We have tried to avoid taking sides on issues of scientific, as distinct from semantic, disagreement.

The Commission is pleased to acknowledge the generous contributions of many scientists who helped by proposing or defining new terms, or by criticizing existing ones. The following have contributed to this revision:

I.P. Beletskaya	N.J. Leonard
T.W. Bentley	R.M. Magid
C.F. Bernasconi	P.C. Maria
E. Bunzel	R.T. Myers
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N. Kallay	

The Commission thanks Mrs. M. Wyss and Dr. S. Motallebi for their help in the preparation of the manuscript of this Glossary.

Arrangement, Abbreviations and Symbols

The arrangement is simply alphabetical, terms beginning with Greek letters following those beginning with Latin ones. Italicized words in the body of a definition, as well as those cited at the end, point to relevant cross-references. No distinction is made between singular and plural in cross-referencing. Literature references should direct the reader either to the original literature where the term was originally defined, or to pertinent references where it is used. Underlining of words means that the words should be emphasized in the particular context of the entry. The appearance of a term in quotation marks in the body of a definition indicates that no further information will be found under that heading. Capitalized names indicate references.

A cross (+) against the title of an entry implies that the Commission recommends discontinuation of the term.

In accordance with general practice Kekulé structures are normally used in this Glossary to represent the formulae of aromatic compounds. A single hexagon with a full circle inside is used in cases where delocalization is emphasized. A full circle is also used in the case of monocyclic aromatic ions, but fused aromatics are represented by Kekulé structures, because in this case each circle would imply the presence of 6π electrons in each hexagon. Thus naphthalene with two circles would appear to have 12π electrons, while it has only 10 in reality. Dashed lines indicate delocalization of positive or negative charge or of the spin of an unpaired electron. Curved singly headed arrows represent formal movement of electron pairs, while doubly headed arrows symbolize resonance.

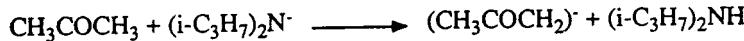
In accordance with previous IUPAC recommendations (IUPAC QUANTITIES (1988)) the symbol ‡ to indicate transition states ("double dagger") is used as a prefix to the appropriate quantities, e.g. $\Delta^{\ddagger}G$ rather than the more often used ΔG^\ddagger .

Relative positions are indicated by post-slashed Arabic numerals. For example, 1/4/dibromo-addition may refer to addition at positions 9 and 10 of anthracene, or at positions 2 and 5 of hexa-2,4-diene (IUPAC TERMINOLOGY FOR TRANSFORMATIONS (1989)).

Alphabetical Entries

abstraction

A *chemical reaction* or *transformation*, the main feature of which is the bimolecular removal of an atom (neutral or charged) from a molecular entity. For example:



(proton abstraction from acetone)



(hydrogen abstraction from methane)

See *detachment*.

acceptor number (AN)

A quantitative measure, devised by GUTMANN (1976), of *Lewis acidity*.

acid

A *molecular entity* or *chemical species* capable of donating a hydron (proton) (see *Brønsted acid*) or capable of forming a covalent bond with an electron pair (see *Lewis acid*).

See also *hard acid*.

acidity

(1) Of a compound:

For *Brønsted acids* it means the tendency of a compound to act as a *hydron* donor. It can be quantitatively expressed by the acid dissociation constant of the compound in water or some other specified medium. For *Lewis acids* it relates to the association constants of *Lewis adducts* and π *adducts*.

(2) Of a medium:

The use of the term is mainly restricted to a medium containing *Brønsted acids*, where it means the tendency of the medium to hydronate a specific reference base. It is quantitatively expressed by the appropriate *acidity function*.

acidity function

Any function that measures the thermodynamic *hydron*-donating or -accepting ability of a solvent system, or a closely related thermodynamic property, such as the tendency of the *lyate ion* of the solvent system to form *Lewis adducts*. (The term "basicity function" is not in common use in connection with basic solutions.) Acidity functions are not unique properties of the solvent system alone, but depend on the solute (or family of closely related solutes) with respect to which the thermodynamic tendency is measured.

Commonly used acidity functions refer to concentrated acidic or basic solutions. Acidity functions are usually established over a range of composition of such a system by UV/VIS spectrophotometric or NMR measurements of the degree of hydronation (protonation or Lewis adduct formation) for the members of a series of structurally similar indicator bases (or acids) of different strength: the best known of these functions is the Hammett acidity function H_0 (for uncharged indicator bases that are primary aromatic amines). For detailed information on other acidity functions, on the evaluation of acidity functions, and on the limitations of the concept, see ROCHESTER (1970), COX and YATES (1983).

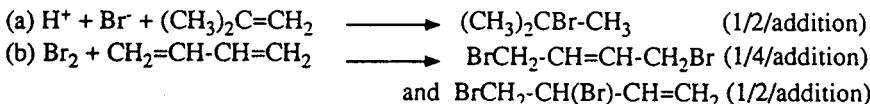
HAMMETT (1940, 1970).

activated complex

An activated complex, often characterized by the superscript \ddagger , is defined as that assembly of atoms which corresponds to an arbitrary infinitesimally small region at or near the col (saddle point) of a potential energy surface.

See also *transition state*.**activation energy**See *energy of activation*.**addend**See *addition reaction*.**addition**(1) Refers to *addition reaction* or *addition transformation*.(2) Loosely, the formation of an *adduct*. (For an example, see *Lewis acid*.)(3) Loosely, any *association* or *attachment*.**addition reaction**

A *chemical reaction* of two or more reacting *molecular entities*, resulting in a single reaction product containing all atoms of all components, with formation of two chemical bonds and a net reduction in bond multiplicity in at least one of the reactants. The reverse process is called an *elimination reaction*. The addition may occur at only one site (α -*addition*, 1/1/*addition*), at two adjacent sites (1/2/*addition*) or at two non-adjacent sites (1/3/- or 1/4/*addition*, etc.). For example



If the reagent or the source of the addends of an addition are not specified, then it is called an *addition transformation*.

See also *addition*, α -*addition*, *cheletropic reaction*, *cycloaddition*.**additivity principle**

The hypothesis that each of several structural features of a *molecular entity* makes a separate and additive contribution to a property of the substance concerned. More specifically, it is the hypothesis that each of the several *substituent* groups in a parent molecule makes a separate and additive contribution to the standard Gibbs energy change (or *Gibbs energy of activation*).

*tion) corresponding to a particular equilibrium (or *rate of reaction*). For further information and examples see BENSON (1976).*

See also *transferability*.

adduct

A new *chemical species AB*, each *molecular entity* of which is formed by direct combination of two separate molecular entities A and B in such a way that there is change in *connectivity*, but no loss, of atoms within the *moieties* A and B. Stoichiometries other than 1:1 are also possible, e.g. a bis-adduct (2:1). An "*intramolecular adduct*" can be formed when A and B are *groups* contained within the same molecular entity.

This is a general term which, whenever appropriate, should be used in preference to the less explicit term *complex*. It is also used specifically for products of an *addition reaction*. For examples see *Lewis adduct*, *Meisenheimer adduct*, π -*adduct*.

A-factor

See *energy of activation*.

agostic

The term designates structures in which a hydrogen atom is bonded to both a carbon atom and a metal atom. The term is also used to characterize the interaction between a CH bond and an unsaturated metal centre, and to describe similar bonding of a transition metal with Si-H compounds. The expression " μ -hydrido-bridged" is also used to describe the bridging hydrogen.

BROOKHART and GREEN (1983); LUO and CRABTREE (1989).

alcoholysis

See *solvolysis*.

allylic substitution reaction

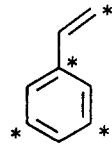
A *substitution reaction* occurring at position 1/ of an allylic system, the double bond being between positions 2/ and 3/. The incoming group may be attached to the same atom 1/ as the *leaving group*, or the incoming group becomes attached at the relative position 3/, with movement of the double bond from 2/3 to 1/2. For example:

(written as a *transformation*).

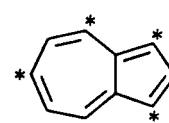
alternant

A *conjugated system* of π -electrons is termed alternant if its atoms can be divided into two sets so that no atom of one set is directly linked to any other atom of the same set.

Example of alternant π system:



Example of non-alternant π system:



(two atoms of unstarred set
are directly linked)

ambident

A description applied to a *chemical species* whose *molecular entities* each possess two alternative and strongly interacting distinguishable reactive centres, to either of which a *bond* may be made in a reaction: the centres must be connected in such a way that reaction at either site stops or greatly retards subsequent attack at the second site. The term is most commonly applied to *coryjugated nucleophiles*, for example the enolate ion



(which may react with *electrophiles* either at the β -carbon atom or at oxygen) or γ -pyridones, and also to the vicinally ambident cyanide ion, cyanate ion, thiocyanate ion, sulfinate ion, nitrite ion, and unsymmetrical hydrazines. Ambident electrophiles are exemplified by carboxylic esters RC(O)OCR_3 which react with nucleophiles either at the carbonyl carbon or the alkoxy carbon.

Molecular entities, such as dianions of dicarboxylic acids, containing two non-interacting (or feebly interacting) reactive centres, are not generally considered to be ambident and are better described as "bifunctional".

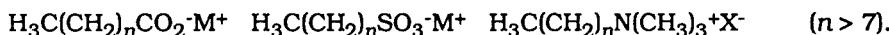
The Latin root of the word implies *two* reactive centres, but the term has in the past also incorrectly been applied to chemical species with more than two reactive centres. For such species the existing term "polydent" (or, better, "multident") is more appropriate.

GOMPPEL (1964); SMITH and DeWALL (1977).

See also *chelation*.

amphiphilic

A compound containing a large organic cation or anion which possesses a long unbranched hydrocarbon chain, e.g.



The existence of distinct polar (hydrophilic) and non polar (hydrophobic) regions in the molecule promotes the formation of *micelles* in dilute aqueous solution.

amphiprotic (solvent)

Self-ionizing solvent possessing both characteristics of *Bronsted acids* and *bases*, for example H_2O and CH_3OH , in contrast to *aprotic solvent*.

amphoteric

A *chemical species* that behaves both as an acid and as a base is called amphoteric. This property depends upon the medium in which the species is investigated: H_2SO_4 is an acid when studied in water, but becomes amphoteric in *superacids*.

anchimeric assistance

See *neighbouring group participation*.

anionotropic rearrangement (or anionotropy)

A rearrangement in which the migrating group moves with its electron pair from one atom to another.

anion radical

See *radical ion*.

annelation

Alternative, but less desirable term for *annulation*. The term is widely used in German and French language.

annulation

A *transformation* involving fusion of a new ring to a molecule via two new bonds.

Some authors use the term "annelation" for the fusion of an additional ring to an already existing one, and "annulation" for the formation of a ring from one or several acyclic precursors, but this distinction is not made generally.

DANHEISER, GERE and SARD (1982), JUNG (1976).

See also *cyclization*.

annulene

Molecule (i.e. having formally the **maximum number of noncumulative double bonds**) monocyclic hydrocarbon without side chains of the general formula C_nH_n (n is an even number) or C_nH_{n+1} (n is an odd number). Note that in systematic nomenclature an annulene with seven or more carbon atoms may be named $[n]\text{annulene}$, where n is the number of carbon atoms, e.g. [9]annulene for cyclonona-1,3,5,7-tetraene.

IUPAC CLASS NAMES (1993).

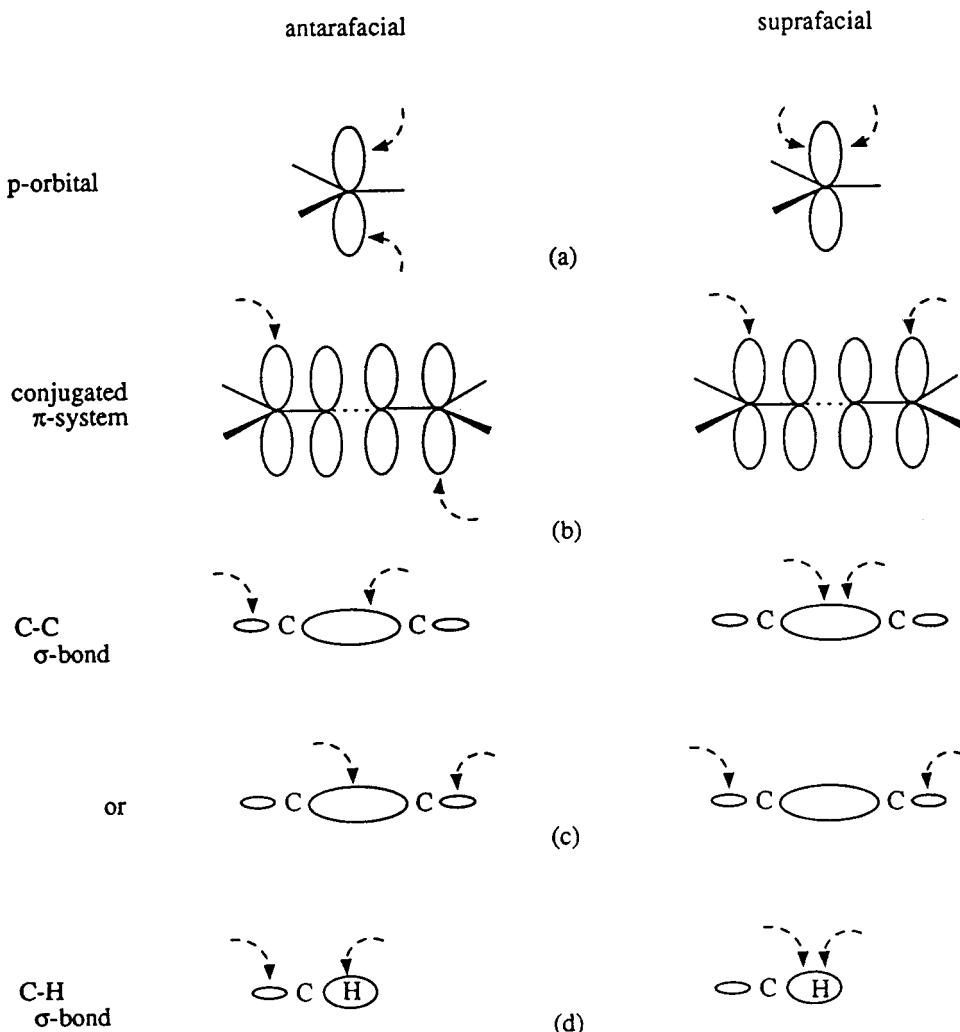
See *aromatic*, Hückel ($4n + 2$) rule.

antarafacial, suprafacial

When a part of a molecule ("molecular fragment") undergoes two changes in bonding (*bond-making* or *bond-breaking*), either to a common centre or to two related centres, external to itself, these bonding changes may be related in one of two spatially different ways. These are designated as "antarafacial" if opposite faces of the molecular fragment are involved, and "suprafacial" if both changes occur at the same face. The concept of "face" is clear from the diagrams in the cases of planar (or approximately planar) frameworks with isolated or interacting p-orbitals (Figs. a and b below).

The terms antarafacial and suprafacial are, however, also employed in cases in which the essential part of the molecular fragment undergoing changes in bonding comprises two atoms linked only by a σ -bond. In these cases it is customary to refer to the phases of the local σ -bonding orbital: occurrence of the two bonding changes at sites of like orbital phase is regarded as suprafacial, whereas that at two sites of opposite phase is antarafacial. The possibilities are shown for C-C and C-H σ -bonds in Figs. c and d. There may be two distinct and alternative stereochemical outcomes of a suprafacial process involving a σ -bond between saturated carbon atoms, i.e. either retention or inversion at both centres. The antarafacial process results in inversion at one centre and retention at the second.

For examples of the use of these terms see *cycloaddition*, *sigmatropic rearrangement*.
See also *anti*, *sigma*, *pi*.

**anti**

In the representation of *stereochemical* relationships "anti" means "on opposite sides" of a reference plane, in contrast to "syn" which means "on the same side", as in the following examples.

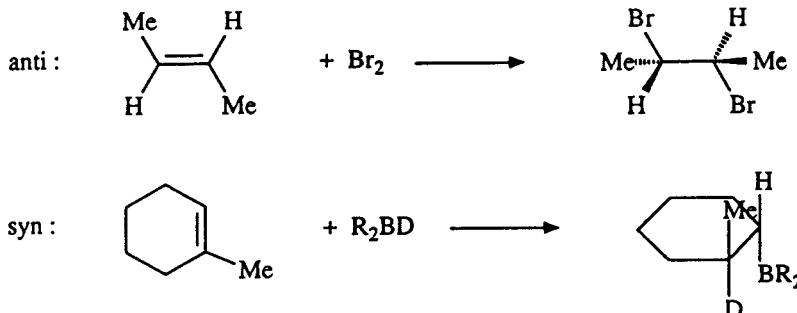
(A) Two substituents attached to atoms joined by a single bond are anti if the torsion angle (dihedral angle) between the bonds to the substituents is greater than 90° , or syn if it is less than 90° . (A further distinction is made between antiperiplanar, synperiplanar, anticlinal and synclinal.)

IUPAC ORGANIC RULES (1979); IUPAC STEREOCHEMICAL TERMINOLOGY (1993); KLYNE and PRELOG (1960).

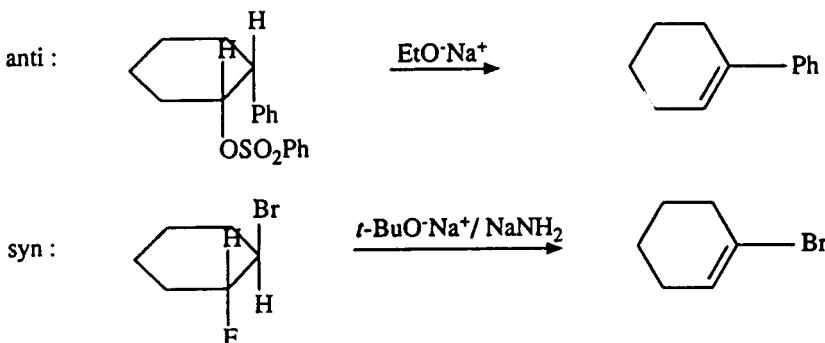
(B) In the older literature the terms anti and syn were used to designate stereoisomers of oximes and related compounds. That usage was superseded by the terms "trans" and "cis" or E and Z, respectively.

(C) When the terms are used in the context of *chemical reactions* or *transformations*, they designate the relative orientation of substituents in the substrate or product:

(1) Addition to a carbon-carbon double bond:



(2) Alkene-forming elimination:



IUPAC ORGANIC RULES (1979).

In the examples described under (1) and (2) anti processes are always *antarafacial*, and syn processes are *suprafacial*. See also IUPAC STEREOCHEMICAL TERMINOLOGY (1993) for further meaning of the term.

antiaromatic

See *aromatic*.

anti-Hammond effect

See *More O'Ferrall-Jencks diagram*.

anti-Markownikoff addition

See *Markownikoff rule*.

aprotic (solvent)

Non-*protogenic* (in a given situation). (With extremely strong Brønsted acids or bases, solvents that are normally aprotic may accept or lose a proton. For example, acetonitrile is in most instances an aprotic solvent, but it is *protophilic* in the presence of concentrated sulfuric acid and *protogenic* in the presence of potassium *tert*-butoxide. Similar considerations apply to benzene, trichloromethane, etc.)

See also *dipolar aprotic solvent*.

aquation

The incorporation of one or more integral molecules of water into another species with or without displacement of one or more other atoms or groups. For example the incorporation of water into the inner ligand sphere of an inorganic *complex* is an aquation reaction.

See also *hydration*.

aromatic, aromaticity

(1) In the traditional sense, "having a chemistry typified by benzene".

(2) A cyclically *conjugated molecular entity* with a stability (due to *delocalization*) significantly greater than that of a hypothetical localized structure (e.g. *Kekulé structure*) is said to possess aromatic character. If the structure is of higher energy (less stable) than such a hypothetical classical structure, the molecular entity is "antiaromatic".

The most widely used method for determining aromaticity is the observation of diatropicity in the ^1H NMR spectrum.

ATKINS (1974); GARRATT (1986).

See also *Hückel* ($4n + 2$) rule, *Möbius aromaticity*.

(3) The terms *aromatic* and *antiaromatic* have been extended to describe the stabilization or destabilization of *transition states* of *pericyclic reactions*. The hypothetical reference structure is here less clearly defined, and use of the term is based on application of the *Hückel* ($4n + 2$) rule and on consideration of the topology of orbital overlap in the transition state. Reactions of molecules in the *ground state* involving antiaromatic transition states proceed, if at all, much less easily than those involving aromatic transition states.

DEWAR (1971); ZIMMERMANN (1971).

Arrhenius equation

See *energy of activation*.

aryne

A hydrocarbon derived from an arene by abstraction of two hydrogen atoms from adjacent carbon atoms; thus 1,2-didehydroarene. Arynes are commonly represented with a formal triple bond. The analogous heterocyclic compounds are called heteroarynes or hetarynes.

E.g., benzyne



Arynes are usually transient species.

IUPAC CLASS NAMES (1993).

association

The assembling of separate *molecular entities* into any aggregate, especially of oppositely charged free ions into *ion pairs* or larger and not necessarily well-defined clusters of ions held together by electrostatic attraction. The term signifies the reverse of *dissociation*, but is not commonly used for the formation of definite *adducts* by *colligation* or *coordination*.

asymmetric induction

The traditional term describing the preferential formation in a *chemical reaction* of one *enantiomer* or *diastereoisomer* over the other as a result of the influence of a chiral feature in the substrate, reagent, *catalyst* or environment. The term also refers to the formation of a new chiral feature preferentially in one *configuration* under such influence.

IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

atomic orbital

A one-electron wavefunction describing an electron in the effective field provided by a nucleus and the other electrons present.

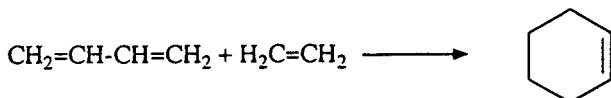
See also *molecular orbital*.

attachment

A *transformation* by which one *molecular entity* (the *substrate*) is converted into another by the formation of one (and only one) two-centre *bond* between the substrate and another *molecular entity* and which involves no other changes in *connectivity* in the substrate. For example, the formation of an acyl cation by attachment of carbon monoxide to a *carbenium ion* (R^+):



The product of an attachment may also be the *adduct* of the two reactants, but not all adducts can be represented as the products of an attachment. (For example, the Diels-Alder *cycloaddition*)



results in an adduct of buta-1,3-diene and ethene, but the reaction cannot be described as an attachment since bonds are formed between more than two centres.)

See also *colligation*, *electron attachment*.

autocatalytic reaction

A chemical reaction in which a product (or a reaction *intermediate*) also functions as *catalyst*. In such a reaction the observed *rate of reaction* is often found to increase with time from its initial value.

See *order of reaction*.

automerization

Synonymous with *degenerate rearrangement*.

autoprotolysis

A proton (hydron) transfer reaction between two identical molecules (usually a solvent), one acting as a *Brønsted acid* and the other as a *Brønsted base*. For example:



autoprotolysis constant

The product of the activities (or, more approximately, concentrations) of the species produced as the result of *autoprotolysis*. For solvents in which no other ionization processes are significant the term is synonymous with "ionic product". The autoprotolysis constant for water, K_w , is equal to the product of activities

$$a(H_3O^+)a(OH^-) = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}.$$

"A" value

The conformational preference of an equatorial compared to an axial substituent in a monosubstituted cyclohexane. This steric substituent parameter equals $\Delta_f G^\circ$ in kcal/mol for the equatorial to axial equilibration on cyclohexane. The values are also known as "Winstein-Holness" A values.

HIRSCH (1967); CAREY and SUNDBERG (1990).

+ azacarbene

See *nitrene*.

+ azene

See *nitrene*.

+ azylene

See *nitrene*.

α -addition (alpha-addition)

A chemical reaction resulting in a single reaction product from two or three reacting chemical species, with formation of two new chemical bonds to the same atom in one of the reactant molecular entities. The synonymous term 1/1/addition is also used. For example:



(This particular example can also be viewed as an *insertion reaction*.) In inorganic chemistry such α -addition reactions, generally to a metallic central atom, are known as "oxidative additions".

α -Addition is the reverse of α -elimination or 1/1/elimination.

See also *addition, elimination*.

α -effect

A positive deviation of an α -nucleophile (a nucleophile bearing an unshared pair of electrons on an atom adjacent to the nucleophilic site) from a Brønsted-type plot of $\log k_{\text{nuc}}$ vs. pK_a constructed for a series of related normal nucleophiles. More generally, it is the influence of the atom bearing a lone pair of electrons on the reactivity at the adjacent site.

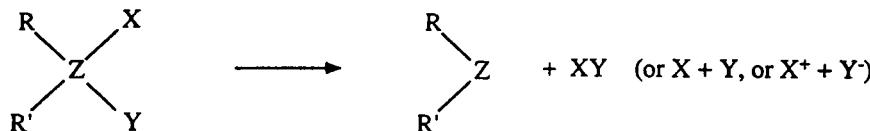
HOZ and BUNCEL (1985).

See also *Brønsted relation*.

The use of the term has been extended to include the effect of any substituent on an adjacent reactive centre, for example in the case of the " α -silicon effect".

α -elimination

A transformation of the general type



where the central atom Z is commonly carbon. The reverse reaction is called α -addition.

Baldwin's rules

A set of empirical rules for certain formations of 3- to 7-membered rings. The predicted pathways are those in which the length and nature of the linking chain enables the terminal atoms to achieve the proper geometries for reaction. The disfavoured cases are subject to severe distortions of bond angles and bond distances.

BALDWIN (1976).

base

A chemical species or molecular entity having an available pair of electrons capable of forming a covalent bond with a hydron (proton) (see Brønsted base) or with the vacant orbital of some other species (see Lewis base).

See also *hard base, superbase*.

basicity

For Brønsted bases it means the tendency of a compound to act as hydron (proton) acceptor. The basicity of a chemical species is normally expressed by the acidity of the conjugate acid (see *conjugate acid-base pair*). For Lewis bases it relates to the association constants of Lewis adducts and π -adducts.

basicity function

See *acidity function*.

bathochromic shift (effect)

Shift of a spectral band to lower frequencies (longer wavelengths) owing to the influence of substitution or a change in environment. It is informally referred to as a red shift and is opposite to *hypsochromic shift* (blue shift).

IUPAC PHOTOCHEMICAL GLOSSARY (1992).

Bell-Evans-Polanyi principle

The linear relation between energy of activation (E_a) and enthalpy of reaction (ΔH_r) sometimes observed within a series of closely related reactions.

$$E_a = A + B\Delta H_r$$

DEWAR (1969), JENCKS (1985).

benzyne

1,2-Didehydrobenzene (the aryne derived from benzene) and its derivatives formed by substitution. The terms *m*- and *p*-benzyne are occasionally used for 1,3- and 1,4-didehydrobenzene, respectively.

IUPAC CLASS NAMES (1993).

bifunctional catalysis

Catalysis (usually for hydron transfer) by a bifunctional *chemical species* involving a mechanism in which both *functional groups* are implicated in the *rate-controlling step*, so that the corresponding *catalytic coefficient* is larger than that expected for catalysis by chemical species containing only one of these functional groups.

The term should not be used to describe the *concerted action* of two different catalysts ("concerted catalysis").

bimolecular

See *molecularity*.

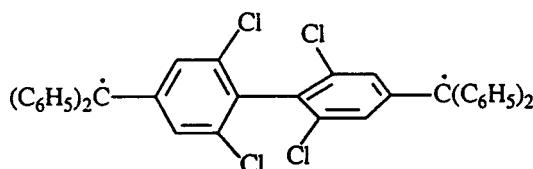
binding site

A specific region (or atom) in a *molecular entity* that is capable of entering into a stabilizing interaction with another molecular entity. An example of such an interaction is that of an active site in an enzyme with its *substrate*. Typical forms of interaction are by *hydrogen bonding*, *coordination*, and *ion pair formation*.

Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

biradical

An even-electron *molecular entity* with two (possibly delocalized) radical centres which act nearly independently of each other, e.g.



Species in which the two radical centres interact significantly are often referred to as "biradicaloids". If the two radical centres are located on the same atom, the species are more properly referred to by their generic names: carbenes, nitrenes, etc.

The lowest-energy triplet state of a biradical lies below or at most only a little above its lowest singlet state (usually judged relative to $k_B T$, the product of the Boltzmann constant k_B and the absolute temperature T). The states of those biradicals whose radical centres interact particularly weakly are most easily understood in terms of a pair of local doublets.

Theoretical descriptions of low-energy states of biradicals display the presence of two unsaturated valences (biradicals contain one fewer bond than permitted by the rules of valence): the dominant valence bond structures have two dots, the low energy molecular orbital configurations have only two electrons in two approximately nonbonding molecular orbitals, two of the natural orbitals have occupancies close to one, etc.

The term is synonymous with "diradical".

IUPAC PHOTOCHEMICAL GLOSSARY (1993).

See also *carbene*, *nitrene*.

Bodenstein approximation

See *steady state*.

bond

There is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent "molecular species". In the context of this Glossary, the term refers usually to the *covalent bond*.

PAULING (1967).

See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.

bond dissociation

See *heterolysis*, *homolysis*.

(In ordinary usage the term refers to homolysis only.)

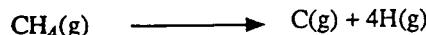
bond-dissociation energy, D (SI unit: kJ mol⁻¹, or J (per molecule))

The enthalpy (per mole) required to break a given *bond* of some specific *molecular entity* by *homolysis*, e.g. for CH₄ → H₃C· + H·, symbolized as D(CH₃-H) (cf. *heterolytic bond dissociation energy*).

See also *bond energy*.

bond energy (mean bond energy)

The average value of the gas-phase *bond dissociation energies* (usually at a temperature of 298 K) for all *bonds* of the same type within the same *chemical species*. The mean bond energy for methane, for example, is one-fourth the enthalpy of reaction for



Tabulated bond energies are generally values of bond energies averaged over a number of selected typical chemical species containing that type of bond.

bond migration

See *migration*.

bond number

The number of electron-pair *bonds* between two nuclei in any given *Lewis formula*. For example in ethene the bond number between the carbon atoms is two, and between the carbon and hydrogen atoms is one.

bond order

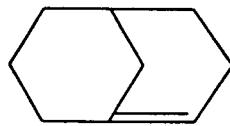
A theoretical index of the degree of bonding between two atoms relative to that of a normal single bond, i.e. the bond provided by one localized electron pair. In the valence-bond theory it is a weighted average of the bond numbers between the respective atoms in the *contributing structures*. In molecular-orbital theory it is calculated from the weights of the atomic orbitals in each of the occupied molecular orbitals. For example, in valence-bond theory (neglecting other than Kekulé structures) the bond order between adjacent carbon atoms in benzene is 1.5; in Hückel molecular orbital theory it is 1.67. Other variants of molecular orbital theory provide other values for bond orders.

borderline mechanism

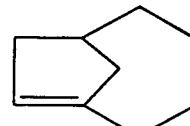
A mechanism intermediate between two extremes, for example a nucleophilic substitution intermediate between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$, or intermediate between electron transfer and $\text{S}_{\text{N}}2$.

Bredt's rule

A double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond without *excessive strain*. For example, while bicyclo[2.2.1]hept-1-ene is only capable of existence as a *transient*, its higher homologues having a double bond at the bridgehead position have been isolated: e.g.



Bicyclo[3.3.1]non-1-ene



Bicyclo[4.2.1]non-1(8)-ene

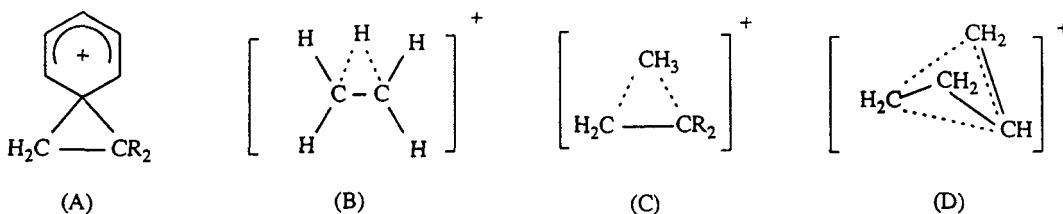
BREDT (1924); see also FAWCETT (1950); WISEMAN (1967); KEESE (1972).
For an alternative formulation see WISEMAN and CHONG (1969).

bridged carbocation

A *carbocation* (real or hypothetical) in which there are two (or more) carbon atoms that could in alternative *Lewis formulae* be designated as *carbenium centres* but which is instead represented by a structure in which a *group* (a hydrogen atom or a hydrocarbon residue, possibly with substituents in non-involved positions) bridges these potential carbenium centres. One may distinguish "electron-sufficient bridged carbocations" and "electron-deficient bridged carbocations". Examples of the former are phenyl-bridged ions (for which the trivial name "phenonium ion" has been used), such as (A). These ions are straightforwardly classified as *carbenium ions*. The latter type of ion necessarily involves three-centre bonding. Structures (C) and (D) contain five-coordinate carbon atoms. The "hydrogen-bridged carbocation" (B) contains a two-co-ordinate hydrogen atom. Hypercoordination, which includes two-coordination for hydrogen and five- but also higher coordination for carbon is generally observed in bridged carbocations.

OLAH, SURYA PRAKASH, WILLIAMSON, FIELD, and WADE (1987).

See also *carbonium ion*, *multi-centre bond*, *neighbouring group participation*.



bridging ligand

A *ligand* attached to two or more, usually metallic, central atoms.
IUPAC INORGANIC NOMENCLATURE (1990).

Brønsted acid (Brönsted acid)

A molecular entity capable of donating a hydron (proton) to a base, (i.e. a "hydron donor") or the corresponding chemical species. For example: H_2O , H_3O^+ , $\text{CH}_3\text{CO}_2\text{H}$, H_2SO_4 , HSO_4^- , HCl , CH_3OH , NH_3 .

See also conjugate acid-base pair.

Brønsted base (Brönsted base)

A molecular entity capable of accepting a *hydron* (proton) from an acid (i.e. a "hydron acceptor") or the corresponding *chemical species*. For example: OH^- , H_2O , CH_3CO_2^- , HSO_4^- , SO_4^{2-} , Cl^- .

See also conjugate acid-base pair.

Brønsted relation (Brönsted relation)

The term applies to either of the equations

$$k_{\text{HA}}/p = G(K_{\text{HA}}q/p)^\alpha$$

$$k_A/q = G(K_{HA}q/p)^{-\beta}$$

(or their logarithmic forms) where α , β and G are constants for a given reaction series (α and β are called "Brønsted exponents"), k_{HA} and k_A are catalytic coefficients (or rate coefficients) of reactions whose rates depend on the concentrations of HA and/or of A^- . K_{HA} is the acid dissociation constant of the acid HA, p is the number of equivalent acidic protons in the acid HA, and q is the number of equivalent basic sites in its conjugate base A^- . The chosen values of p and q should always be specified. (The charge designations of HA and A^- are only illustrative.)

The Brønsted relation is often termed the "Brønsted catalysts law" (or the "Catalysis Law"). Although justifiable on historical grounds, this name is not recommended, since Brønsted relations are known to apply to many uncatalysed and pseudo-catalysed reactions (such as simple proton (*hydron*) transfer reactions). The term "pseudo-Brønsted relation" is sometimes used for reactions which involve nucleophilic catalysis instead of acid-base catalysis. Various types of Brønsted parameters have been proposed such as β_{lg} , β_{nuc} , β_{eq} for leaving group, nucleophile and equilibrium constants, respectively.

See also linear free-energy relation.

Bunnett-Olsen equations

The equations for the relation between $\lg([SH^+]/[S]) + H_o$ and $H_o + \lg[H^+]$ for base S in aqueous mineral acid solution, where H_o is Hammett's acidity function and $H_o + \lg[H^+]$ represents the activity function $\lg(\gamma_{SH^+}/\gamma_{H^+})$ for the nitroaniline reference bases to build H_o .

$$\lg([SH^+]/[S]) - \lg[H^+] = (\Phi - 1)(H_o + \lg[H^+]) + pK_{SH^+}$$

$$\lg([SH^+]/[S]) + H_o = \Phi(H_o + \lg[H^+]) + pK_{SH^+}$$

BUNNETT and OLSEN (1966); HAMMETT (1970).

See also Cox-Yates equation.

cage

An aggregate of molecules, generally in the condensed phase, that surrounds the fragments formed, for example, by thermal or photochemical dissociation. Because the cage hinders the separation of the fragments by diffusion, they may preferentially react with one another ("cage effect") but not necessarily to re-form the precursor species. For example,



See also *geminate recombination*.

cage compound

A polycyclic compound having the shape of a cage (see OLAH, 1990). The term is also used for inclusion compounds.

canonical form

See *contributing structure*.

captodative effect

Effect on the stability of a carbon centred radical determined by the combined action of a captor (electron withdrawing) and a dative (electron releasing) substituent, both attached to the radical centre. The term is also used for certain unsaturated compounds.

BORDWELL and LYNCH (1989); SUSTMANN and KORTH (1990); VIEHE, JANOUSEK, MERENYI, and STELLA (1985).

carbanion

Generic name for anions containing an even number of electrons and having an unshared pair of electrons on a tervalent carbon atom (e.g. Cl_3C^- or $\text{HC}\equiv\text{C}^-$) or - if the ion is mesomeric (see *mesomerism*) - having at least one significant contributing structure with an unshared pair of electrons on a tervalent carbon atom, for example,



See also *radical ion*.

carbene

Generic name for the species H_2C : and substitution derivatives thereof, containing an electrically neutral bivalent carbon atom with two nonbonding electrons. The nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (triplet state). Use of the alternative name "methylene" as a generic term is not recommended.

See also *biradical*.

carbenium centre

The three-coordinate carbon atom in a carbenium ion to which the excess positive charge of the ion (other than that located on heteroatoms) may be formally considered to be largely attributed, i.e., which has one vacant p-orbital. (N.B. It is not always possible to uniquely identify such an atom.) This formal attribution of charge often does not express the real charge distribution.

carbenium ion

A generic name for carbocations, real or hypothetical, that have at least one important contributing structure containing a tervalent carbon atom with a vacant p-orbital. (The name implies a protonated carbene or a substitution derivative thereof.)

The term was proposed (and rejected) as a replacement for the traditional usage of the name *carbonium ion*.

To avoid ambiguity, the name should not be used as the root for the systematic nomenclature of carbocations. The corresponding difficulty confused carbonium ion nomenclature for many years. For example, the term "ethylcarbonium ion" has at times been used to refer either to CH_3CH_2^+ (ethyl cation) or (correctly) to $\text{CH}_3\text{CH}_2\text{CH}_2^+$ (propyl cation).

For the nomenclature of carbenium ions see IUPAC NOMENCLATURE GUIDE (1993).

carbenoid

A carbene like chemical species but with properties and reactivity differing from the free carbene itself, e.g.



carbocation

A cation containing an even number of electrons with a significant portion of the excess positive charge located on one or more carbon atoms. This is a general term embracing carbenium ions, all types of carbonium ions, vinyl cations, etc. Carbocations may be named by adding the word "cation" to the name of the corresponding radical [IUPAC ORGANIC RULES (1979), IUPAC NOMENCLATURE GUIDE (1993).] Such names do not imply structure (e.g. whether three-coordinated or five-coordinated carbon atoms are present).

OLAH and SCHLEYER (1972).

See also *bridged carbocation, radical ion.*

carbonium ion

The term should be used with great care since several incompatible meanings are currently in use. It is not acceptable as the root for systematic nomenclature for carbocations.

(1) In most of the existing literature the term is used in its traditional sense for what is here defined as *carbenium ion*.

(2) A carbocation, real or hypothetical, that contains at least one five-coordinate carbon atom.

(3) A carbocation, real or hypothetical, whose structure cannot adequately be described by two-electron two-centre bonds only. (The structure may involve carbon atoms with a coordination number greater than five.)

OLAH and SCHLEYER (1972).

carbyne

Generic name for the species



and substitution derivatives thereof, such as



containing an electrically neutral univalent carbon atom with three non-bonding electrons. Use of the alternative name "methylidyne" as a generic term is not recommended.

catalysis

The action of a *catalyst*.

catalysis law

See *Brønsted relation*.

catalyst

A substance that participates in a particular *chemical reaction* and thereby increases its rate but without a net change in the amount of that substance in the system. At the molecular level, the catalyst is used and regenerated during each set of *microscopic chemical events* leading from a *molecular entity* of reactant to a *molecular entity* of product.

See also *autocatalytic reaction, bifunctional catalysis, catalytic coefficient, electron-transfer catalysis, general acid catalysis, general base catalysis, intramolecular catalysis, micellar catalysis, Michaelis-Menten kinetics, phase-transfer catalysis, pseudo-catalysis, rate of reaction, specific catalysis.*

catalytic coefficient

If the *rate of reaction* (v) is expressible in the form

$$v = (k_0 + \sum k_i [C_i]^{n_i}) [A]^{\alpha} [B]^{\beta} \dots$$

where A, B, ... are reactants and C_i represents one of a set of catalysts, then the proportionality factor k_i is the catalytic coefficient of the particular *catalyst* C_i . Normally the *partial order* of reaction (n_i) with respect to a catalyst will be unity, so that k_i is an $(\alpha+\beta+\dots+1)$ th order rate coefficient. The proportionality factor k_0 is the $(\alpha+\beta+\dots)$ th order rate coefficient of the uncatalysed component of the total reaction.

cation radical

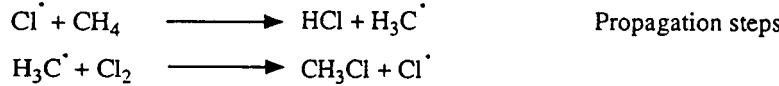
See *radical ion*.

cationotropic rearrangement (cationotropy)

See *tautomerism*.

chain reaction

A reaction in which one or more reactive reaction *intermediates* (frequently radicals) are continuously regenerated, usually through a repetitive cycle of elementary steps (the "propagation step"). For example, in the chlorination of methane by a radical mechanism, Cl· is continuously regenerated in the chain propagation steps:



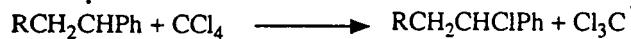
In chain polymerization reactions, reactive intermediates of the same types, generated in successive steps or cycles of steps, differ in relative molecular mass, as in



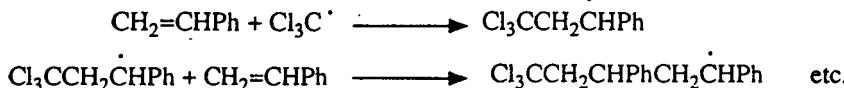
See also *chain transfer, initiation, termination*.

chain transfer

The abstraction, by the *radical end* of a growing chain-polymer, of an atom from another molecule. The growth of the polymer chain is thereby terminated but a new radical, capable of chain propagation and polymerization, is simultaneously created. For the example of alkene polymerization cited for a *chain reaction*, the reaction



represents a chain transfer, the radical Cl₃C· inducing further polymerization:



The phenomenon occurs also in other chain reactions such as cationic polymerization.
See also *telomerization*.

charge density

See *electron density*.

charge population

The net electric charge on a specified atom in a *molecular entity*, as determined by some prescribed definition, e.g. that of MULLIKEN (1955).

See also *electron density*.

charge-transfer complex

A ground state *adduct* which exhibits an observable charge transfer absorption band.
IUPAC PHOTOCHEMICAL GLOSSARY (1992).

chelation

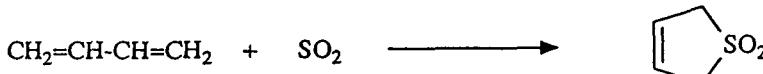
The formation or presence of *bonds* (or other attractive interactions) between two or more separate *binding sites* within the same ligand and a single central atom. A *molecular entity* in which there is chelation (and the corresponding *chemical species*) is called a "chelate". The terms bidentate (or didentate), tridentate, tetradeinate... multidente are used to indicate the number of potential binding sites of the ligand, at least two of which must be used by the ligand in forming a "chelate". For example, the bidentate ethylenediamine forms a chelate with CuI in which both nitrogen atoms of ethylenediamine are bonded to copper. (The use of the term is often restricted to metallic central atoms.)

The phrase "separate binding sites" is intended to exclude cases such as [PtCl₃(CH₂=CH₂)], ferrocene, and (benzene)tricarbonylchromium in which ethene, the cyclopentadienyl group, and benzene, respectively, are considered to present single binding sites to the respective metal atom, and which are not normally thought of as chelates (see *haptic*).

See also *cryptand*.

cheletropic reaction

A form of *cycloaddition* across the terminal atoms of a fully *conjugated system* with formation of two new σ -bonds to a single atom of the ("monocentric") reagent. There is formal loss of one π -bond in the substrate and an increase in *coordination number* of the relevant atom of the reagent. An example is the *addition* of sulfur dioxide to butadiene:



The reverse of this type of reaction is designated "cheletropic elimination".
WOODWARD and HOFFMANN (1969).

cheletropic reaction

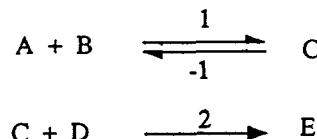
Alternative (and etymologically more correct) name for *cheletropic reaction*.
DEWAR (1971).

chemical flux

A concept related to *rate of reaction*, particularly applicable to the progress in one direction only of component reaction steps in a complex system or to the progress in one direction of reactions in a system at dynamic equilibrium (in which there are no observable concentration changes with time). Chemical flux (ϕ) is a derivative with respect to time, and has the dimensions of amount of substance per unit volume transformed per unit time.

The sum of all the chemical fluxes leading to destruction of B is designated the "total chemical flux out of B" (symbol $\Sigma\phi_{-B}$); the corresponding formation of B by concurrent elementary reactions is the "total chemical flux into B or A" (symbol $\Sigma\phi_B$).

For the mechanism



the total chemical flux into C is caused by the single reaction (1):

$$\Sigma\phi_C = \phi_1$$

whereas the chemical flux out of C is a sum over all reactions that remove C:

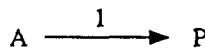
$$\Sigma\phi_{-C} = \phi_{-1} + \phi_2$$

where ϕ_{-1} is the "chemical flux out of C into B (and/or A)" and ϕ_2 is the "chemical flux out of C into E". The rate of appearance of C is then given by

$$d[C]/dt = \Sigma\phi_C - \Sigma\phi_{-C}$$

In this system ϕ_1 (or $\Sigma\phi_A$) can be regarded as the hypothetical rate of decrease in the concentration of A due to the single (unidirectional) reaction (1) proceeding in the assumed absence of all other reactions.

For a non-reversible reaction



$$-d[\text{A}]/dt = \phi_1$$

If two substances A and P are in *chemical equilibrium*



then

$$\Sigma\phi_A = \Sigma\phi_{-A} = \Sigma\phi_P = \Sigma\phi_{-P}$$

and

$$-d[\text{A}]/dt = d[\text{P}]/dt = 0$$

GOLD (1979).

See also *order of reaction*, *rate-limiting step*, *steady state*.

chemical reaction

A process that results in the interconversion of *chemical species*. Chemical reactions may be *elementary reactions* or *stepwise reactions*. (It should be noted that this definition includes experimentally observable interconversions of conformers.)

Detectable chemical reactions normally involve *sets* of *molecular entities*, as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. "microscopic chemical events").

See also *identity reaction*.

chemical relaxation

If the equilibrium mixture of a *chemical reaction* is disturbed by a sudden change, especially of some external parameter (such as temperature, pressure, or electrical field strength), the system will readjust itself to a new position of the chemical equilibrium or return to the original position, if the perturbation is temporary. The readjustment is known as *chemical relaxation*.

In many cases, and in particular when the displacement from equilibrium is slight, the progress of the system towards equilibrium can be expressed as a first-order law

$$[C_t - (C_{eq})_2] = [(C_{eq})_1 - (C_{eq})_2] e^{-t/\tau}$$

where $(C_{eq})_1$ and $(C_{eq})_2$ are the equilibrium concentrations of one of the chemical species involved in the reaction before and after the change in the external parameter, and c_t is its concentration at time t . The time parameter τ , named *relaxation time*, is related to the *rate constants* of the chemical reaction involved.

Measurements of the relaxation times by relaxation methods [involving a temperature jump (T-jump), pressure jump, electric field jump or a periodic disturbance of an external parameter, as in ultrasonic techniques] are commonly used to follow the kinetics of very fast reactions.

See BERNASCONI (1976); LEFFLER and GRUNWALD (1963); see also *relaxation*.

chemical shift (NMR), δ (SI unit: 1)

The variation of the resonance frequency of a nucleus in nuclear magnetic resonance (NMR) spectroscopy in consequence of its magnetic environment. The chemical shift of a nucleus, δ , is expressed in ppm by its frequency, v_{cpd} , relative to a standard, v_{ref} , and defined as

$$\delta = \frac{v_{cpd} - v_{ref}}{v_o} \times 10^6$$

where v_o is the operating frequency of the spectrometer. For ^1H and ^{13}C NMR the reference signal is usually that of tetramethylsilane (SiMe_4). Other references are used in the older literature and in other solvents, such as D_2O .

If a resonance signal occurs at lower frequency or higher applied field than an arbitrarily selected reference signal, it is said to be upfield, and if resonance occurs at higher frequency or lower applied field, the signal is downfield. Resonance lines upfield from SiMe_4 have positive, and resonance lines downfield from SiMe_4 have negative δ -values.

chemical species

An ensemble of chemically identical *molecular entities* that can explore the same set of molecular energy levels on the time scale of the experiment. The term is applied equally to a set of chemically identical atomic or molecular structural units in a solid array.

For example, two conformational *isomers* may be interconverted sufficiently slowly to be detectable by separate NMR spectra and hence to be considered to be separate chemical species on a time scale governed by the radiofrequency of the spectrometer used. On the other hand, in a slow chemical reaction the same mixture of conformers may behave as a single chemical species, i.e. there is virtually complete equilibrium population of the total set of molecular energy levels belonging to the two conformers.

Except where the context requires otherwise, the term is taken to refer to a set of molecular entities containing isotopes in their natural abundance.

The wording of the definition given in the first paragraph is intended to embrace both cases such as graphite, sodium chloride, or a surface oxide, where the basic structural units may not be capable of isolated existence, as well as those cases where they are.

In common chemical usage, and in this Glossary, generic and specific chemical names (such as *radical* or *hydroxide ion*) or chemical formulae refer either to a chemical species or to a *molecular entity*.

chemically induced dynamic nuclear polarization (CIDNP)

See *CIDNP*.

chemoselective, chemoselectivity

Chemoselectivity is the preferential reaction of a chemical reagent with one of two or more different functional groups. A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium tetrahydroborate is a more chemoselective reducing agent than is lithium tetrahydroaluminate. The concept has not been defined in more quantitative terms. The term is also applied to reacting molecules or intermediates which exhibit selectivity towards chemically different reagents.

Some authors use the term chemospecificity for 100 % chemoselectivity. However, this usage is discouraged.

See TROST (1980).

See also *regioselectivity, stereoselectivity, stereospecificity*.

+ chemospecificity

See *chemoselectivity*.

chromophore

The part (atom or group of atoms) of a *molecular entity* in which the electronic transition responsible for a given spectral band is approximately localized. The term arose in the dyestuff industry, referring originally to the groupings in the molecule that are responsible for the dye's colour.

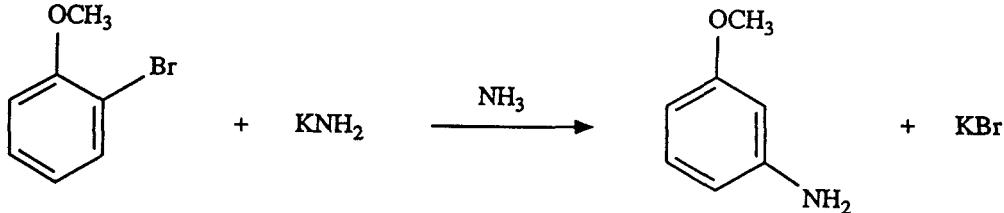
WITT (1876).

CIDNP (Chemically Induced Dynamic Nuclear Polarization)

Non-Boltzmann nuclear spin state distribution produced in thermal or photochemical reactions, usually from *colligation* and diffusion, or *disproportionation of radical pairs*, and detected by NMR spectroscopy by enhanced absorption or emission signals.

cine-substitution

A *substitution reaction* (generally *aromatic*) in which the entering group takes up a position adjacent to that occupied by the *leaving group*. For example,



See also *tele-substitution*.

class (a) metal ion

A metal ion that combines preferentially with *ligands* containing ligating atoms that are the lightest of their Periodic Group.

See also *class (b) metal ion, hard acid*.

class (b) metal ion

A metal ion that combines preferentially with *ligands* containing ligating atoms other than the lightest of their Periodic Group.

See also *class (a) metal ion, hard acid*.

clathrate

See *host, inclusion compound*.

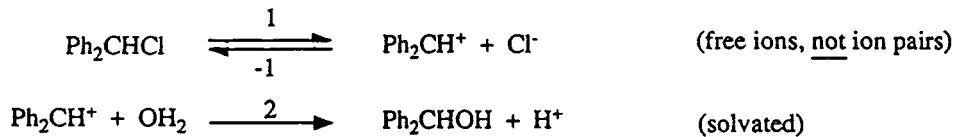
colligation

The formation of a covalent bond by the combination or recombination of two *radicals* (the reverse of *unimolecular homolysis*). For example:



common-ion effect (on rates)

A reduction in the *rate* of certain reactions of a *substrate RX* in solution [by a path that involves a *pre-equilibrium* with formation of R⁺ (or R⁻) ions as reaction intermediates] caused by the addition to the reaction mixture of an electrolyte solute containing the "common ion" X⁻ (or X⁺). For example, the rate of solvolysis of diphenylmethyl chloride in acetone-water is reduced by the addition of salts of the common ion Cl⁻ which causes a decrease in the quasi-equilibrium concentration of the diphenylmethyl cation in the scheme:



This phenomenon is a direct consequence of the *mass-law effect* on ionization equilibria in electrolytic solution.

More generally, the common-ion effect is the influence of the "common ion" on the reactivity due to the shift of the dissociation equilibrium. It may also lead to an enhancement of the *rate of reaction*.

compensation effect

In a considerable number of cases plots of $T\Delta fS$ vs. ΔfH , for a series of reactions, e.g. for a reaction in a range of different solvents, are straight lines of approximately unit slope. Therefore, the terms ΔfH and $T\Delta fS$ in the expression partially compensate, and $\Delta fG = \Delta fH - T\Delta fS$ often is a much simpler function of solvent (or other) variation than ΔfH or $T\Delta fS$ separately.

CONNOR (1991).

See also *isokinetic relationship*.

complementary binding sites

See *binding site*.

complex

A molecular entity formed by loose association involving two or more component molecular entities (ionic or uncharged), or the corresponding *chemical species*. The bonding between the components is normally weaker than in a covalent bond.

The term has also been used with a variety of shades of meaning in different contexts: it is therefore best avoided when a more explicit alternative is applicable. In inorganic chemistry the term "coordination entity" is recommended instead of "complex" (IUPAC INORGANIC NOMENCLATURE (1990)). For the different usage of "complex" in inorganic chemistry, see IUPAC INORGANIC RULES (1970); Rule 2.24.

See also *activated complex, adduct, charge transfer complex, electron-donor-acceptor complex, encounter complex, inclusion complex, σ-adduct, π-adduct, transition state*.

composite reaction

A *chemical reaction* for which the expression for the rate of disappearance of a reactant (or rate of appearance of a product) involves rate constants of more than a single *elementary reaction*. Examples are "opposing reactions" (where rate constants of two opposed *chemical reactions* are involved), "parallel reactions" (for which the rate of disappearance of any reactant is governed by the rate constants relating to several simultaneous reactions to form different respective products from a single set of reactants), and *stepwise reactions*.

comproportionation

The reverse of *disproportionation*. The term "symproportionation" is also used.

HARTMANN, KLENKE, and METZGER (1986).

concerted process

Two or more *primitive changes* are said to be concerted (or to constitute a concerted process) if they occur within the same *elementary reaction*. Such changes will normally (though perhaps not inevitably) be "energetically coupled". (In the present context the term "energetically coupled" means that the simultaneous progress of the primitive changes involves a *transition state* of lower energy than that for their successive occurrence.) In a concerted process the primitive changes may be *synchronous* or *asynchronous*.

See also *bifunctional catalysis, potential energy (reaction) surface*.

condensation reaction

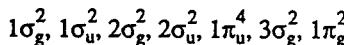
A (usually stepwise) reaction in which two or more reactants (or remote reactive sites within the same *molecular entity*) yield a single main product with accompanying formation of water or of some other small molecule, e.g. ammonia, ethanol, acetic acid, hydrogen sulfide.

The mechanism of many condensation reactions has been shown to comprise consecutive *addition* and *elimination reactions*, as in the base-catalysed formation of (*E*)-but-2-enal (crotonaldehyde) from acetaldehyde, via 3-hydroxybutanal (aldol). The overall reaction in this example is known as the aldol condensation.

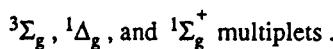
The term is sometimes also applied to cases where the formation of water or another simple molecule does not occur, as in "benzoin condensation".

configuration (electronic)

A distribution of the electrons of an atom or a *molecular entity* over a set of one-electron wavefunctions called *orbitals*, according to the Pauli principle. From one configuration several states with different multiplicities may result. For example, the ground electronic configuration of the oxygen molecule (O_2) is



resulting in the



IUPAC PHOTOCHEMICAL GLOSSARY (1992).

configuration (molecular)

In the context of stereochemistry, the term is restricted to the arrangements of atoms of a *molecular entity* in space that distinguishes stereoisomers, the isomerism of which is not due to conformational differences.

IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

conformation

The spatial arrangements of atoms affording distinction between stereoisomers which can be interconverted by rotation about formally single bonds. Some authorities extend the term to include inversion at trigonal bipyramidal centres and other "polytopal rearrangements".

IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

conjugate acid-base pair

The Brønsted acid BH^+ formed on protonation of a base B is called the conjugate acid of B, and B is the conjugate base of BH^+ . (The conjugate acid always carries one unit of positive charge more than the base, but the absolute charges of the species are immaterial to the definition.) For example: the Brønsted acid HCl and its conjugate base Cl^- constitute a conjugate acid-base pair.

conjugated system, conjugation

In the original meaning a conjugated system is a molecular entity whose structure may be represented as a system of alternating single and multiple bonds: e.g.



In such systems, conjugation is the interaction of one p-orbital with another across an intervening σ -bond in such structures. (In appropriate molecular entities d-orbitals may be involved.) The term is also extended to the analogous interaction involving a p-orbital containing an unshared electron pair, e.g.



See also *delocalization, homoconjugation, resonance*.

conjugative mechanism

See *electronic effect*.

connectivity

In a chemical context, the information content of a *line formula*, but omitting any indication of *bond* multiplicity.

constitution

The description of the identity and connectivity (and corresponding bond multiplicities) of the atoms in a *molecular entity* (omitting any distinction from their spatial arrangement).

conrotatory

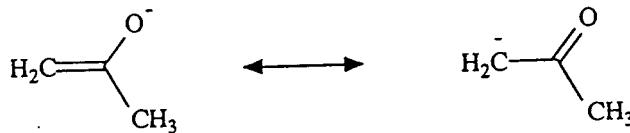
See *electrocyclic reaction*.

contact ion pair

See *ion pair*.

contributing structure

The definition is based on the valence-bond formulation of the quantum mechanical idea of the wavefunction of a molecule as composed of a linear combination of wavefunctions, each representative of a formula containing bonds that are only single, double or triple with a particular pairing of electron spins. Each such formula represents a contributing structure, also called "resonance structure" to the total wavefunction, and the degree to which each contributes is indicated by the square of its coefficient in the linear combination. The contributing structures, also called "canonical forms", themselves thus have a purely formal significance: they are the components from which wavefunctions can be built. Structures may be covalent (or non-polar) or ionic (or polar). The representation is frequently kept qualitative so that we speak of important or major contributing structures and minor contributing structures. For example, two major non-equivalent contributing structures for the conjugate base of acetone are



See also *delocalization*, *Kekulé structure*, *resonance*.

coordinate covalence (coordinate link)

See *coordination*.

coordination

The formation of a covalent bond, the two shared electrons of which have come from only one of the two parts of the *molecular entity* linked by it, as in the reaction of a *Lewis acid* and a *Lewis base* to form a *Lewis adduct*; alternatively, the bonding formed in this way. In the former sense, it is the reverse of *unimolecular heterolysis*. "Coordinate covalence" and "coordinate link" are synonymous (obsolete) terms. The synonym "dative bond" is obsolete.

(The origin of the bonding electrons has by itself no bearing on the character of the bond formed. Thus, the formation of methyl chloride from a methyl cation and a chloride ion involves coordination; the resultant bond obviously differs in no way from the C-Cl bond in methyl chloride formed by any other path, e.g. by colligation of a methyl radical and a chlorine atom.)

The term is also used to describe the number of ligands around a central atom without necessarily implying two-electron bonds.

See also *dipolar bond*, *π -adduct*.

coordination number

The coordination number of a specified atom in a *chemical species* is the number of other atoms directly linked to that specified atom [cf. IUPAC INORGANIC NOMENCLATURE (1990); Rule I-10.2.5]. For example, the coordination number of carbon in methane is four, and it is five in protonated methane, CH_5^+ . (The term is used in a different sense in the crystallographic description of ionic crystals.)

coordinatively saturated

A transition metal complex that has formally 18 outer shell electrons at the central metal atom.

coordinatively unsaturated

A transition metal complex that possesses fewer ligands than exist in the coordinatively saturated complex. These complexes usually have fewer than 18 outer shell electrons at the central metal atom.

coronate

See *crown*.

correlation analysis

The use of empirical correlations relating one body of experimental data to another, with the objective of finding quantitative estimates of the factors underlying the phenomena involved. Correlation analysis in organic chemistry often uses *linear free-energy relations* for rates or equilibria of reactions, but the term also embraces similar analysis of physical (most commonly spectroscopic) properties and of biological activity.

CHAPMAN and SHORTER (1972, 1978).

See also *Quantitative Structure-Activity Relationships (QSAR)*.

cosphere

See *cybotactic region*.

coupling constant (spin-spin coupling constant), *J* (SI unit: Hz (NMR))

A quantitative measure for nuclear spin-spin, nuclear-electron (hyperfine coupling) and electron-electron (fine coupling in EPR) coupling in magnetic resonance spectroscopy. The "indirect" or scalar NMR coupling constants are in a first approximation independent of the external magnetic field and are expressed in Hz.

covalent bond

A region of relatively high electron density between nuclei which arises at least partly from sharing of electrons and gives rise to an attractive force and characteristic internuclear distance.

See also *agostic, coordination, hydrogen bond, multi-centre bond*.

Cox-Yates equation

A modification of the *Bunnett-Olsen equation* of the form

$$\lg ([\text{SH}^+]/[\text{S}]) - \lg [\text{H}^+] = m^* X + pK_{\text{SH}^+}$$

where *X* is the activity function $\lg(\gamma_{\text{S}}\gamma_{\text{H}^+})/\gamma_{\text{SH}^+}$ for an arbitrary reference base. The function *X* is called the excess acidity because it gives a measure of the difference between the acidity of a solution and that of an ideal solution of the same concentration. In practice $X = - (H_0 + \lg[\text{H}^+])$ and $m^* = 1 - \Phi$.

COX and YATES (1978, 1981); LUCCHINI, MODENA, SCORRANO, COX and YATES (1982).

See also *Bunnett-Olsen equations*.

critical micelle concentration (cmc)

There is a relatively small range of concentrations separating the limit below which virtually no *micelles* are detected and the limit above which virtually all additional surfactant molecules form micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the critical micellization concentration (critical micelle concentration), symbol c_M , abbreviation cmc (or c.m.c.). As values obtained using different properties are not quite identical, the method by which the cmc is determined should be clearly stated.

See IUPAC MANUAL APPENDIX II (1972).

See also *inverted micelle*.

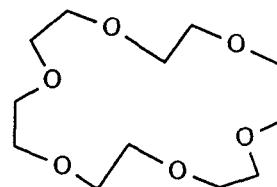
cross-conjugation

In a system $\text{XC}_6\text{H}_4\text{GY}$ this is conjugation involving the substituent *X*, the benzene ring, and the side-chain connective-plus-reaction site *GY*, i.e. either *X* is a $+R$ group and *GY* is a $-R$ group, or *X* is a $-R$ group and *GY* is a $+R$ group. In Hammett correlations this situation can lead to the need to apply exalted substituent constants σ^+ or σ^- , respectively, as in electrophilic or nucleophilic aromatic substitution, respectively. The term "through resonance" is synonymous. Cross conjugation has also been used to describe the interactions occurring in 2-phenylallyl and similar systems (DEWAR (1969)).

crown

A molecular entity comprising a monocyclic *ligand* assembly that contains three or more *binding sites* held together by covalent bonds and capable of binding a *guest* in a central (or nearly central) position. The *adducts* formed are sometimes known as "coronates". The best known members of this group are macrocyclic polyethers, such as "18-crown-6", containing several repeating units $-\text{CR}_2\text{-CR}_2\text{O}-$ (where R is most commonly H), and known as crown ethers.

PEDERSEN (1967); CRAM et al. (1986).
See also *host*.

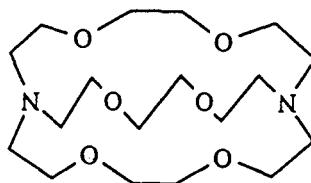


"18-crown-6"

cryptand

A molecular entity comprising a cyclic or polycyclic assembly of *binding sites* that contains three or more *binding sites* held together by *covalent bonds*, and which defines a molecular cavity in such a way as to bind (and thus "hide" in the cavity) another molecular entity, the *guest* (a cation, an anion or a neutral species), more strongly than do the separate parts of the assembly (at the same total concentration of binding sites). The *adduct* thus formed is called a "cryptate". The term is usually restricted to bicyclic or oligocyclic molecular entities.

Example



Corresponding monocyclic ligand assemblies (crowns) are sometimes included in this group, if they can be considered to define a cavity in which a guest can hide. The terms "podand" and "spherand" are used for certain specific ligand assemblies. Coplanar cyclic polydentate ligands, such as porphyrins, are not normally regarded as cryptands.

DIETRICH, LEHN and SAUVAGE (1969).

See also *host*.

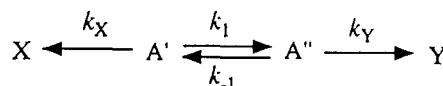
For a contribution to the evolving terminology, see also VÖGTLÉ (1980).

Curtin-Hammett principle

In a *chemical reaction* that yields one product (X) from one conformational isomer (A') and a different product (Y) from another conformational isomer (A'') (and provided these two isomers are rapidly interconvertible relative to the rate of product formation, whereas the products do not undergo interconversion) the product composition is not in direct proportion to the relative concentrations of the conformational isomers in the *substrate*; it is controlled only by the difference in standard free energies ($\delta\Delta fG$) of the respective *transition states*.

It is also true that the product composition is formally related to the relative concentrations of the conformational isomers A' and A'' (i.e. the conformational equilibrium constant) and the respective rate constants of their reactions; these parameters are generally - though not invariably - unknown.

The diagram below represents the energetic situation for transformation of interconverting isomers A and A' into products X and Y.



$$k_1 \gg k_X \quad k_{-1} \gg k_Y$$

ELIEL (1962); see also SEEMAN et al. (1980), SEEMAN (1983).

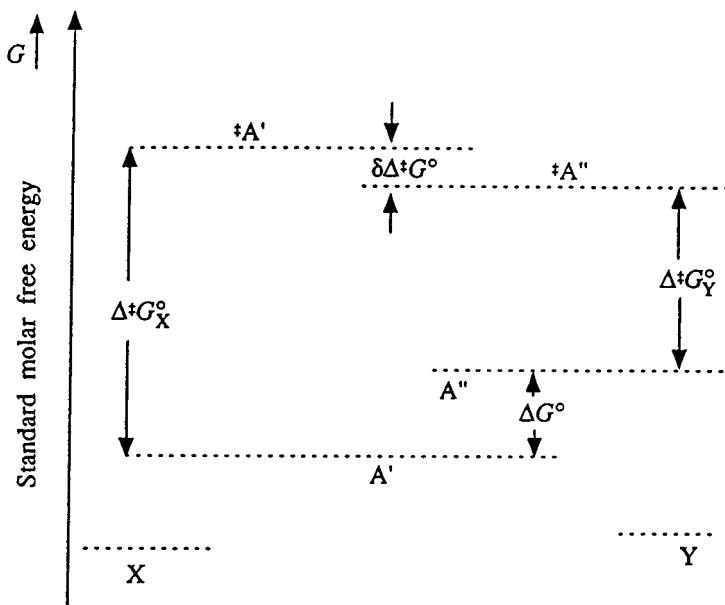


Figure. Curtin-Hammett principle. Transformation of interconverting isomers A' and A'' into products X and Y .

cybotactic region

That part of a solution in the vicinity of a solute molecule in which the ordering of the solvent molecules is modified by the presence of the solute molecule. The term solvent "cosphere" of the solute has also been used.

KOSOWER (1968); STEWART and MORROW (1927).

See also *solvation*.

cyclization

Formation of a ring compound from a chain by formation of a new bond.

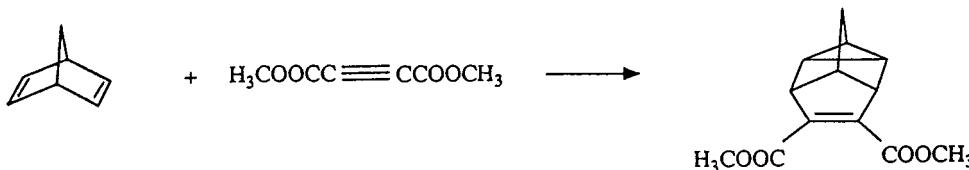
See also *annulation*.

cycloaddition

A reaction in which two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic *adduct* in which there is a net reduction of the bond multiplicity.

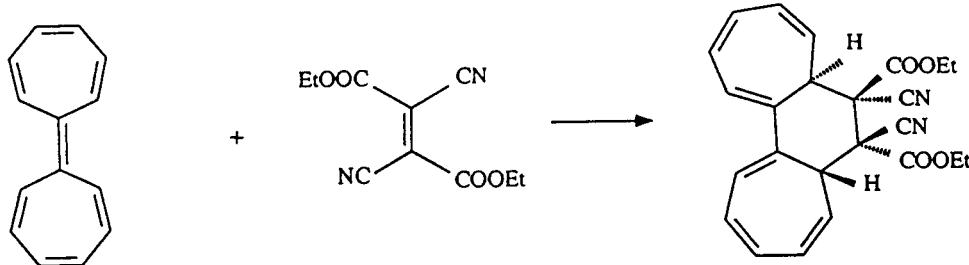
The following two systems of notations have been used for the more detailed specification of cycloadditions, of which the second, more recent system (described under (2)) is preferred:

(1) A $(i+j+\dots)$ cycloaddition is a reaction in which two or more molecules (or parts of the same molecule), respectively, provide units of i , j ,... linearly connected atoms: these units become joined at their respective termini by new σ -bonds so as to form a cycle containing $(i+j+\dots)$ atoms. In this notation, (a) a Diels-Alder reaction is a $(4+2)$ cycloaddition, (b) the initial reaction of ozone with an alkene is a $(3+2)$ cycloaddition, and (c) the reaction shown below is a $(2+2+2)$ cycloaddition. (N.B.: parentheses (...) are used in the description based on numbers of atoms.)



(2) The symbolism $[i+j+\dots]$ for a cycloaddition identifies the numbers i , j ,... of electrons in the interacting units that participate in the transformation of reactants to products. In this notation the reaction (a) and (b) of the preceding paragraph would both be described as $[2+4]$ cycloadditions, and (c) as a $[2+2+2]$ cycloaddition. The symbol a or s ($a =$ *antarafacial*, $s =$ *suprafacial*) is often added (usually as a subscript after the number to designate the stereochemistry of addition to each fragment. A subscript specifying the orbitals, viz., σ , π (sigma, pi) with their usual significance) or n (for an orbital associated with a single atom only), may be

added as a subscript before the number. Thus the normal Diels-Alder reaction is a $[4_s+2_s]$ or $[\pi 4_s + \pi 2_s]$ cycloaddition, whilst the reaction



would be a $[14_a+2_s]$ or $[\pi 14_a + \pi 2_s]$ cycloaddition. (N.B. Square brackets [...] are used in the descriptions based on numbers of electrons.)

Cycloadditions may be *pericyclic reactions* or (non-concerted) stepwise reactions. The term "dipolar cycloaddition" is used for cycloadditions of 1,3-dipolar compounds.

HUISGEN (1968); HUISGEN, GRASHEY and SAUER (1964); WOODWARD and HOFFMANN (1969).

See also *cheletropic reactions*.

cycloelimination

The reverse of *cycloaddition*. The term is preferred to the synonyms "cycloreversion", "retro-addition", and "retrocycloaddition".

+ cycloreversion

See *cycloelimination*.

+ dative bond

See *coordination*.

decomposition, chemical

The breakdown of a single entity (normal molecule, reaction *intermediate*, etc.) into two or more fragments.

+ de-electronation

See *oxidation* (1).

degenerate chemical reaction

See *identity reaction*.

degenerate rearrangement

A *molecular rearrangement* in which the principal product is indistinguishable (in the absence of isotopic labelling) from the principal reactant. The term includes both "degenerate intramolecular rearrangements" and reactions that involve *intermolecular* transfer of atoms or groups ("degenerate intermolecular rearrangements"); both are degenerate *isomerizations*. The occurrence of degenerate rearrangements may be detectable by isotopic labelling or by dynamic NMR techniques. For example: the [3,3]*sigmatropic* rearrangement of hexa-1,5-diene (Cope rearrangement),



Synonymous but less preferable terms are "automerization", "permutational isomerism", "isodynamic transformation", "topomerization".

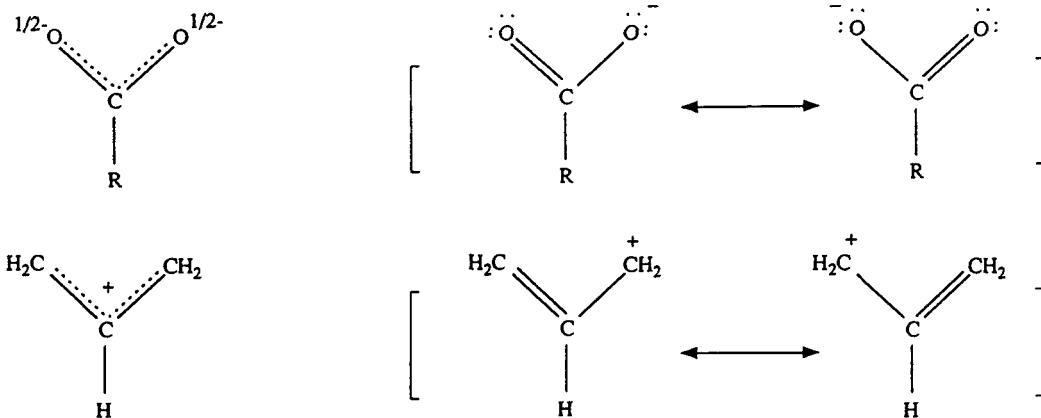
BINSCH, ELIEL, and KESSLER (1971).

See also *fluxional, molecular rearrangement, valence isomer*.

delocalization

A quantum mechanical concept most usually applied in organic chemistry to describe the π -bonding in a *corygated system*. This bonding is not localized between two atoms: instead, each link has a "fractional double bond character" or *bond order*. There is a corresponding "delocalization energy", identifiable with the stabilization of the system compared with a

hypothetical alternative in which formal (localized) single and double bonds are present. Some degree of delocalization is always present and can be estimated by quantum mechanical calculations. The effects are particularly evident in *aromatic* systems and in symmetrical molecular entities in which a lone pair of electrons or a vacant p-orbital is conjugated with a double bond (e.g. carboxylate ions, nitro compounds, enamines, the allyl cation). Delocalization in such species may be represented by partial bonds or as resonance (here symbolized by a two-headed arrow) between contributing structures.



These examples also illustrate the concomitant delocalization of charge in ionic conjugated systems. Analogously, delocalization of the spin of an unpaired electron occurs in conjugated radicals.

See also *mesomerism*.

deshielding

See *shielding*.

detachment

The reverse of an *attachment*.

See also *electron attachment*.

detailed balancing, principle of

When equilibrium is reached in a reaction system (containing an arbitrary number of components and reaction paths), as many atoms, in their respective *molecular entities*, will pass forward, as well as backwards, along each individual path in a given finite time interval. Accordingly, the reaction path in the reverse direction must in every detail be the reverse of the reaction path in the forward direction (provided always that the system is at equilibrium).

The principle of detailed balancing is a consequence for macroscopic systems of the principle of *microscopic reversibility*.

diamagnetic

Substances having a negative magnetic susceptibility are diamagnetic. They are repelled out of a magnetic field.

See also *paramagnetic*.

diastereoisomerism

Stereoisomerism other than *enantiomerism*. Diastereoisomers (or diastereomers) are stereoisomers not related as mirror images. Diastereoisomers are characterized by differences in physical properties, and by some differences in chemical behaviour toward achiral as well as chiral reagents.

IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

dielectric constant

A measure for the effect of a medium on the potential energy of interaction between two charges. It is measured by comparing the capacity of a capacitor with and without the sample present.

dienophile

The olefin component of a Diels-Alder reaction.

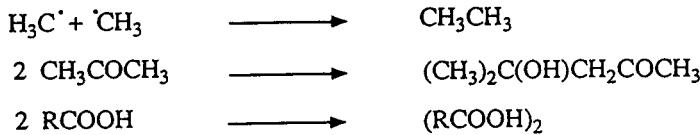
See *cycloaddition*.

diffusion-controlled rate

See *encounter-controlled rate*, *microscopic diffusion control*. See also *mixing control*.

dimerization

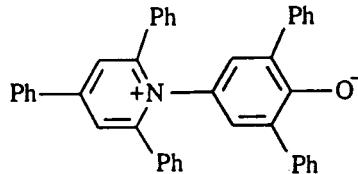
The transformation of a molecular entity A to give a molecular entity A₂. For example:



See also *association*.

Dimroth-Reichardt E_T parameter

A measure of the *ionizing power* (loosely *polarity*) of a solvent, based on the maximum wavenumber of the longest wavelength electronic absorption band of



in a given solvent. E_T, called E_T(30) by its originators, is given by

$$\begin{aligned} E_T &= 2.859 \times 10^{-3}\nu \\ &= 2.859 \times 10^4\lambda^{-1} \end{aligned}$$

where E_T is in kcal/mol, ν is in cm⁻¹ and λ is in nm.

The so-called normalized E_T^N scale is defined as

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{SiMe}_4)}{E_T(\text{water}) - E_T(\text{SiMe}_4)} = [E_T(\text{solvent}) - 30.7] / 32.4$$

DIMROTH, REICHARDT, SIEPMANN and BOHLMANN (1963); REICHARDT (1988).
See also *Grunwald-Winstein equation*, *Z-value*.

dipolar aprotic solvent

A solvent with a comparatively high relative permittivity (or dielectric constant), greater than ca. 15, and a sizable permanent dipole moment, that cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds, e.g. dimethyl sulfoxide. The term (and its alternative "polar aprotic solvent") is a misnomer and is therefore discouraged. Such solvents are usually not *aprotic*, but *protophilic* (and at most weakly *protogenic*). In describing a solvent it is better to be explicit about its essential properties, e.g. dipolar and non-*protogenic*.

dipolar bond

A bond formed (actually or conceptually) by coordination of two neutral moieties, the combination of which results in charge-separated structures, e.g.,



The term is preferred to the obsolescent synonyms "coordinate link", "co-ordinate co-valence", "dative bond", "semipolar bond".

dipolar cycloaddition

See *cycloaddition*.

dipole-dipole interaction

Intermolecular or intramolecular interaction between molecules or groups having a permanent electric dipole moment. The strength of the interaction depends on the distance and relative orientation of the dipoles. The term applies also to intramolecular interactions between bonds having permanent dipole moments.

See also *van der Waals forces*.

dipole-induced dipole forces

See *van der Waals forces*.

diradical

See *biradical*.

direct effect

See *field effect*.

dismutation

See *disproportionation*.

dispersion forces

See *London forces*.

disproportionation

Any chemical reaction of the type $A + A \rightarrow A' + A''$ where A , A' and A'' are different chemical species. For example:

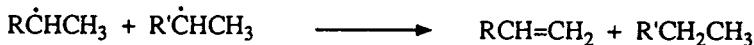


The reverse of disproportionation is called *comproportionation*.

A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by



Reactions of the more general type



are also loosely described as radical disproportionations.

(A somewhat more restricted usage of the term prevails in inorganic chemistry.)

disrotatory

See *electrocyclic reaction*.

dissociation

(1) The separation of a molecular entity into two or more molecular entities (or any similar separation *within* a polyatomic molecular entity). Examples include *unimolecular heterolysis* and *homolysis*, and the separation of the constituents of an *ion pair* into free ions.

(2) The separation of the constituents of any aggregate of molecular entities.
In both senses dissociation is the reverse of association.

distonic radical cation

A radical cation in which charge and radical sites are separated.
YATES, BOUMA and RADOM (1986).

donor number (DN)

A quantitative measure of *Lewis basicity* devised by GUTMANN (1976).

driving force (also called the affinity) of a reaction, A (SI unit: kJ mol^{-1})

The decrease in Gibbs energy on going from the reactants to the products of a chemical reaction ($-\Delta G$).

downfield

See *chemical shift*.

dual substituent-parameter equation

In a general sense, this is any equation which expresses substituent effects in terms of two parameters. However, in practice the term is used more specifically for an equation for summarizing the effects of *meta*- or *para*-substituents ($i = m$ or p) X on chemical reactivity, spectroscopic properties, etc. of a probe site Y in benzene or other aromatic system.

$$P^1 = \rho_I \sigma_I + \rho_R \sigma_R$$

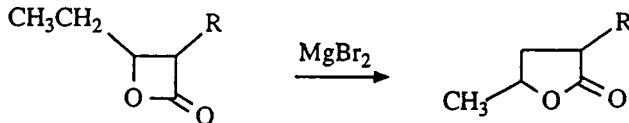
P is the magnitude of the property Y for substituent X , expressed relative to the property for $X=H$; σ_I and σ_R are inductive or polar and resonance substituent constants, respectively, there being various scales for σ_R ; ρ_I and ρ_R are the corresponding regression coefficients.

EHRENSON, BROWNLEE, and TAFT (1973); TAFT and TOPSOM (1987).

See also *extended Hammett equation*.

dyotropic rearrangement

An uncatalyzed process in which two σ -bonds simultaneously migrate intramolecularly, e.g.



REETZ (1972).

E_T -value

See *Dimroth-Reichardt E_T parameter, Z-value*.

+ educt

Term used mainly in the German literature for starting material (reactant). It should be avoided in English, because there it means "something that comes out" and not "something that goes in". The german use of the term is in fact also incorrect.

effective charge

Change in effective charge is a quantity obtained by comparison of the *polar effect* of substituents on the free energies of rate or equilibrium processes with that on a standard ionization equilibrium. Provided the effective charge on the states in the standard equilibrium are defined, then it is possible to measure effective charges for states in the reaction or equilibrium under consideration.

WILLIAMS (1984, 1992).

effective molarity (or effective concentration)

The ratio of the first-order rate constant of an *intramolecular* reaction involving two functional groups within the same *molecular entity* to the second-order *rate constant* of an analogous *intermolecular elementary reaction*. This ratio has the dimension of concentration. The term can also apply to an equilibrium constant.

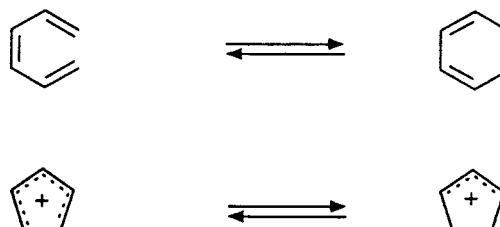
See also *intramolecular catalysis*.

eighteen-electron rule

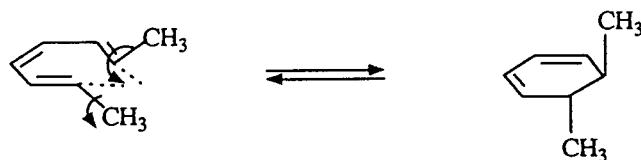
An electron-counting rule to which an overwhelming majority of stable diamagnetic transition metal complexes adhere. The number of nonbonded electrons at the metal plus the number of electrons in the metal-ligand bonds should be 18. The 18 electron rule in transition metal chemistry is a full analogue of the "Lewis octet rule".

electrocyclic reaction

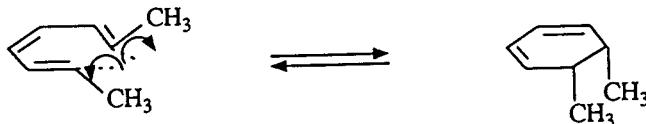
A *molecular rearrangement* that involves the formation of a σ -bond between the termini of a fully conjugated linear π -electron system (or a linear fragment of a π -electron system) and a decrease by one in the number of π -bonds, or the reverse of that process. For example:



The stereochemistry of such a process is termed "conrotatory" or *antarafacial* if the substituents at the interacting termini of the conjugated system both rotate in the same sense, e.g.



or "disrotatory" (or *suprafacial*) if one terminus rotates in a clockwise and the other in a counter-clockwise sense, e.g.



See also *pericyclic reaction*.

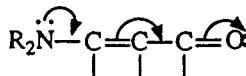
electrofuge

A *leaving group* that does not carry away the bonding electron pair. For example, in the nitration of benzene by NO_2^+ , H^+ is the electrofuge. The adjective of electrofuge is electrofugal.

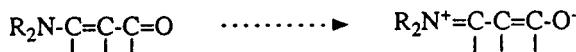
See also *electrophile, nucleofuge*.

electromeric effect

A molecular polarizability effect occurring by an *intramolecular* electron displacement (sometimes called the "conjugative mechanism" and, previously, the "tautomeric mechanism") characterized by the substitution of one electron pair for another within the same atomic octet of electrons. It can be indicated by curved arrows symbolizing the displacement of electron pairs, as in



which represents the hypothetical electron shift



INGOLD (1953).

The term has been deemed obsolescent or even obsolete (see *mesomeric effect, resonance effect*). It has long been custom to use phrases such as "enhanced substituent resonance effect" which imply the operation of the electromeric effect, without using the term, and various modern theoretical treatments parametrize the response of substituents to "electronic demand", which amounts to considering the electromeric effect together with the *inductomereric effect*.

EHRENSON, BROWNLEE and TAFT (1973); TAFT and TOPSOM (1987); CHARTON (1987).

electron acceptor

(1) A substance to which an electron may be transferred; for example 1,4-dinitrobenzene or the dication 1,1'-dimethyl-4,4'-bipyridyldium .

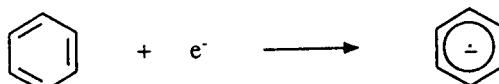
+ (2) A Lewis acid. This usage is discouraged.

electron affinity

The energy released when an additional electron (without excess energy) attaches itself to a *molecular entity* (usually an electrically neutral molecular entity). (The direct measurement of this quantity involves molecular entities in the gas phase.)

electron attachment

The transfer of an electron to a *molecular entity*, resulting in a molecular entity of (algebraically) increased negative charge. (It is not an *attachment*, as defined in this Glossary.)



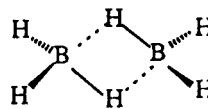
See also *oxidation (1), reduction*.

electron configuration

See *configuration (electronic)*.

electron-deficient bond

A single bond between adjacent atoms that is formed by less than two electrons, as in B_2H_6 :



The B-H-B bonds are called a "two-electron three-centre bonds".

electron density

If $P(x,y,z) dx dy dz$ is the probability of finding an electron in the volume element $dx dy dz$ at the point of a molecular entity with coordinates x,y,z , then $P(x,y,z)$ is the electron density at this point. For many purposes (e.g., X-ray scattering, forces on atoms) the system behaves exactly as if the electrons were spread out into a continuously distributed charge. The term has frequently been wrongly applied to negative charge population.

See also *charge density*.

electron detachment

The reverse of an *electron attachment*.

electron donor

(1) A *molecular entity* that can transfer an electron to another *molecular entity*, or to the corresponding *chemical species*.

+ (2) A Lewis base. This use is discouraged.

+ electron-donor-acceptor complex

A term sometimes employed instead of *charge-transfer complex* or *Lewis adduct*.

See also *adduct*, *coordination*

electron-pair acceptor

A synonym for *Lewis acid*.

electron-pair donor

A synonym for *Lewis base*.

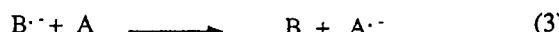
electron transfer

The transfer of an electron from one *molecular entity* to another, or between two localized sites in the same *molecular entity*.

See also *inner sphere (electron transfer)*, *outer sphere (electron transfer)*, *Marcus equation*.

electron-transfer catalysis

The term indicates a sequence of reactions such as shown in equations (1)-(3), leading from A to B:



An analogous sequence involving radical cations ($\text{A}^{\cdot+}$, $\text{B}^{\cdot+}$) is also observed.

The most notable example of electron-transfer catalysis is the $\text{S}_{\text{RN}}1$ (or $\text{T}+\text{D}_N+\text{A}_N$) reaction of aromatic halides.

The term has its origin in a suggested analogy to acid-base catalysis, with the electron instead of the proton. However, there is a difference between the two catalytic mechanisms, since the electron is not a true catalyst, but rather behaves as the initiator of a *chain reaction*. "Electron-transfer induced chain reaction" is a more appropriate term for the situation described by equations (1)-(3).

EBERSON (1987).

electronation

See electron attachment, reduction.

electronegativity

A measure of the power of an atom or a group of atoms to attract electrons from other parts of the same *molecular entity*. The concept has been quantified by a number of authors, including especially Pauling and Mulliken.

See ATKINS (1974).

electroneutrality principle

The principle expresses the fact that all pure substances carry a net charge of zero.

electronic effect of substituents: symbols and signs

The inductive effect has universally been represented by the symbol I. This is now commonly taken to include both through-bonds and through-space transmission, but I is also used specifically for through-bonds transmission; through-space transmission is then symbolized as F (for field effect). The symbols for the influence of substituents exerted through electron delocalization have variously been M (mesomeric), E (electromeric), T (tautomeric), C (conjugative), K (konjugativ), and R (resonance). Since the present fashion is to use the term resonance effect, R is the most commonly used symbol, although M is still seen quite often.

Both the possible sign conventions are in use. The Ingold sign convention associates electronegativity (relative to hydrogen atom) with a negative sign, electropositivity with a positive sign. Thus the nitro group is described as electron-withdrawing by virtue of its $-I$ and $-M$ effects; chloro is described as a $-I$, $+M$ substituent, etc. For correlation analysis and linear free-energy relationships this convention has been found inconvenient, for it is in contradiction to the sign convention for polar substituent constants (σ -constants). Authors concerned with these fields often avoid this contradiction by adopting the opposite sign convention originally associated with Robinson, for electronic effects. This practice is almost always associated with the use of R for the electron delocalization effect: thus the nitro group is a $+I$, $+R$ substituent; chloro a $+I$, $-R$ substituent, etc.

electrophile, electrophilic

An electrophile (or electrophilic reagent) is a reagent that forms a bond to its reaction partner (the nucleophile) by accepting both bonding electrons from that reaction partner.

An "electrophilic substitution reaction" is a heterolytic reaction in which the reagent supplying the entering group acts as an electrophile. For example



Electrophilic reagents are *Lewis acids*. "Electrophilic catalysis" is catalysis by Lewis acids.

The term "electrophilic" is also used to designate the apparent polar character of certain radicals, as inferred from their higher relative reactivities with reaction sites of higher electron density.

See also *electrophilicity*.

electrophilicity

(1) The property of being electrophilic (see *electrophile*).

(2) The relative reactivity of an electrophilic reagent. (It is also sometimes referred to as "electrophilic power".) Qualitatively, the concept is related to Lewis acidity. However, whereas Lewis acidity is measured by relative equilibrium constants, electrophilicity is measured by relative *rate constants* for reactions of different electrophilic reagents towards a common substrate (usually involving attack at a carbon atom).

See also nucleophilicity.

element effect

The ratio of the rate constants of two reactions that differ only in the identity of the element of the atom in the *leaving group*, e.g., $k_{\text{Br}}/k_{\text{Cl}}$. As for *isotope effects*, a ratio of unity is regarded as a "null effect".

elementary reaction

A reaction for which no *reaction intermediates* have been detected or need to be postulated in order to describe the chemical reaction on a molecular scale. An elementary reaction is assumed to occur in a single step and to pass through a single *transition state*.

IUPAC CHEMICAL KINETICS (1981).

See also *stepwise reaction*.

elimination

The reverse of an *addition reaction* or *transformation*.

In an elimination two groups (called *eliminands*) are lost most often from two different centres (1/2/elimination or 1/3/elimination, etc.) with concomitant formation of an unsaturation in the molecule (double bond, triple bond) or formation of a new ring.

If the groups are lost from a single centre (α -elimination, 1/1/elimination) the resulting product is a *carbene* or a "carbene analogue".

See also α -elimination.

enantiomer

One of a pair of *molecular entities* which are mirror images of each other and non-superimposable.

enantioselectivity

See stereoselectivity.

encounter complex

A *complex* of *molecular entities* produced at an *encounter-controlled rate*, and which occurs as an intermediate in a reaction mechanism. When the complex is formed from two molecular entities it is called an "encounter pair". A distinction between encounter pairs and (larger) encounter complexes may be relevant in some cases, e.g. for mechanisms involving *pre-association*.

encounter-controlled rate

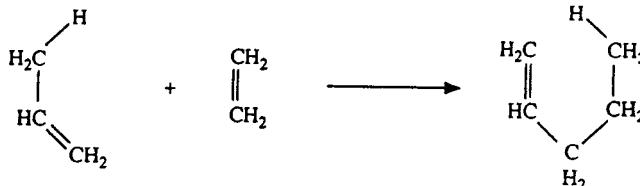
A *rate of reaction* corresponding to the rate of encounter of the reacting *molecular entities*. This is also known as "diffusion-controlled rate" since rates of encounter are themselves controlled by diffusion rates (which in turn depend on the viscosity of the *medium* and the dimensions of the reactant molecular entities).

For a *bimolecular* reaction between solutes in water at 25 °C an encounter-controlled rate is calculated to have a second-order *rate constant* of about $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

See also microscopic diffusion control.

ene reaction

The addition of a compound with a double bond having an allylic hydrogen (the "ene") to a compound with a multiple bond (the "enophile") with transfer of the allylic hydrogen and a concomitant reorganization of the bonding, as illustrated below for propene (the "ene") and ethene (the "enophile"). The reverse is a "retro-ene" reaction.

**energy of activation (Arrhenius energy of activation; activation energy), E_a (SI unit: kJ mol⁻¹)**

An operationally defined quantity expressing the dependence of a rate constant on temperature according to

$$E_a = RT^2(\partial \ln k / \partial T)_p$$

as derived from the "Arrhenius equation", $k = A \exp(-E_a/RT)$, where A (SI unit: as for the corresponding rate constant) is termed the "pre-exponential factor".

See also enthalpy of activation.

energy profile

See Gibbs energy diagram, potential-energy profile.

enforced concerted mechanism

Variation of reaction parameters in a series of reactions proceeding in non-concerted steps may lead to a situation, where the putative intermediate will possess a lifetime shorter than a bond vibration, so that the steps become concerted. The *transition state structure* will lie on the coordinate of the *More O'Ferrall-Jencks diagram* leading to that of the putative intermediate.

enophile

See *ene reaction*.

entering group

An atom or group that forms a bond to what is considered to be the main part of the *substrate* during a reaction. For example: the attacking *nucleophile* in a bimolecular nucleophilic substitution reaction.

enthalpy of activation (standard enthalpy of activation), $\Delta\ddagger H^\circ$ (SI unit: kJ mol⁻¹)

The standard enthalpy difference between the *transition state* and the ground state of the reactants at the same temperature and pressure. It is related to the temperature coefficient of the rate constant according to the equation:

$$\begin{aligned}\Delta\ddagger H &= RT^2(\partial \ln k / \partial T)_p - RT = E_a - RT \\ &= -R(\partial \ln(k/T) / \partial(1/T))_p\end{aligned}$$

where E_a is the *energy of activation*, providing that the rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm⁻³, measured at a fixed temperature and pressure). If $\ln k$ is expressed as

$$\ln k = (a/T) + b + c \ln T + dT,$$

then

$$\Delta\ddagger H = -aR + (c - 1)RT + dRT^2.$$

If enthalpy of activation and *entropy of activation* are assumed to be temperature independent, then

$$\Delta\ddagger H = -aR$$

If the concentration units are mol dm⁻³, the true and apparent enthalpies of activation differ by $(n - 1)/(\alpha RT^2)$, where n is the *order of reaction* and α the thermal expansivity.

See also *entropy of activation*, *Gibbs energy of activation*.

entropy of activation, (standard entropy of activation), $\Delta\ddagger S^\circ$ (SI unit: J mol⁻¹ K⁻¹)

The standard entropy difference between the *transition state* and the ground state of the reactants, at the same temperature and pressure.

It is related to the *Gibbs energy of activation* and *enthalpy of activation* by the equations

$$\begin{aligned}\Delta\ddagger S &= (\Delta\ddagger H - \Delta\ddagger G)/T \\ &= \Delta\ddagger H/T - R \ln(k_B/h) + R \ln(k/T)\end{aligned}$$

or, if $\ln k$ is expressed as $\ln k = a/T + b + c \ln T + dT$,

$$\Delta\ddagger S = R [b - \ln(k_B/h) + (c - 1)(1 + \ln T) + 2dT]$$

provided that rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm⁻³, measured at a fixed temperature and pressure). The numerical value of $\Delta\ddagger S$ depends on the standard state (and therefore on the concentration units selected). If entropy of activation and *enthalpy of activation* are assumed to be temperature-independent,

$$\Delta\ddagger S = R[b - \ln(k_B/h)]$$

Strictly speaking, the quantity defined is the entropy of activation at constant pressure from which the entropy of activation at constant volume can be deduced.

The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A (see *energy of activation*).

epimer

A *diastereoisomer* that has the opposite configuration at only one of two or more tetrahedral "stereogenic" centres present in the respective *molecular entity*.

IUPAC STEREOCHEMICAL GLOSSARY (1993).

epimerization

Interconversion of epimers by reversal of the configuration at one of the "stereogenic" centres.

equilibrium, chemical

Reversible processes (processes which may be made to proceed in the forward or reverse direction by the (infinitesimal) change of one variable, ultimately reach a point where the rates in both directions are identical, so that the system gives the appearance of having a static composition at which the Gibbs energy, G , is a minimum. At equilibrium the sum of the chemical potentials of the reactants equals that of the products, so that

$$\Delta G_r = \Delta G_r^\circ + RT \ln K = 0$$

$$\Delta G_r^\circ = -RT \ln K$$

The equilibrium constant, K , is given by the *mass-law effect*.

equilibrium control

See *thermodynamic control*.

equilibrium isotope effect

See *isotope effect*.

excess acidity

See *Burnett-Olsen equations, Cox-Yates equation*.

excimer

An excited dimer, "non-bonding" in the ground state. For example, a complex formed by the interaction of an excited *molecular entity* with a ground state counterpart of this entity.

IUPAC PHOTOCHEMICAL GLOSSARY (1992).

See also *exciplex*.

exciplex

An electronically excited complex of definite stoichiometry, "non-bonding" in the ground state. For example, a complex formed by the interaction of an excited *molecular entity* with a ground state counterpart of a different structure.

IUPAC PHOTOCHEMICAL GLOSSARY (1992).

See also *excimer*.

excited state

State of a system with energy higher than that of the ground state. This term is most commonly used to characterize a molecule in one of its electronically excited states, but can also refer to vibrational and/or rotational excitation in the electronic ground state.

IUPAC ANALYTICAL CHEMISTRY (1982).

extended Hammett equation

This term applies in a general way to any multiparametric extension of the *Hammett equation*. It is sometimes used specifically for a form of *dual substituent-parameter equation* in which the actual value of the correlated property P under the influence of the substituent X is used, rather than the value relative to that for $X = H$. An intercept term h corresponding to the value of P for $X = H$ is introduced, e.g.

$$P = \alpha\sigma_I + \beta\sigma_R + h$$

The equation may be applied to systems for which the inclusion of further terms to represent other effects, e.g. steric, is appropriate

CHAPMAN and SHORTER (1972, 1978); CHARTON (1987).

external return

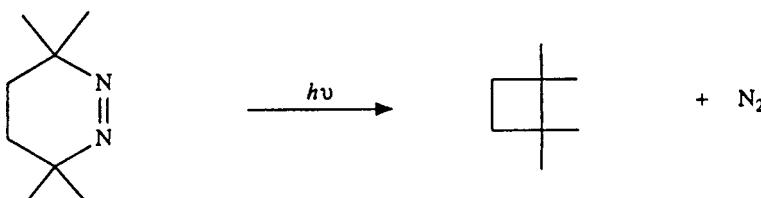
See *ion-pair return*.

extrusion transformation

A *transformation* in which an atom or group Y connected to two other atoms or groups X and Z is lost from a molecule, leading to a product in which X is bonded to Z , e.g.,



or



The reverse of an extrusion is called *insertion*.
See *cheletropic reaction*.

η -symbol ("eta")

See *hapto*.

fast-atom bombardment (FAB) mass spectroscopy

A method in which ions are produced in a mass spectrometer from nonvolatile or thermally fragile organic molecules by bombarding the compound in the condensed phase with energy-rich neutral particles.

IUPAC MASS SPECTROSCOPY (1991).

field effect

An experimentally observable effect symbolized by F (on reaction rates, etc.) of intramolecular coulombic interaction between the centre of interest and a remote unipole or dipole, by direct action through space rather than through bonds. The magnitude of the field effect (or "direct effect") depends on the unipolar charge/dipole moment, orientation of dipole, shortest distance between the centre of interest and the remote unipole or dipole, and on the effective dielectric constant. An approach to its calculation was described by KIRKWOOD and WESTHEIMER (1938) and has been elaborated in more recent years.

See also *electronic effect, inductive effect, polar effect*.

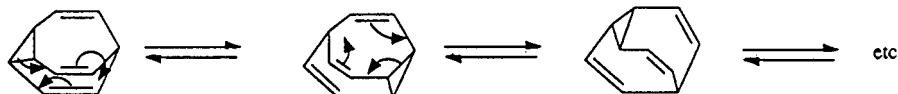
flash vacuum pyrolysis (FVP)

Thermal reaction of a molecule by exposing it to a short thermal shock at high temperature, usually in the gas phase.

fluxional

A chemical species is said to be fluxional if it undergoes rapid degenerate rearrangements (generally detectable by methods which allow the observation of the behaviour of individual nuclei in a rearranged chemical species, e.g. NMR, X-ray).

Example: Bulvalene (1 209 600 interconvertible arrangements of the ten CH groups).



The term is also used to designate positional change among ligands of complex compounds and organometallics. In these cases, the change is not necessarily degenerate.

See also *valence tautomerization*.

force-field calculations

See *molecular mechanics calculation*.

fractionation factor, isotopic

The ratio $(x_1/x_2)_A/(x_1/x_2)_B$, where x is the abundance, expressed as the atom fraction of the isotope distinguished by the subscript numeral, when the two isotopes are equilibrated between two different chemical species A and B (or between specific sites A and B in the same or different chemical species). The term is most commonly met in connection with deuterium solvent isotope effects, when the fractionation factor Φ expresses the ratio

$$\Phi = (x_D/x_H)_{\text{solute}} / (x_D/x_H)_{\text{solvent}}$$

for the exchangeable hydrogen atoms in the chemical species (or sites) concerned. The concept is also applicable to *transition states*.

GOLD (1969).

fragmentation

(1) The *heterolytic* cleavage of a molecule according to the general reaction



where *a-b* is an *electrofuge* and *X* is a *nucleofuge* (which may emerge from the reaction in combined form), and the middle group affords the unsaturated fragment *c=d*. For example,

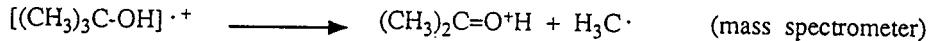


GROB (1969).

(2) The breakdown of a *radical* into a diamagnetic molecule or ion and a smaller radical, e.g.,



(3) The breakdown of a *radical ion* in a mass spectrometer or in solution, forming an ion of lower molar mass and a radical, e.g.,



free radical

See *radical*.

frontier orbitals

The Highest-energy Occupied Molecular Orbital (HOMO) (filled or partly filled) and Lowest-energy Unoccupied Molecular Orbital (LUMO) (completely or partly vacant) of a *molecular entity*. Examination of the mixing of frontier molecular orbitals of reacting molecular entities affords an approach to the interpretation of reaction behaviour; this constitutes a simplified perturbation *molecular orbital* theory of chemical behaviour.

FUKUI, YONEZAWA, and SHINGU (1952); FLEMING (1976).

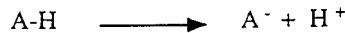
See also *SOMO*, *subjacent orbital*.

functional group

Organic compounds are thought of as consisting of a relatively unreactive backbone, for example a chain of sp^3 hybridized carbon atoms, and one or several functional groups. The functional group is an atom, or a group of atoms that has similar chemical properties whenever it occurs in different compounds. It defines the characteristic physical and chemical properties of families of organic compounds.

gas-phase acidity

The negative of the Gibbs energy (ΔG_f^\ominus) change for the reaction



in the gas phase.

BARTMESS and MC IVER (1979).

gas-phase basicity

The negative of the Gibbs energy (ΔG_f^\ominus) change associated with the reaction



in the gas phase. Also called absolute or intrinsic basicity.

See also *proton affinity*.

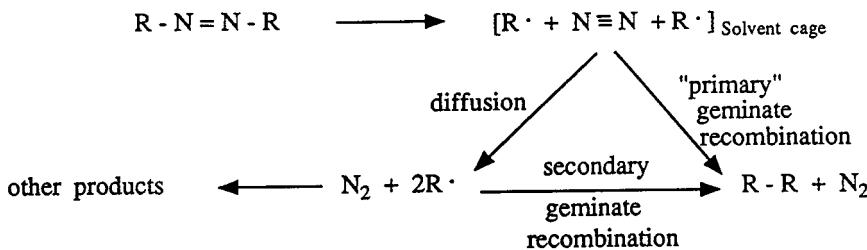
geminate pair

Pair of *molecular entities* in close proximity in solution within a solvent cage and resulting from reaction (e.g. bond scission, electron transfer, group transfer) of a precursor that constitutes a single kinetic entity.

See also *ion pair, radical pair*.

geminate recombination

The reaction with each other of two *transient molecular entities* produced from a common precursor in solution. If reaction occurs before any separation by diffusion has occurred, this is termed "primary geminate recombination". If the mutually reactive entities have been separated, and come together by diffusion, this is termed "secondary geminate recombination".



general acid catalysis

The *catalysis* of a chemical reaction by a series of *Brønsted acids* (which may include the solvated hydrogen ion) so that the rate of the catalysed part of the reaction is given by $\Sigma k_{HA}[HA]$ multiplied by some function of *substrate* concentrations. (The acids HA are unchanged by the overall reaction.) General catalysis by acids can be experimentally distinguished from *specific catalysis* by hydrogen cations (*hydrons*) by observation of the *rate of reaction* as a function of buffer concentration.

See also *catalysis, catalytic coefficient, intramolecular catalysis, pseudo-catalysis, specific catalysis*.

general base catalysis

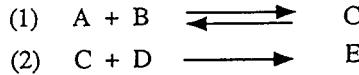
The *catalysis* of a *chemical reaction* by a series of *Brønsted bases* (which may include the *lyate* ion) so that the rate of the catalysed part of the reaction is given by $\Sigma k_B[B]$ multiplied by some function of *substrate* concentration.

See also *general acid catalysis*.

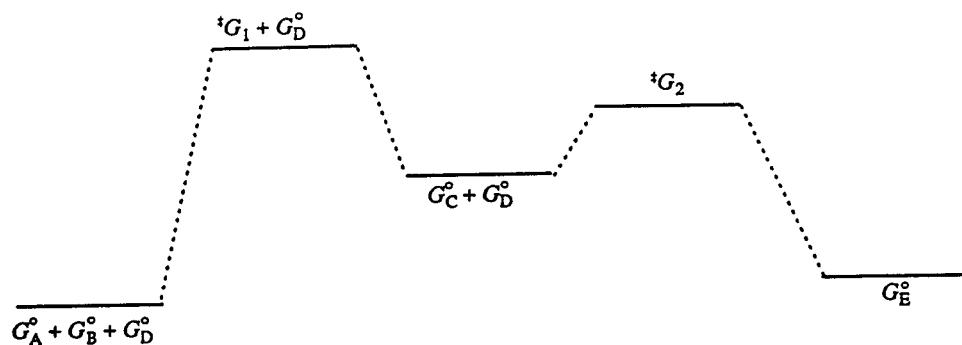
Gibbs energy diagram

A diagram showing the relative standard Gibbs energies of reactants, *transition states*, reaction *intermediates*, and products, in the same sequence as they occur in a chemical reaction. These points are often connected by a smooth curve (a "Gibbs energy profile", commonly still referred to as a "free energy profile") but experimental observation can provide information on relative standard Gibbs energies only at the maxima and minima and not at the configurations between them. The abscissa expresses the sequence of reactants, products, reaction intermediates and transition states and is usually undefined or only vaguely defined by the *reaction coordinate* (extent of bond breaking or bond making). In some adaptations the abscissas are however explicitly defined as *bond orders, Brønsted exponents, etc.*

Contrary to statements in many text books, the highest point on a Gibbs energy diagram does not necessarily correspond to the transition state of the *rate-limiting step*. For example, in a *stepwise reaction* consisting of two reaction steps



one of the transition states of the two reaction steps must (in general) have a higher standard Gibbs energy than the other, whatever the concentration of D in the system. However, the value of that concentration will determine which of the reaction steps is rate-limiting. If the particular concentrations of interest, which may vary, are chosen as the standard state, then the rate-limiting step is the one of highest Gibbs energy.



See also *potential energy profile*, *potential energy (reaction) surface*, *reaction coordinate*.

Gibbs energy of activation (standard free energy of activation), $\Delta\ddagger G$ (SI unit: kJ mol⁻¹)

The standard Gibbs energy difference between the *transition state* of a reaction (either an *elementary reaction* or a *stepwise reaction*) and the ground state of the reactants. It is calculated from the experimental rate constant k via the conventional form of the absolute rate equation:

$$\Delta\ddagger G = RT [\ln(k_B/h) - \ln(k/T)]$$

where k_B is the Boltzmann constant and h the Planck constant ($k_B/h = 2.08358 \times 10^{10}$ K⁻¹ s⁻¹). The values of the rate constants, and hence Gibbs energies of activation, depend upon the choice of concentration units (or of the thermodynamic standard state).

See also *enthalpy of activation*, *entropy of activation*.

ground state

The state of lowest Gibbs energy of a system.

IUPAC ANALYTICAL CHEMISTRY (1982).

See also *excited state*.

group

A defined linked collection of atoms or a single atom within a *molecular entity*. This use of the term in physical organic and general chemistry is less restrictive than the definition adopted for the purpose of nomenclature of organic compounds. [See IUPAC ORGANIC RULES (1979), Section C]

See also *substituent*.

Grunwald-Winstein equation

The *linear free energy relation*

$$\log(k_s/k_0) = mY$$

expressing the dependence of the rate of solvolysis of a substrate on ionizing power of the solvent. The rate constant k_0 applies to the reference solvent (ethanol-water, 80:20, v/v) and k_s to the solvent s , both at 25 °C. The parameter m is characteristic of the substrate and is assigned the value unity for *tert*-butyl chloride. The value Y is intended to be a quantitative measure of the *ionizing power* of the solvent s . The equation was later extended by WINSTEIN, GRUNWALD and JONES (1951) to the form

$$\log(k_s/k_0) = mY + lN$$

where N is the *nucleophilicity* of the solvent and l its susceptibility parameter. The equation has also been applied to reactions other than solvolysis. [For the definition of other Y -scales, see BENTLEY and SCHLEYER (1977), BENTLEY and LLEWELLYN (1990).]

GRUNWALD and WINSTEIN (1948); FAINBERG and WINSTEIN (1956).

See also *Dimroth-Reichardt E_T parameter*, *polarity*, *Z-value*.

guest

An organic or inorganic ion or molecule that occupies a cavity, cleft or pocket within the molecular structure of a *host molecular entity* and forms a *complex* with it or that is trapped in a cavity within the crystal structure of a host.

See also *crown*, *cryptand*, *inclusion compound*.

half-life, $t_{1/2}$ (SI unit: s)

In a kinetic experiment, the time required for the concentration of a particular reacting species to fall to one-half of its initial value. (Its dependence on initial concentration depends upon the *order of reaction*. It is independent of initial concentration only for a first-order process.)

See also *lifetime*.

halochromism

Halochromism means the colour change which occurs on addition of acid (or base, or a salt) to a solution of a compound. A chemical reaction (e.g. ion formation) transforms a colourless compound into a coloured one.

FALBE and REGITZ (1990); REICHARDT, ASHARIN-FORD, and SCHAEFER. (1993).

Hammett acidity function

See *acidity function*.

Hammett equation (or Hammett relation)

The equation in the form

$$\lg(k/k_0) = \rho\sigma$$

or

$$\lg(K/K_0) = \rho\sigma$$

applied to the influence of *meta*- or *para*-substituents X on the reactivity of the functional group Y in the benzene derivative *m*- or *p*-XC₆H₄Y. k or K is the rate or equilibrium constant, respectively, for the given reaction of *m*- or *p*-XC₆H₄Y; k₀ or K₀ refers to the reaction of C₆H₅Y, i.e. X = H; σ is the *substituent constant* characteristic of *m*- or *p*-X; ρ is the *reaction constant* characteristic of the given reaction of Y. The equation is often encountered in a form with lg k₀ or lg K₀ written as a separate term on the right hand side, e.g.

$$\lg k = \rho\sigma + \lg k_0$$

or

$$\lg K = \rho\sigma + \lg K_0$$

It then signifies the intercept corresponding to X = H in a regression of lg k or lg K on σ.

HAMMETT (1940, 1970).

See also *ρ-value*, *σ-constant*, *Taft equation*, *Yukawa-Tsuno equation*.

Hammond principle (or Hammond postulate)

The hypothesis that, when a *transition state* leading to an unstable *reaction intermediate* (or product) has nearly the same energy as that intermediate, the two are interconverted with only a small reorganization of molecular structure. Essentially the same idea is sometimes referred to as "Leffler's assumption", namely, that the transition state bears the greater resemblance to the less stable species (reactant or reaction intermediate/product). Many text books and physical organic chemists, however, express the idea in Leffler's form, but attribute it to Hammond.

As a corollary, it follows that a factor stabilising a reaction *intermediate* will also stabilize the *transition state* leading to that *intermediate*.

The acronym "Bemahapothle" (Bell, Marcus, Hammond, Polanyi, Thornton, Leffler) is sometimes used in recognition of the principal contributors towards expansion of the original idea of the Hammond postulate.

HAMMOND (1955); LEFFLER (1953); WILLIAMS (1984). See also FARCASIU (1975).

See also *More O'Ferrall-Jencks diagram*.

Hansch constant

A measure of the capability of a solute for *hydrophobic (lipophilic)* interaction based on the partition coefficient P for distribution of the solute between octan-1-ol and water. The most general way of applying P in *correlation analysis*, QSAR, etc. is as log P, but the behaviour of substituted benzene derivatives may be quantified by a substituent constant scale, π, which is defined in a way analogous to the Hammett σ scale. There are various π scales, depending on the substrate series used as reference.

HANSCH and LEO (1979).

hapto

The hapto symbol, η with numerical superscript, provides a topological description for the bonding of hydrocarbons and other π -electron systems to metals, by indicating the connectivity between the ligand and the central atom. For example, η^3 indicates that three atoms of the ligand are bonded to the central atom.

IUPAC INORGANIC NOMENCLATURE (1990).

hard acid

A Lewis acid with an acceptor centre of low polarizability. Other things being approximately equal, complexes of hard acids and bases or soft acids and bases have an added stabilization (sometimes called "HSAB" rule). For example the hard O⁻ (or N⁻) bases are preferred to their S⁻ (or P⁻) analogues by hard acids. Conversely a "soft acid" possesses an acceptor centre of high polarizability and exhibits the reverse preference for coordination of a soft base. These preferences are not defined in a quantitative sense.

See PEARSON (1963, 1973); HO (1977).

See also class (a) metal ion, hard base.

hard base

A Lewis base with a donor centre (e.g. an oxygen atom) of low polarizability; the converse applies to "soft bases".

See also hard acid.

heat capacity of activation, $\Delta^\ddagger C_p^\circ$ (SI unit: J mol⁻¹ K⁻¹)

A quantity related to the temperature coefficient of $\Delta^\ddagger H$ (enthalpy of activation) and $\Delta^\ddagger S$ (entropy of activation) according to the equations:

$$\Delta^\ddagger C_p = (\partial \Delta^\ddagger H / \partial T)_p = T (\partial \Delta^\ddagger S / \partial T)_p$$

If the rate constant is expressible in the form $\ln k = a/T + b + c \ln T + dT$,

then

$$\Delta^\ddagger C_p = (c - 1) R + 2dRT$$

See KOHNSTAM (1967).

+ hemileptic

See homoleptic.

Henderson-Hasselbach equation

An equation of the form

$$pH = pK_a - \lg([HA]/[A^-])$$

for the calculation of the pH of solutions where the ratio [HA]/[A⁻] is known.

heterobimetallic complex

A metal complex having two different metal atoms.

heteroconjugation

+(1) Association between a base and the conjugate acid of a different base through a hydrogen bond (B⁻...HB⁺ or A⁻H ...A⁻). The term has its origin in the conjugate acid-base pair and is in no way related to conjugation of orbitals. Heteroassociation is a more appropriate term.

+(2) Some authors refer to conjugated systems containing a heteroatom, e.g. pyridine, as "heteroconjugated systems". This usage is discouraged since it inappropriately suggests an analogy to homoconjugation (2), and conflicts with the currently accepted definition of that term.

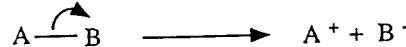
heteroleptic

Transition metal or Main Group compounds having more than one type of ligand.

See also homoleptic.

heterolysis, heterolytic

The cleavage of a covalent bond so that both bonding electrons remain with one of the two fragments between which the bond is broken, e.g.



Heterolytic bond fission is a feature of many *bimolecular reactions* in solution (e.g., *electrophilic substitution, nucleophilic substitution*).

See also *homolysis, heterolytic bond-dissociation energy*.

heterolytic bond-dissociation energy

The energy required to break a given *bond* of some specific compound by *heterolysis*. For the *dissociation* of a neutral molecule AB in the gas phase into A⁺ and B⁻ the heterolytic *bond-dissociation energy* D(A⁺B⁻) is the sum of the bond dissociation energy, D(A-B), and the adiabatic ionization energy of the radical A[·] minus the electron affinity of the radical B[·].

heterovalent hyperconjugation

See *hyperconjugation*.

hidden return

See *ion-pair return*.

Hildebrand parameter

A parameter measuring the cohesion of a solvent (energy required to create a cavity in the solvent).

CHASTRETTE, RAJZMANN, CHANON, and PURCELL (1985).

Hofmann rule

"The principal alkene formed in the decomposition of quaternary ammonium hydroxides that contain different primary alkyl groups is always ethylene, if an ethyl group is present." Originally given in this limited form by A.W. Hofmann, the rule has since been extended and modified as follows: "When two or more alkenes can be produced in a β -elimination reaction, the alkene having the smallest number of alkyl groups attached to the double bond carbon atoms will be the predominant product." This orientation described by the Hofmann rule is observed in elimination reactions of quaternary ammonium salts and tertiary sulfonium salts, and in certain other cases.

HOFMANN (1851).

See also *Zaitsev rule*.

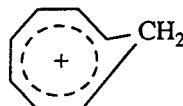
homo

(1) An acronym for *Highest Occupied Molecular Orbital*. See *frontier orbitals*.

(2) A prefix (consisting of lower case letters, homo,) used to indicate a higher homologue of a compound.

homoaromatic

Whereas in an *aromatic* molecule there is continuous overlap of p-orbitals over a cyclic array of atoms, in a *homoaromatic* molecule there is a formal discontinuity in this overlap resulting from the presence of a single sp³ hybridized atom at one or several positions within the ring; p-orbital overlap apparently bridges these sp³ centres, and features associated with aromaticity are manifest in the properties of the compound. Pronounced *homoaromaticity* is not normally associated with neutral molecules, but mainly with species bearing an electrical charge, e.g., the "homotropylium" cation, C₈H₉⁺,



In bis, tris, (etc.) *homoaromatic* species, two, three, (etc.) single sp³ centres separately interrupt the π -electron system.

See also *homoconjugation* (2).

homoconjugation

+ (1) Association between a base and its *conjugate acid* through a *hydrogen bond* (B···HB⁺ or AH···A⁻). *Homoassociation* is a more appropriate term for this phenomenon.

(2) The orbital overlap of two π -systems separated by a non-conjugating group, such as CH₂.

See also *conjugate acid-base pair, conjugated system, homoaromatic*.

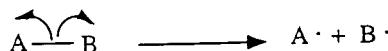
homoleptic

Transition metal or Main Group compounds having only one type of *ligand* are said to be *homoleptic*, e.g. TaMe₅.

See also *heteroleptic*.

homolysis, homolytic

The cleavage of a *bond* ("homolytic cleavage" or "homolytic fission") so that each of the molecular fragments between which the bond is broken retains one of the bonding electrons. A *unimolecular reaction* involving homolysis of a bond (not forming part of a cyclic structure) in a *molecular entity* containing an even number of (paired) electrons results in the formation of two radicals:



It is the reverse of *colligation*. Homolysis is also commonly a feature of *bimolecular substitution reactions* (and of other reactions) involving radicals and molecules.

See also *bond dissociation energy, heterolysis*.

host

A *molecular entity* that forms *complexes* with organic or inorganic guests, or a chemical species that can accommodate guests within cavities of its crystal structure. Examples include *cryptands* and *crowns* (where there are ion-dipole attractions between heteroatoms and positive ions), *hydrogen-bonded* molecules that form "clathrates" (e.g. hydroquinone and water), and host molecules of *inclusion compounds* (e.g. urea or thiourea). *van der Waals forces* and *hydrophobic interactions* bind the guest to the host molecule in clathrates and inclusion compounds.

Hückel ($4n + 2$) rule

Monocyclic planar (or almost planar) systems of trigonally (or sometimes digonally) hybridized atoms that contain $(4n + 2)$ π -electrons (where n is a non-negative integer) will exhibit *aromatic character*. The rule is generally limited to $n = 0\text{--}5$.

This rule is derived from the Hückel MO calculation on planar monocyclic conjugated hydrocarbons $(CH)_m$, where m is an integer equal to or greater than 3 according to which $(4n + 2)$ π -electrons are contained in a closed-shell system. Examples of systems that obey the Hückel rule include:



Cyclopropenyl cation
($m = 3, n = 0$)



Cyclopentadienyl anion
($m = 5, n = 1$)



Benzene
($m = 6, n = 1$)

Systems containing $4n$ π -electrons (such as cyclobutadiene and the cyclopentadienyl cation) are "antiaromatic".

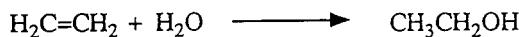
See also *conjugation, Möbius aromaticity*.

hybridization

Linear combination of *atomic orbitals* on an atom. Hybrid orbitals are often used in organic chemistry to describe the bonding molecules containing tetrahedral (sp^3), trigonal (sp^2), and digonal (sp) atoms.

hydration

Addition of water or of the elements of water (i.e. H and OH) to a *molecular entity*. For example, hydration of ethene:



The term is also used in a more restricted sense for the process:



cf. the use of the term in inorganic/physical chemistry to describe the state of the ions of an electrolyte in aqueous solution.

AHRLAND (1979).

See also *aquation, solvation*.

hydrogen bond

The hydrogen bond is a form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e., N, O, or F. Hydrogen bonds may be *intermolecular* or *intramolecular*. With a few exceptions, usually involving fluorine, the associated energies are less than 20–25 kJ mol⁻¹ (5–6 kcal mol⁻¹).

hydrolysis

Solvolytic by water.

hydron

General name for the ion H⁺ either in natural abundance, or where it is not desired to distinguish between the isotopes, as opposed to proton for ¹H⁺, deuteron for ²H⁺ and triton for ³H⁺.

IUPAC NAMES FOR HYDROGEN ATOMS (1988).

hydrophilic

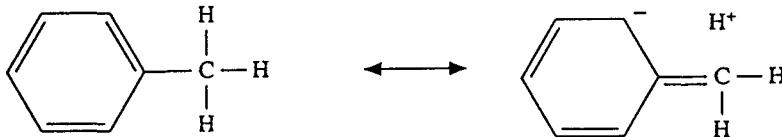
"Water loving". The capacity of a *molecular entity* or of a *substituent* to interact with polar solvents, in particular with water, or with other polar groups.

hydrophobic interaction

The tendency of hydrocarbons (or of *lipophilic* hydrocarbon-like groups in solutes) to form *intermolecular* aggregates in an aqueous *medium*, and analogous intramolecular interactions. The name arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons. However, the phenomenon ought to be attributed to the effect of the hydrocarbon-like groups on the water-water interaction. The misleading alternative term "hydrophobic bond" is discouraged.

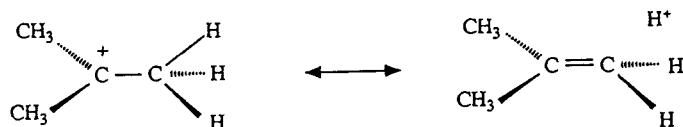
hyperconjugation

In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of σ -bonds (e.g. C-H, C-C, etc.) with a π network. This interaction is customarily illustrated by *contributing structures*, e.g. for toluene (below), sometimes said to be an example of "heterovalent" or "sacrificial hyperconjugation", so named because the contributing structure contains one two-electron bond less than the normal *Lewis formula* for toluene



At present, there is no evidence for sacrificial hyperconjugation in neutral hydrocarbons.

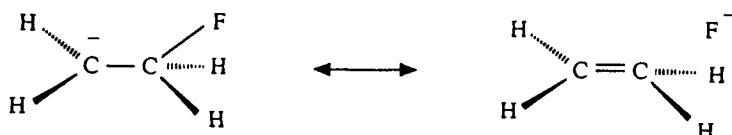
The concept of hyperconjugation is also applied to *carbenium ions* and *radicals*, where the interaction is now between σ -bonds and an unfilled or partially filled π - or p-orbital. A contributing structure illustrating this for the *tert*-butyl cation is:



This latter example is sometimes called an example of "isovalent hyperconjugation" (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula).

Both structures shown on the right hand side are also examples of "double bond- no-bond resonance".

The interaction between filled π or p orbitals and adjacent antibonding σ^* orbitals is referred to as "negative hyperconjugation", as for example in the fluoroethyl anion:



RADOM (1982).

See also *sigma*, *pi*, *n-σ** delocalization.

hypsochromic shift

Shift of a spectral band to higher frequency or shorter wavelength upon substitution or change in medium. It is informally referred to as blue shift.

IUPAC PHOTOCHEMICAL GLOSSARY (1988).

See also *bathochromic shift*.

identity reaction

A *chemical reaction* whose products are chemically identical with the reactants, for example the bimolecular self exchange reaction of CH_3I with I^- .

See also *degenerate rearrangement*.

imbalance

The situation in which *reaction parameters* that characterize different bond forming or bond breaking processes in the same reaction have developed to different extents as the *transition state* is approached along some arbitrarily defined reaction coordinate. For example, in the nitroalkane anomaly, the Brønsted β exponent for proton removal is smaller than the Brønsted α for the nitroalkane, because of imbalance between the amount of bond breaking and resonance delocalization in the transition state. Imbalance is common in reactions such as elimination, addition and other complex reactions that involve proton (hydron) transfer.

BERNASCONI (1992).

See also *synchronous*, *synchronization (principle of imperfect synchronization)*.

+ imene

See *nitrene*.

+ imidogen

See *nitrene*.

+ imidonium ion

See *nitrenium ion*.

+ imin

See *nitrene*.

+ imine radical

See *nitrene*.

inclusion compound (or inclusion complex)

A *complex* in which one component (the *host*) forms a cavity or, in the case of a crystal, a crystal lattice containing spaces in the shape of long tunnels or channels in which molecular entities of a second *chemical species* (the *guest*) are located. There is no covalent bonding between guest and host, the attraction being generally due to *van der Waals forces*. If the spaces in the host lattice are enclosed on all sides so that the guest species is "trapped" as in a cage, such compounds are known as "clathrates" or "cage" compounds".

induction period

The initial slow phase of a *chemical reaction* which later accelerates. Induction periods are often observed with radical reactions, but they may also occur in other systems (for example before steady-state concentration of the reactants is reached).

inductive effect

In strict definition, an experimentally observable effect (on rates of reaction, etc.) of the transmission of charge through a chain of atoms by electrostatic induction. A theoretical distinction may be made between the *field effect*, and the inductive effect as models for the Coulomb interaction between a given site within a *molecular entity* and a remote unipole or

dipole within the same entity. The experimental distinction between the two effects has proved difficult, except for molecules of peculiar geometry, which may exhibit "reversed field effects". Ordinarily the inductive effect and the field effect are influenced in the same direction by structural changes in the molecule and the distinction between them is not clear. This situation has led many authors to include the field effect in the term "inductive effect". Thus the separation of σ values into inductive and resonance components does not imply the exclusive operation of a through-bonds route for the transmission of the non-conjugative part of the substituent effect. To indicate the all-inclusive use of the term inductive, the phrase "so-called inductive effect" is sometimes used. Certain modern theoretical approaches suggest that the "so-called inductive effect" reflects a field effect rather than through-bonds transmission.

EHRENSON, BROWNLEE and TAFT (1973); TAFT and TOPSOM (1987).

See also *field effect, mesomeric effect, polar effect*.

inductomeric effect

A molecular polarizability effect occurring by the inductive mechanism of electron displacement. The consideration of such an effect and the descriptive term have been regarded as obsolescent or even obsolete, but in recent years theoretical approaches have reintroduced substituent polarizability as a factor governing reactivity, etc. and its parametrization has been proposed.

See TAFT and TOPSOM (1987); INGOLD (1953).

inert

Stable and unreactive under specified conditions.

inhibition

The decrease in *rate of reaction* brought about by the addition of a substance (inhibitor), by virtue of its effect on the concentration of a reactant, *catalyst* or *reaction intermediate*. For example, molecular oxygen and *p*-benzoquinone can react as "inhibitors" in many reactions involving *radicals* as *intermediates* by virtue of their ability to act as *scavengers* toward these radicals.

If the rate of a reaction in the absence of inhibitor is v_0 and that in the presence of a certain amount of inhibitor is v , the degree of inhibition (i) is given by

$$i = (v_0 - v)/v_0$$

See also *mechanism based inhibition*.

initiation

A reaction or process generating free *radicals* (or some other *reactive reaction intermediates*) which then induce a *chain reaction*. For example, in the chlorination of alkanes by a radical mechanism the initiation step is the dissociation of molecular chlorine.

inner-sphere (electron transfer)

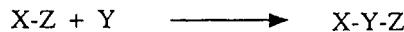
Historically an electron transfer between two metal centres sharing a ligand or atom in their respective coordination shells. The definition has more recently been extended to any situation in which the interaction between the donor and acceptor centres in the *transition state* is significant ($>20 \text{ kJ mol}^{-1}$).

IUPAC PHOTOCHEMICAL GLOSSARY (1992).

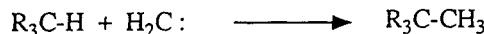
See also *outer-sphere electron transfer*.

insertion

A chemical reaction or transformation of the general type



in which the connecting atom or group Y replaces the bond joining the parts X and Z of the reactant XZ. An example is the carbene insertion reaction



The reverse of an insertion is called an *extrusion*.

See also α -addition.

intermediate

A molecular entity with a lifetime appreciably longer than a molecular vibration (corresponding to a local potential energy minimum of depth greater than RT) that is formed (directly or indirectly) from the reactants and reacts further to give (either directly or indirectly) the products of a chemical reaction; also the corresponding *chemical species*.

See *reaction step*, *elementary reaction*, *stepwise reaction*.

intermolecular

(1) Descriptive of any process that involves a transfer (of atoms, groups, electrons, etc.) or interactions between two or more *molecular entities*.

(2) Relating to a comparison between different molecular entities.

See also *intramolecular*.

internal return

See *ion-pair return*.

intimate ion pair

See *ion pair*.

intramolecular

(1) Descriptive of any process that involves a transfer (of atoms, groups, electrons, etc.) or interactions between different parts of the same *molecular entity*.

(2) Relating to a comparison between atoms or groups within the same molecular entity.

See also *intermolecular*.

intramolecular catalysis

The acceleration of a chemical transformation at one site of a *molecular entity* through the involvement of another *functional ("catalytic") group* in the same molecular entity, without that group appearing to have undergone change in the reaction product. The use of the term should be restricted to cases for which analogous *intermolecular catalysis* by *chemical species* bearing that catalytic group is observable. Intramolecular catalysis can be detected and expressed in quantitative form by a comparison of the reaction rate with that of a comparable model compound in which the catalytic group is absent, or by measurement of the *effective molarity* of the catalytic group.

See also *effective molarity*, *neighbouring group participation*.

intrinsic barrier

The Gibbs energy of activation ($\Delta^{\ddagger}G$) in the limiting case where $\Delta G^\circ = 0$, i.e. when the effect of thermodynamic driving force is eliminated. According to the *Marcus equation*, the intrinsic barrier is related to the *reorganization energy*, λ , of the reaction by the equation

$$\Delta^{\ddagger}G = \lambda/4$$

CANNON (1980); SCHLEENER, AMATORE and KOCHI (1986).

inverse kinetic isotope effect

See *isotope effect*.

inverted micelle

The reversible formation of association colloids from surfactants in non-polar solvents leads to aggregates termed inverted (or inverse, reverse or reversed) *micelles*. Such association is often of the type



and the phenomenon of critical micelle concentration (or an analogous effect) is consequently not observed.

In an inverted micelle the polar *groups* of the surfactants are concentrated in the interior and the *lipophilic* groups extend towards and into the non-polar solvent.

ion pair

A pair of oppositely charged ions held together by Coulomb attraction without formation of a *covalent bond*. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centres closer together than a distance

$$q = 8.36 \times 10^6 z^+ z^- / (\epsilon_r T) \text{ pm}$$

are considered to constitute an ion pair ("Bjerrum ion pair"). [z^+ and z^- are the charge numbers of the ions, and ϵ_r is the relative permittivity (or dielectric constant) of the medium.]

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^- .

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a "loose ion pair", symbolically represented as $X^+ \parallel Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g., by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs.

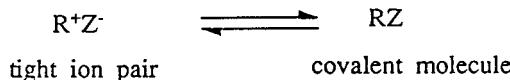
A further conceptual distinction has sometimes been made between two types of loose ion pairs. In "solvent-shared ion pairs" the ionic constituents of the pair are separated by only a single solvent molecule, whereas in "solvent-separated ion pairs" more than one solvent molecule intervenes. However, the term "solvent-separated ion pair" must be used and interpreted with care since it has also widely been used as a less specific term for "loose" ion pair.

See also *common-ion effect*, *dissociation*, *ion-pair return*, *special salt effect*.

ion pair return

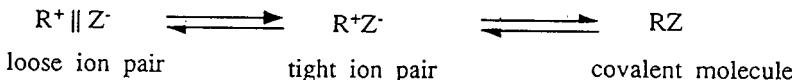
The recombination of a pair of ions R^+ and Z^- formed from ionization of RZ .

If the ions are paired as a tight ion pair and recombine without prior separation into a loose ion pair this is called "internal ion-pair return":



It is a special case of "primary geminate recombination".

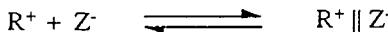
If the ions are paired as a loose ion pair and form the covalent chemical species via a tight ion pair, this is called "external ion-pair return":



It is a special case of "secondary geminate recombination".

When the covalent molecule RZ is reformed without direct evidence of prior partial racemization or without other direct evidence of prior formation of a tight ion pair, (e.g., without partial racemization if the group R is suitably chiral) the internal ion-pair return is sometimes called a "hidden return".

External (unimolecular) ion-pair return is to be distinguished from "external (bimolecular) ion return", the (reversible) process whereby dissociated ions are converted into loose ion pairs:

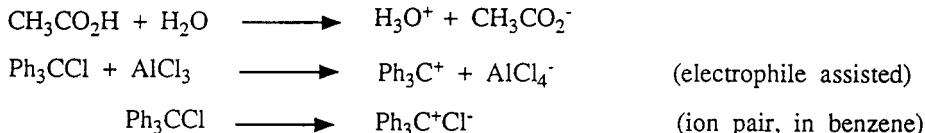


ionic strength, I (SI unit: mol dm⁻³)

In a solution of fully dissociated electrolytes the ionic strength is defined as $I = 0.5 \sum_i c_i z_i^2$, in which c_i is the concentration and z_i the charge number of ionic species i . μ is also defined as $I_m = 0.5 \sum_i m_i z_i^2$, where m_i is the molality.

ionization

The generation of one or more ions. It may occur, e.g. by loss of an electron from a neutral molecular entity, by the unimolecular heterolysis of such an entity into two or more ions, or by a heterolytic substitution reaction involving neutral molecules, such as



The loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization. This terminology is used especially in mass spectroscopy.
See also *dissociation*, *ionization energy*.

ionization energy, E_i (SI unit kJ mol⁻¹ or J per molecule)

The minimum energy required to remove an electron from an isolated *molecular entity* (in its vibrational ground state) in the gaseous phase. If the resulting molecular entity is considered to be in its vibrational ground state, one refers to the energy as the "adiabatic ionization energy". If the molecular entity produced possesses the vibrational energy determined by the Franck-Condon principle (according to which the electron ejection takes place without an accompanying change in molecular geometry), the energy is called the "vertical ionization energy". The name ionization energy is preferred to the somewhat misleading earlier name "ionization potential".

See also *ionization*.

ionizing power

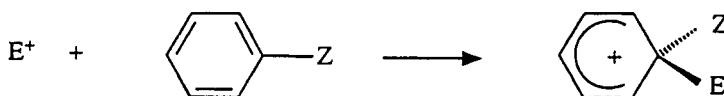
A term to denote the tendency of a particular solvent to promote *ionization* of an uncharged or, less often, charged solute. The term has been used both in a kinetic and in a thermodynamic context.

See also *Dimroth-Reichardt E_T parameter, Grunwald-Winstein equation, Z-value*.

ipso-attack

The attachment of an entering group to a position in an aromatic compound already carrying a *substituent group* (other than hydrogen). The entering group may displace that substituent group but may also itself be expelled or migrate to a different position in a subsequent step. The term "ipso-substitution" is not used, since it is synonymous with substitution.

For example:



where E⁺ is an *electrophile* and Z is a substituent (other than hydrogen).
See also *cine-substitution, tele-substitution*.

isodesmic reaction

A reaction (actual or hypothetical) in which the types of bonds that are made in forming the products are the same as those which are broken in the reactants, e.g.

- (a) PhCOOH + p-ClC₆H₄COO⁻ → PhCOO⁻ + p-ClC₆H₄COOH
- (b) ClCH=CH₂ + ClCH₂CH₂Cl → CH₂=CH₂ + Cl₂CHCH₂Cl

Such processes have advantages for theoretical treatment. The *Hammett equation* as applied to equilibria (cf. (a)) essentially deals with isodesmic processes.

For the use of isodesmic processes in quantum chemistry, see HEHRE et al. (1970).

isoelectronic

Two or more *molecular entities* are described as isoelectronic if they have the same number of valence electrons and the same structure, i.e. number and *connectivity* of atoms, but differ in some of the elements involved. thus

CO, N₂ and NO⁺ are isoelectronic
CH₂=C=O and CH₂=N=N are isoelectronic

CH₃COCH₃ and CH₃N=NCH₃ have the same number of electrons, but have different structures, hence they are not described as isoelectronic.

isoentropic

A reaction series is said to be isoentropic if the individual reactions of the series have the same standard *entropy of activation*.

isoequilibrium relationship

A relationship analogous to the *isokinetic relationship* but applied to equilibrium data. The equation defining the isoequilibrium temperature β is

$$\Delta_r H - \beta \Delta_r S = \text{constant}$$

where Δ_rH and Δ_rS are enthalpy and entropy of reaction, respectively.

See also *isokinetic relationship*.

isokinetic relationship

When a series of structurally related substrates undergo the same general reaction or when the reaction conditions for a single substrate are changed in a systematic way, the enthalpies and entropies of activation sometimes satisfy the relation

$$\Delta^{\ddagger}H - \beta\Delta^{\ddagger}S = \text{constant}$$

where the parameter β is independent of temperature. This equation (or some equivalent form) is said to represent an "isokinetic relationship". The temperature $T = \beta$ (at which all members of a series obeying the isokinetic relationship react at the same rate) is termed the "isokinetic temperature".

Supposed isokinetic relationships as established by direct correlation of $\Delta^{\ddagger}H$ with $\Delta^{\ddagger}S$ are often spurious and the calculated value of β is meaningless, because errors in $\Delta^{\ddagger}H$ lead to compensating errors in $\Delta^{\ddagger}S$. Satisfactory methods of establishing such relationships have been devised.

EXNER (1973); LEFFLER (1955).

See also compensation effect, isoequilibrium relationship, isoselective relationship.

isolobal

The term is used to compare molecular fragments with each other and with familiar species from organic chemistry. Two fragments are isolobal if the number, symmetry properties, approximate energy, and shape of the frontier orbitals and the number of electrons in them are similar.

See isoelectronic.

isomer

One of several species (or molecular entities) that have the same atomic composition (molecular formula) but different line formulae or different stereochemical formulae and hence different physical and/or chemical properties.

isomerization

A chemical reaction, the principal product of which is isomeric with the principal reactant. An intramolecular isomerization that involves the breaking or making of bonds is a special case of a molecular rearrangement.

Isomerization does not necessarily imply molecular rearrangement (e.g. in the case of the interconversion of conformational isomers).

isosbestic point

This term is usually employed with reference to a set of absorption spectra, plotted on the same chart for a set of solutions in which the sum of the concentrations of two principal absorbing components, A and B, is constant. The curves of absorbance against wavelength (or frequency) for such a set of mixtures often all intersect at one or more points, called isosbestic points.

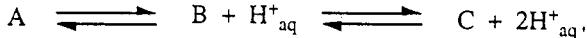
Isosbestic points are commonly met when electronic spectra are taken (a) on a solution in which a chemical reaction is in progress (in which case the two absorbing components concerned are a reactant and a product, A + B), or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g., an acid-base indicator equilibrium.



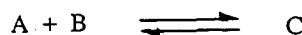
The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. In all these examples, A (and/or B) may be either a single chemical species or a mixture of chemical species present in invariant proportion.

If A and B are single chemical species, isosbestic points will appear at all wavelengths at which their molar absorption coefficients (formerly called extinction coefficients) are the same. (A more involved identity applies when A and B are mixtures of constant proportion.)

If absorption spectra of the types considered above intersect not at one or more isosbestic points but over progressively changing wavelength, this is prima facie evidence in case (a) for the formation of a reaction intermediate in substantial concentration ($A \rightarrow C \rightarrow B$), in case (b) for the involvement of a third absorbing species in the equilibrium, e.g.



or in case (c) for some interaction of A and B, e.g.,



isoselective relationship

A relationship analogous to the *isokinetic relationship*, but applied to *selectivity* data of reactions. At the isoselective temperature, the selectivities of the series of reactions following the relationship are identical.

GIESE (1984).

See also *isoequilibrium relationship*, *isokinetic relationship*.

isotope effect

The effect on the rate or equilibrium constant of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components is referred to as a kinetic isotope effect (see *isotope effect, kinetic*) or a thermodynamic (or equilibrium) isotope effect (see *isotope effect, thermodynamic*), respectively.

isotope effect, equilibrium

see *isotope effect, thermodynamic*.

isotope effect, heavy atom

An isotope effect due to isotopes other than those of hydrogen.

isotope effect, intramolecular

A kinetic isotope effect observed when a single substrate, in which the isotopic atoms occupy equivalent reactive positions, reacts to produce a non-statistical distribution of *isotopomeric* products. In such a case the isotope effect will favor the pathway with lower force constants for displacement of the isotopic nuclei in the *transition state*.

isotope effect, inverse

A kinetic isotope effect which $k^l/k^h < 1$, i.e. the heavier substrate reacts more rapidly than the lighter one, as opposed to the more usual "normal" isotope effect, in which $k^l/k^h > 1$. The isotope effect will normally be "normal" when the frequency differences between the isotopic *transition states* are smaller than in the reactants. Conversely, an inverse isotope effect can be taken as evidence for an increase in the corresponding force constants on passing from the reactant to the transition state.

isotope effect, kinetic

The effect of isotopic substitution on a rate constant is referred to as a kinetic isotope effect.

For example in the reaction



the effect of isotopic substitution in reactant A is expressed as the ratio of rate constants k^l/k^h , where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively.

Within the framework of *transition state theory* in which the reaction is rewritten as



and with neglect of isotopic mass on tunnelling and the transmission coefficient, k^l/k^h can be regarded as if it were the equilibrium constant for an isotope exchange reaction between the transition state $[TS]^{\ddagger}$ and the isotopically substituted reactant A, and calculated from their vibrational frequencies as in the case of a thermodynamic isotope effect (see *isotope effect, thermodynamic*).

Isotope effects like the above, involving a direct or indirect comparison of the rates of reaction of *isotopologues*, are called "intermolecular", in contrast to intramolecular isotope effects (see *isotope effect, intramolecular*), in which a single substrate reacts to produce a non-statistical distribution of *isotopomeric* product molecules.

See WOLFSBERG (1972).

isotope effect, primary

A kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in the *rate-controlling step* or in a *pre-equilibrium* step of a specified reaction is

termed a primary isotope effect. The corresponding isotope effect on the equilibrium constant of a reaction in which one or more bonds to isotopic atoms are broken, is called a "primary equilibrium isotope effect".

See also *isotope effect, secondary*.

isotope effect, secondary

A kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the *rate-controlling step* or in a *pre-equilibrium* step of a specified reaction, and is therefore not a primary isotope effect, is termed a secondary isotope effect. One speaks of α , β (etc.) secondary isotope effects, where α , β (etc.) denote the position of isotopic substitution relative to the reaction centre. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "secondary equilibrium isotope effect".

Secondary isotope effects have been discussed in terms of the conventional electronic effects of physical organic chemistry, e.g. induction, *hyperconjugation*, *hybridization*, etc., since these properties are determined by the electron distribution, that depends on vibrationally averaged bond lengths and angles which vary slightly with isotopic substitution. While this usage is legitimate, the term "electronic isotope effect" should be avoided, because of the misleading implication that such an effect is electronic rather than vibrational in origin.

See also *isotope effect, steric*.

isotope effect, solvent

A kinetic or equilibrium isotope effect resulting from change in the isotopic composition of the solvent.

isotope effect, steric

A secondary isotope effect attributed to the different vibrational amplitudes of *isotopologues*. For example, both the mean and mean-square amplitudes of vibrations associated with C-H bonds are greater than those of C-D bonds. The greater effective bulk of molecules containing the former may be manifested by a *steric effect* on a rate or equilibrium constant.

isotope effect, thermodynamic

The effect of isotopic substitution on an equilibrium constant is referred to as a thermodynamic (or equilibrium) isotope effect.

For example, the effect of isotopic substitution in reactant A that participates in the equilibrium:



is the ratio K^l/K^h of the equilibrium constant for the reaction in which A contains the light isotope to that in which it contains the heavy isotope. The ratio can be expressed as the equilibrium constant for the isotopic exchange reaction:



in which reactants such as B that are not isotopically substituted do not appear.

The potential energy surfaces of isotopic molecules are identical to a high degree of approximation, so thermodynamic isotope effects can only arise from the effect of isotopic mass on the nuclear motions of the reactants and products, and can be expressed quantitatively in terms of partition function ratios for nuclear motion:

$$\frac{K^l}{K^h} = \frac{(Q_{\text{nuc}}^l / Q_{\text{nuc}}^h)_C}{(Q_{\text{nuc}}^l / Q_{\text{nuc}}^h)_A}$$

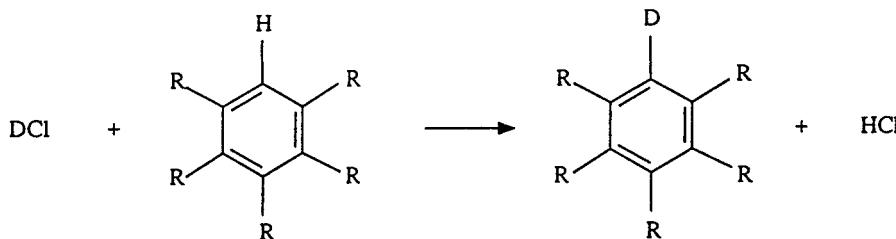
Although the nuclear partition function is a product of the translational, rotational and vibrational partition functions, the isotope effect is determined almost entirely by the last named, specifically by vibrational modes involving motion of isotopically different atoms. In the case of light atoms (i.e. protium *vs.* deuterium or tritium) at moderate temperatures, the isotope effect is dominated by zero-point energy differences.

WOLFSBERG (1972).

See also *fractionation factor*.

isotope exchange

A chemical reaction in which the reactant and product *chemical species* are chemically identical but have different isotopic composition. In such a reaction the isotope distribution tends towards equilibrium (as expressed by fractionation factors) as a result of transfers of isotopically different atoms or groups. For example,

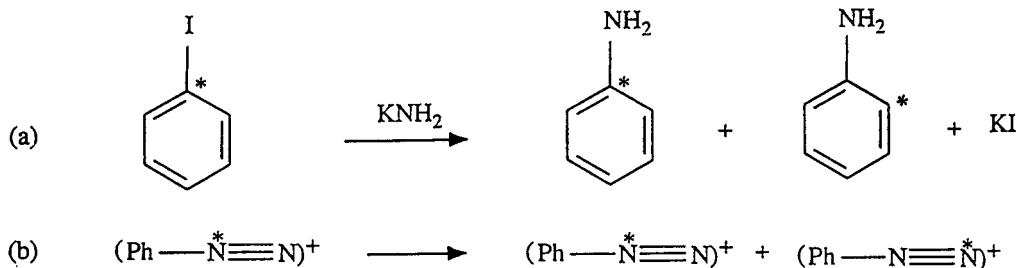
**isotopic perturbation, method of**

NMR shift difference measurement of the isotope effect on a fast (degenerate) equilibrium between two species which are equivalent except for isotopic substitution. This can be used to distinguish a rapidly equilibrating mixture with time-averaged symmetry from a single structure with higher symmetry.

SIEHL (1987).

isotopic scrambling

The achievement, or the process of achieving, an equilibrium distribution of isotopes within a specified set of atoms in a *chemical species* or group of chemical species. For example,



(* denotes position of an isotopically different atom.)
See also *fractionation factor*.

isotopologue

A molecular entity that differs only in isotopic composition (number of isotopic substitutions), e.g. CH₄, CH₃D, CH₂D₂...

isotopomer

Isomers having the same number of each isotopic atom but differing in their positions. The term is a contraction of "isotopic isomer".

Isotopomers can be either constitutional isomers (e.g. CH₂DCH=O and CH₃CD=O) or isotopic stereoisomers (e.g. (R)- and (S)-CH₃CHDOH or (Z)- and (E)-CH₃CH=CHD).

IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

isovalent hyperconjugation

See *hyperconjugation*.

Kamlet-Taft solvent parameters

Parameters of the Kamlet-Taft solvatochromic relationship which measure separately the hydrogen bond donor (α), hydrogen bond acceptor (β), and dipolarity/polarizability (π^*) properties of solvents as contributing to overall solvent *polarity*.

KAMLET, ABBOUD and TAFT (1981).

Kekulé structure (for aromatic compounds)

A representation of an *aromatic molecular entity* (such as benzene), with fixed alternating single and double bonds, in which interactions between multiple bonds are assumed to be absent.

For benzene,



and



are the Kekulé structures.

kinetic control (of product composition)

The term characterizes conditions (including reaction times) that lead to reaction products in a proportion governed by the relative rates of the parallel (forward) reactions in which the products are formed, rather than by the respective overall equilibrium constants.

See also *thermodynamic control*.

kinetic electrolyte effect (kinetic ionic-strength effect)

The general effect of an added electrolyte (i.e. an effect other than, or in addition to, that due to its possible involvement as a reactant or catalyst) on the observed rate constant of a reaction in solution. At low concentrations (when only long-range coulombic forces need to be considered) the effect on a given reaction is determined only by the *ionic strength* of the solution and not by the chemical identity of the ions. For practical purposes, this concentration range is roughly the same as the region of validity of the Debye-Hückel limiting law for activity coefficients. At higher concentrations, the effect of an added electrolyte depends also on the chemical identity of the ions. Such specific action can usually be interpreted as the incursion of a *reaction path* involving an ion of the electrolyte as reactant or catalyst, in which case the action is not properly to be regarded just as a kinetic electrolyte effect.

Kinetic electrolyte effects are usually (too restrictively and therefore incorrectly) referred to as "kinetic salt effects".

A kinetic electrolyte effect ascribable solely to the influence of the ionic strength on activity coefficients of ionic reactants and transition states is called a "primary kinetic electrolyte effect".

A kinetic electrolyte effect arising from the influence of the ionic strength of the solution upon the *pre-equilibrium* concentration of an ionic species that is involved in a subsequent *rate-limiting step* of a reaction is called a "secondary kinetic electrolyte effect". A common case encountered in practice is the effect on the concentration of hydrogen ion (acting as catalyst) produced from the *ionization* of a weak acid in a buffer solution.

See also *common-ion effect, order of reaction*.

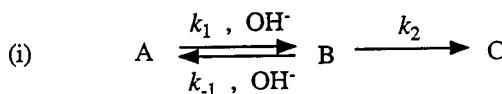
kinetic ambiguity

Synonymous with *kinetic equivalence*.

kinetic equivalence

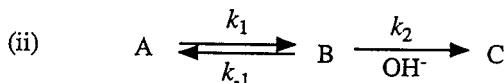
Two reaction schemes are kinetically equivalent if they imply the same *rate law*.

For example, consider the two schemes (i) and (ii) for the formation of C from A:



Providing that B does not accumulate as a *reaction intermediate*.

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A] [\text{OH}^-]}{k_2 + k_{-1}[\text{OH}^-]} \quad (1)$$



Providing that B does not accumulate as a reaction intermediate

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A] [\text{OH}^-]}{k_{-1} + k_2 [\text{OH}^-]} \quad (2)$$

Both equations for $d[C]/dt$ are of the form

$$\frac{d[C]}{dt} = \frac{r[A][OH^-]}{1 + s[OH^-]} \quad (3)$$

where r and s are constants (sometimes called "coefficients in the rate equation"). The equations are identical in their dependence on concentrations and do not distinguish whether OH^- catalyses the formation of B , and necessarily also its reversion to A , or is involved in its further transformation to C . The two schemes are therefore kinetically equivalent under conditions to which the stated provisos apply.

kinetic isotope effect

See *isotope effect*.

Koppel-Palm solvent parameters

Parameters to measure separately the ability of a solvent to enter into non-specific solvent-solute interactions (permittivity ϵ and refractive index n_D) and specific solvent-solute interaction (solvent basicity or nucleophilicity B and solvent acidity or electrophilicity E) as contributing to overall solvent polarity.

KOPPEL and PALM (1972).

Kosower Z-value

See *Z-value*.

labile

The term has loosely been used to describe a relatively *unstable* and *transient chemical species* or (less commonly) a relatively *stable* but reactive species. It must therefore not be used without explanation of the intended meaning.

See also *inert, persistent, reactive, unreactive*.

least nuclear motion, principle of

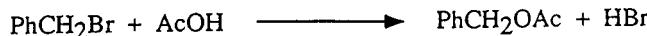
The hypothesis that, for given reactants, the reactions involving the smallest change in nuclear positions will have the lowest *energy of activation*. (It is also often simply referred to as principle of least motion.)

HINE (1977).

leaving group

An atom or *group* (charged or uncharged) that becomes detached from an atom in what is considered to be the residual or main part of the *substrate* in a specified reaction.

For example, in the heterolytic solvolysis of benzyl bromide in acetic acid



the leaving group is Br^- ; in the reaction



the leaving group is NMe_3 ; in the *electrophilic* nitration of benzene, it is H^+ . The term has meaning only in relation to a specified reaction. The leaving group is not, in general, the same as the *substituent group* present in the substrate (e.g. bromo and trimethylammonio in the substrates of the first two examples above.)

A slightly different usage of the term prevails in the (non-mechanistic) naming of transformations, where the actual substituent group present in the substrate (and also in the product) is referred to as the leaving group.

See also *electrofuge, entering group, nucleofuge*.

Leffler's assumption

See *Hammond principle*.

left-to-right convention

Arrangement of the structural formulae of the reactants so that the bonds to be made or broken form a linear array in which the electrons move from left to right.

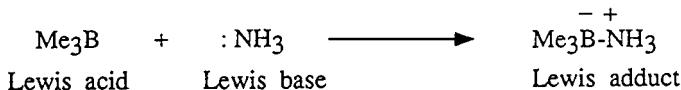
IUPAC REACTION MECHANISMS (1989).

levelling effect

The tendency of a solvent to make all *Bronsted acids* whose acidity exceeds a certain value appear equally acidic. It is due to the complete transfer to a *protophilic* solvent of a hydron from a dissolved acid stronger than the *conjugate acid* of the solvent. The only acid present to any significant extent in all such solutions is the *lyonium ion*. For example, the solvent water has a levelling effect on the acidities of HClO_4 , HCl , and HI : aqueous solutions of these acids at the same (moderately low) concentrations have the same acidities. A corresponding levelling effect applies to strong bases in *protogenic* solvents.

Lewis acid

A molecular entity (and the corresponding chemical species) that is an electron-pair acceptor and therefore able to react with a *Lewis base* to form a *Lewis adduct*, by sharing the electron pair furnished by the Lewis base. For example:



See also *coordination*, *dipolar bond*.

Lewis acidity

The thermodynamic tendency of a substrate to act as a *Lewis acid*. Comparative measures of this property are provided by the equilibrium constants for Lewis adduct formation of a series of Lewis acids with a common reference *Lewis base*.

See also *acceptor number (AN)*, *electrophilicity*.

Lewis adduct

The *adduct* formed between a *Lewis acid* and a *Lewis base*.

Lewis base

A molecular entity (and the corresponding chemical species) able to provide a pair of electrons and thus capable of *coordination* to a *Lewis acid*, thereby producing a *Lewis adduct*.

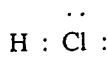
Lewis basicity

The thermodynamic tendency of a substance to act as a *Lewis base*. Comparative measures of this property are provided by the equilibrium constants for *Lewis adduct* formation for a series of Lewis bases with a common reference *Lewis acid*.

See also *donor number (DN)*, *nucleophilicity*.

Lewis formula (electron dot or Lewis structure)

Molecular structure in which the valency electrons are shown as dots so placed between the bonded atoms that one pair of dots represents two electrons or one covalent (single) bond, e.g.



A double bond is represented by two pairs of dots, etc. Dots representing non-bonded outer-shell electrons are placed adjacent to the atoms with which they are associated, but not between the atoms. Formal charges (e.g. +, -, 2+, etc.) are attached to atoms to indicate the difference between the positive nuclear charge (atomic number) and the total number of electrons (including those in the inner shells), on the formal basis that bonding electrons are shared equally between atoms they join. (Bonding pairs of electrons are usually denoted by lines, representing *covalent bonds*, as in *line formulae*.)

lifetime (mean lifetime), τ

The lifetime of a *chemical species* which decays in a first-order process is the time needed for a concentration of this species to decrease to $1/e$ of its original value. Statistically, it represents the mean life expectancy of an excited species. In a reacting system in which the decrease in concentration of a particular chemical species is governed by a first-order *rate law*, it is equal to the reciprocal of the sum of the (pseudo)unimolecular rate constants of all processes which cause the decay. When the term is used for processes which are not first order, the lifetime depends on the initial concentration of the species, or of a quencher, and should be called apparent lifetime instead.

See also *chemical relaxation*, *half-life*, *rate of reaction*.

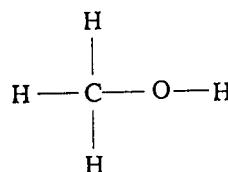
ligand

If it is possible to indicate a "central atom" in a polyatomic *molecular entity*, the atoms or *groups* bound to that atom are called ligands. (Cf. IUPAC INORGANIC NOMENCLATURE (1990); Rule I-10.2.3.) The term is generally used in connection with metallic "central atoms".

In biochemistry a part of a polyatomic molecular entity may be considered central, and atoms, groups or molecules bound to that part are considered ligands (Cf. BIOCHEMICAL NOMENCLATURE (1992)).

line formula

A two-dimensional representation of *molecular entities* in which atoms are shown joined by lines representing single or multiple bonds, without any indication or implication concerning the spatial direction of bonds. For example, methanol is represented as



(The term should not be confused with the representation of chemical formulae by the "Wiswesser line notation", a method of string notation. Formulae in this notation are also known as "Wiswesser line formulae".)

linear free-energy relation

A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy relations) are the *Brønsted relation*, and the *Hammett equation* (see also σ -value).

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a standard free energy (Gibbs energy) change, and the logarithm of a rate constant is a linear function of the free energy (Gibbs energy) of activation.

It has been suggested (IUPAC PHYSICAL ORGANIC GLOSSARY (1983)) that this name should be replaced by *Linear Gibbs Energy Relation*, but at present there is little sign of acceptance of this change.

The area of physical organic chemistry which deals with such relations is commonly referred to as "Linear Free-Energy Relationships".

linear Gibbs energy relation

See *linear free-energy relation*.

linear solvation energy relationships

Equations involving the application of *solvent parameters* in linear or multiple (linear) regression expressing the solvent effect on the rate or equilibrium constant of a reaction.

See *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft solvent parameter*, *Koppel-Palm solvent parameter*, *Z-value*.

line-shape analysis

Determination of rate constants for a chemical exchange from the shapes of spectroscopic lines of dynamic processes. The method is most often used in nuclear magnetic resonance spectroscopy.

Lineweaver-Burk plot

See *Michaelis-Menten kinetics*.

lipophilic

Literally "fat-loving". Applied to *molecular entities* (or parts of molecular entities) having a tendency to dissolve in fat-like (e.g. hydrocarbon) solvents.

See also *hydrophilic*, *hydrophobic interaction*.

London forces

Attractive forces between apolar molecules, due to their mutual polarizability. They are also components of the forces between polar molecules. Also called "dispersion forces".

See also *van der Waals forces*.

lone (electron) pair

Two paired electrons localized in the valence shell on a single atom. Lone pairs should be designated with two dots.

The term "nonbonding electron pair" is more appropriate, and is found in many modern text books.

loose ion pair

See *ion pair*.

LUMO

See *frontier orbitals*.

lyate ion

The anion produced by hydron removal from a solvent molecule. For example, the hydroxide ion is the lyate ion of water.

lyonium ion

The cation produced by hydronation of a solvent molecule. For example, CH_3OH_2^+ is the lyonium ion of methanol.

See also *onium ion*.

macroscopic diffusion control

See *mixing control*.

magic acid

See superacid.

magnetic equivalence

Nuclei having the same resonance frequency in nuclear magnetic resonance spectroscopy and also identical spin-spin interactions with the nuclei of a neighbouring group are magnetically equivalent. The spin-spin interaction between magnetically equivalent nuclei does not appear, and thus has no effect on the multiplicity of the respective NMR signals. Magnetically equivalent nuclei are necessarily also chemically equivalent, but the reverse is not necessarily true.

magnetization transfer

NMR method for determining kinetics of chemical exchange by perturbing the magnetization of nuclei in a particular site or sites and following the rate at which magnetic equilibrium is restored. The most common perturbations are saturation and inversion, and the corresponding techniques are often called "saturation transfer" and "selective inversion-recovery".

See also *saturation transfer*.

Marcus equation

A general expression which correlates the Gibbs energy of activation ($\Delta_f^{\ddagger}G$) with the driving force (Δ_rG°) of the reaction:

$$\Delta_f^{\ddagger}G = (\lambda/4)(1 + \Delta_rG^{\circ}/\lambda)^2$$

where λ is the *reorganization energy* and Δ_rG° is the standard free energy of the reaction corrected for the electrostatic work required to bring the reactants together. $\lambda/4$ is the *intrinsic barrier of the reaction*. Originally developed for *outer-sphere electron transfer* reactions, the Marcus equation has later been applied also to atom and group transfer reactions.

MARCUS (1964); ALBERY (1980).

Markownikoff rule

"In the addition of hydrogen halides to unsymmetrically constituted [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms." Originally formulated by Markownikoff (Markovnikov) to generalize the orientation in additions of hydrogen halides to simple alkenes, this rule has been extended to polar *addition reactions* as follows. "In the *heterolytic* addition of a polar molecule to an alkene or alkyne, the more electronegative (nucleophilic) atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms."

This is an indirect statement of the common mechanistic observation, that the more electropositive (electrophilic) atom (or part) of the polar molecule becomes attached to the end of the multiple bond that would result in the more stable *carbenium ion* (whether or not a carbe-

nium ion is actually formed as a *reaction intermediate* in the addition reaction). Addition in the opposite sense is commonly called "anti-Markovnikov addition".

MARKOWNIKOFF (1870).

mass-law effect

At equilibrium, the product of the activities (or concentrations) of the reacting species is constant. Thus for the equilibrium



$$K = [C]^\gamma [D]^\delta / [A]^\alpha [B]^\beta$$

GULDBERG and WAAGE (1879).

See also *common-ion effect, equilibrium*.

matrix isolation

A term which refers to the isolation of a reactive or unstable species by dilution in an inert matrix (argon, nitrogen, etc.), usually condensed on a window or in an optical cell at low temperature, to preserve its structure for identification by spectroscopic or other means.

IUPAC ATMOSPHERIC GLOSSARY (1990).

mean lifetime

See *lifetime*.

mechanism

A detailed description of the process leading from the reactants to the products of a reaction, including a characterization as complete as possible of the composition, structure, energy and other properties of *reaction intermediates*, products, and *transition states*. An acceptable mechanism of a specified reaction (and there may be a number of such alternative mechanisms not excluded by the evidence) must be consistent with the reaction stoichiometry, the *rate law*, and with all other available experimental data, such as the stereochemical course of the reaction. Inferences concerning the electronic motions which dynamically interconvert successive species along the *reaction path* (as represented by curved arrows, for example) are often included in the description of a mechanism.

It should be noted that for many reactions all this information is not available and the suggested mechanism is based on incomplete experimental data. It is not appropriate to use the term *mechanism* to describe a statement of the probable sequence in a set of stepwise reactions. That should be referred to as a *reaction sequence*, and not a *mechanism*.

See also *Gibbs energy diagram*.

mechanism-based inhibition

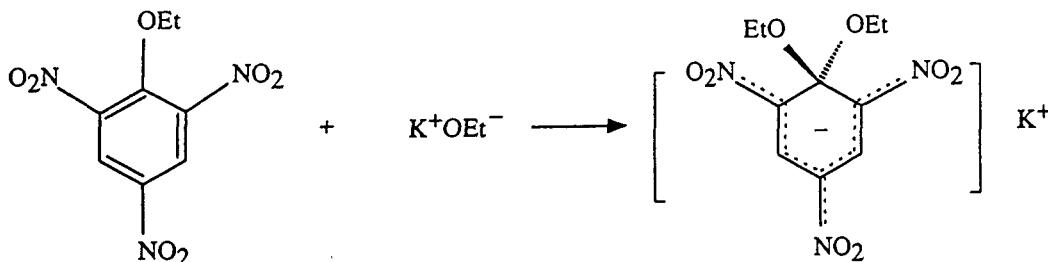
Irreversible *inhibition* of an enzyme due to its catalysis of the reaction of an artificial substrate. Also called "suicide inhibition".

medium

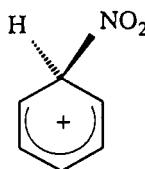
The phase (and composition of the phase) in which *chemical species* and their reactions are studied in a particular investigation.

Meisenheimer adduct

A cyclohexadienyl derivative formed as *Lewis adduct* from a *nucleophile* (*Lewis base*) and an *aromatic* or *heteroaromatic* compound, also called Jackson-Meisenheimer adduct. In earlier usage the term "Meisenheimer complex" was restricted to the typical Meisenheimer alkoxide adducts of nitro-substituted aromatic ethers, e.g.,



Analogous cationic adducts, such as



considered to be *reaction intermediates* in *electrophilic aromatic substitution reactions*, are called "Wheland intermediates", and sometimes, inappropriately, σ -complexes.

JACKSON and GAZZOLO (1900); BUNCEL, CRAMPTON, STRAUSS and TERRIER. (1984).
See also σ -adduct.

melting point (corrected/uncorrected)

The term originally signified that a correction was made (not made) for the emergent stem of the thermometer. In current usage it often means that the accuracy of the thermometer was (was not) verified. This current usage is inappropriate and should be abandoned.

mesolytic cleavage

Cleavage of a bond in a *radical ion* whereby a *radical* and an *ion* are formed. The term reflects the mechanistic duality of the process, which can be viewed as homolytic or heterolytic depending on how the electrons are attributed to the fragments.

See MASLAK and NARVAEZ (1990).

mesomeric effect

The effect (on reaction rates, ionization equilibria, etc.) attributed to a substituent due to overlap of its p - or π -orbitals with the p - or π -orbitals of the rest of the *molecular entity*. *Delocalization* is thereby introduced or extended, and electronic charge may flow to or from the substituent. The effect is symbolized by M.

Strictly understood, the mesomeric effect operates in the ground electronic state of the molecule. When the molecule undergoes electronic excitation or its energy is increased on the way to the *transition state* of a *chemical reaction*, the mesomeric effect may be enhanced by the *electromeric effect*, but this term is not much used, and the mesomeric and electromeric effects tend to be subsumed in the term *resonance effect of a substituent*.

See also *electronic effect*, *field effect*, *inductive effect*.

mesomerism

Essentially synonymous with *resonance*. The term is particularly associated with the picture of π -electrons as less localized in an actual molecule than in a *Lewis formula*.

The term is intended to imply that the correct representation of a structure is intermediate between two or more Lewis formulae.

See also *aromatic (2)*, *delocalization*.

mesophase

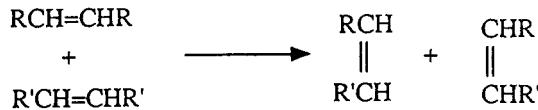
The phase of a liquid crystalline compound between the crystalline and the isotropic liquid phase.

metastable (chemical species)

See *transient (chemical species)*.

metathesis

A *bimolecular* process formally involving the exchange of a bond (or bonds) between similar interacting *chemical species* so that the bonding affiliations in the products are identical (or closely similar) to those in the reactants. For example:



(The term has its origin in inorganic chemistry with a different meaning, but this older usage is not applicable in physical organic chemistry.)

+ methylene

See *carbene*.

+ methylidyne

See *carbyne*.

micellar catalysis

The acceleration of a *chemical reaction* in solution by the addition of a surfactant at a concentration higher than its *critical micelle concentration* so that the reaction can proceed in the environment of surfactant aggregates (*micelles*). (Rate enhancements may be due, for example, to higher concentration of the reactants in that environment, more favourable orientation and solvation of the species, or enhanced rate constants in the micellar pseudophase of the surfactant aggregate.) Micelle formation can also lead to a decreased reaction rate.

See also *catalyst*.

micelle

Surfactants in solution are often association colloids, that is, they tend to form aggregates of colloidal dimensions, which exist in equilibrium with the molecules or ions from which they are formed. Such aggregates are termed *micelles*.

See also *inverted micelle*.

IUPAC MANUAL APPENDIX II (1972).

Michaelis-Menten kinetics

The dependence of an initial *rate of reaction* upon the concentration of a *substrate S* that is present in large excess over the concentration of an enzyme or other *catalyst* (or reagent) *E* with the appearance of saturation behaviour following the Michaelis-Menten equation,

$$v = V[S]/(K_m + [S]),$$

where *v* is the observed initial rate, *V* is its limiting value at substrate saturation (i.e., $[S] \gg K_m$), and K_m the substrate concentration when $v = V/2$. The definition is experimental, i.e., it applies to any reaction that follows an equation of this general form. The symbols V_{\max} or v_{\max} are sometimes used for *V*.

The parameters *V* and K_m (the "Michaelis constant") of the equation can be evaluated from the slope and intercept of a linear plot of v^{-1} against $[S]^{-1}$ (a "Lineweaver-Burk plot") or from slope and intercept of a linear plot of *v* against $v/[S]$ ("Eadie-Hofstee plot").

A Michaelis-Menten equation is also applicable to the condition where *E* is present in large excess, in which case the concentration $[E]$ appears in the equation instead of $[S]$.

The term has sometimes been used to describe reactions that proceed according to the scheme



in which case $K_m = (k_{-1} + k_{\text{cat}})/k_1$ (Briggs-Haldane conditions). It has more usually been applied only to the special case in which $k_{-1} \gg k_{\text{cat}}$ and $K_m = k_{-1}/k_1 = K_s$; in this case K_m is a true dissociation constant (Michaelis-Menten conditions).

See also *rate-determining step*.

microscopic chemical event

See *chemical reaction, molecularity*.

microscopic diffusion control (encounter control)

The observable consequence of the limitation that the rate of a bimolecular *chemical reaction* in a homogeneous medium cannot exceed the rate of encounter of the reacting *molecular entities*.

If (hypothetically) a *bimolecular* reaction in a homogeneous medium occurred instantaneously when two reactant molecular entities made an encounter, the *rate of reaction* would be an *encounter-controlled rate*, determined solely by rates of diffusion of reactants. Such a hypothetical "fully diffusion controlled rate" is also said to correspond to "total microscopic diffusion control", and represents the asymptotic limit of the rate of reaction as the rate constant for the chemical conversion of the encounter pair into product (or products) becomes large relative to the rate constant for separation (or dissociation) of the encounter pair.

"Partial microscopic diffusion control" is said to operate in a homogeneous reaction when the rates of chemical conversion and of separation are comparable. (The degree of microscopic diffusion control cannot usually be determined with any precision.)

See also *mixing control*.

microscopic reversibility, principle of

In a reversible reaction, the mechanism in one direction is exactly the reverse of the mechanism in the other direction. This does not apply to reactions that begin with a photochemical excitation.

See also *chemical reaction, detailed balancing*.

migration

(1) The (usually *intramolecular*) transfer of an atom or group during the course of a *molecular rearrangement*.

(2) The movement of a bond to a new position, within the same *molecular entity*, is known as "bond migration".

Allylic rearrangements, e.g.,



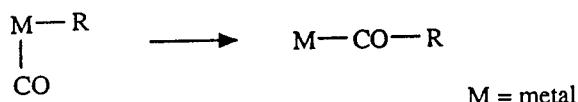
exemplify both types of migration.

migratory aptitude

The term is applied to characterize the relative tendency of a group to participate in a rearrangement. In nucleophilic rearrangements (*migration* to an electron-deficient centre), the migratory aptitude of a group is loosely related to its capacity to stabilize a partial positive charge, but exceptions are known, and the position of hydrogen in the series is often unpredictable.

migratory insertion

A combination of *migration* and *insertion*. The term is mainly used in organometallic chemistry.



minimum structural change, principle of

See *molecular rearrangement*.

mixing control

The experimental limitation of the *rate of reaction* in solution by the rate of mixing of solutions of the two reactants. It can occur even when the reaction rate constant is several powers of 10 less than that for an *encounter-controlled* rate. Analogous (and even more important) effects of the limitation of reaction rates by the speed of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas) systems.

See also *microscopic diffusion control, stopped flow*.

Möbius aromaticity

A monocyclic array of orbitals in which there is a single out-of-phase overlap (or, more generally, an odd number of out-of-phase overlaps) reveals the opposite pattern of *aromatic* character to Hückel systems; with $4n$ electrons it is stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic). In the excited state $4n + 2$ Möbius π -electron systems are stabilized, and $4n$ systems are destabilized. No examples of ground-state Möbius π -systems are known, but the concept has been applied to *transition states of pericyclic reactions* [see *aromatic (3)*].

The name is derived from the topological analogy of such an arrangement of orbitals to a Möbius strip.

HEILBRONNER (1964); ZIMMERMAN (1971).

See also *Hückel (4n + 2) rule*.

moiety

In physical organic chemistry moiety is generally used to signify part of a molecule, e.g. in an ester R^1COOR^2 the alcohol moiety is R^2O . The term should not be used for a small fragment of a molecule.

molecular entity

Any constitutionally or isotopically distinct atom, *molecule*, ion, *ion pair*, *radical*, *radical ion*, *complex*, *conformer* etc., identifiable as a separately distinguishable entity.

Molecular entity is used in this glossary as a general term for singular entities, irrespective of their nature, while *chemical species* stands for sets or ensembles of molecular entities. Note that the name of a compound may refer to the respective molecular entity or to the chemical species, e.g. methane, may mean a single molecule of CH₄ (molecular entity) or a molar amount, specified or not (chemical species), participating in a reaction.

The degree of precision necessary to describe a molecular entity depends on the context. For example "hydrogen molecule" is an adequate definition of a certain molecular entity for some purposes, whereas for others it is necessary to distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the hydrogen molecule.

molecular mechanics calculation

An empirical calculational method intended to give estimates of structures and energies for conformations of molecules. The method is based on the assumption of "natural" bond lengths and angles, deviation from which leads to strain, and the existence of torsional interactions and attractive and/or repulsive *van der Waals* and dipolar forces between non-bonded atoms. The method is also called "(empirical) force-field calculations".

BURKERT and ALLINGER (1982).

molecular metal

A non-metallic material whose properties resemble those of metals, usually following oxidative doping; e.g. polyacetylene following oxidative doping with iodine.

molecular orbital

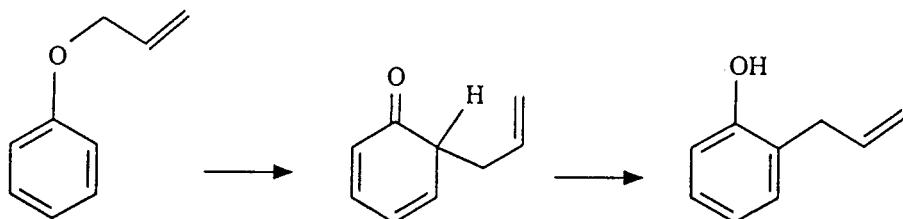
A one-electron wavefunction describing an electron moving in the effective field provided by the nuclei and all other electrons of a *molecular entity* of more than one atom. Such molecular orbitals can be transformed in prescribed ways into component functions to give "localized molecular orbitals". Molecular orbitals can also be described, in terms of the number of nuclei (or "centres") encompassed, as two-centre, multi-centre, etc. molecular orbitals, and are often expressed as a linear combination of *atomic orbitals*.

An orbital is usually depicted by sketching contours on which the wavefunction has a constant value (contour map) or by indicating schematically the envelope of the region of space in which there is an arbitrarily fixed high (say 96%) probability of finding the electron occupying the orbital, giving also the algebraic sign (+ or -) of the wavefunction in each part of that region.

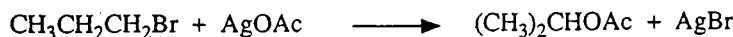
molecular rearrangement

The term is traditionally applied to any reaction that involves a change of connectivity (sometimes including hydrogen), and violates the so-called "principle of minimum structural change". According to this oversimplified principle, *chemical species* do not isomerize in the course of a *transformation*, e.g. *substitution*, or the change of a functional *group* of a chemical species into a different functional group is not expected to involve the making or breaking of more than the minimum number of bonds required to effect that transformation. For example, any new substituents are expected to enter the precise positions previously occupied by displaced groups.

The simplest type of rearrangement is an *intramolecular* reaction in which the product is isomeric with the reactant (one type of "intramolecular isomerization"). An example is the first step of the Claisen rearrangement:



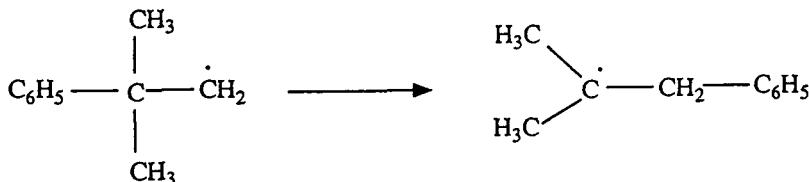
The definition of molecular rearrangement includes changes in which there is a *migration* of an atom or bond (unexpected on the basis of the principle of minimum structural change), as in the reaction



where the *rearrangement stage* can formally be represented as the "1,2-shift" of hydride between adjacent carbon atoms in the carbocation



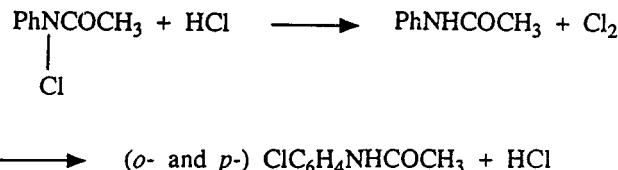
Such migrations occur also in radicals, e.g.:



The definition also includes reactions in which an *entering group* takes up a different position from the *leaving group*, with accompanying bond migration. An example of the latter type is the "allylic rearrangement":



A distinction is made between "intramolecular rearrangements" (or "true molecular rearrangements") and "intermolecular rearrangements" (or "apparent rearrangements"). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage (i.e. the change is intramolecular), whereas in an "intermolecular rearrangement" a migrating group is completely free from the parent molecule and is re-attached to a different position in a subsequent step, as in the Orton reaction:



MAYO (1980).

molecularity

The number of reactant *molecular entities* that are involved in the "microscopic chemical event" constituting an *elementary reaction*. (For reactions in solution this number is always taken to exclude molecular entities that form part of the *medium* and which are involved solely by virtue of their solvation of solutes.) A reaction with a molecularity of one is called "unimolecular", one with a molecularity of two "bimolecular" and of three "termolecular".

See also *chemical reaction, order of reaction*.

molecule

An electrically neutral entity consisting of more than one atom ($n > 1$). Rigorously, a molecule, in which $n > 1$ must correspond to a depression on the potential energy surface that is deep enough to confine at least one vibrational state.

See also *molecular entity*.

More O'Ferrall-Jencks diagram

Visualization of the potential energy surfaces for a reacting system, as a function of two chosen coordinates. It is particularly useful to discuss structural effects on the *transition state geometry* for processes occurring either by stepwise or concerted routes. The use of such diagrams, first suggested for elimination reactions (MORE O'FERRALL (1970)), was later extended to acid-base catalysis and to certain other reactions (JENCKS (1972, 1980)).

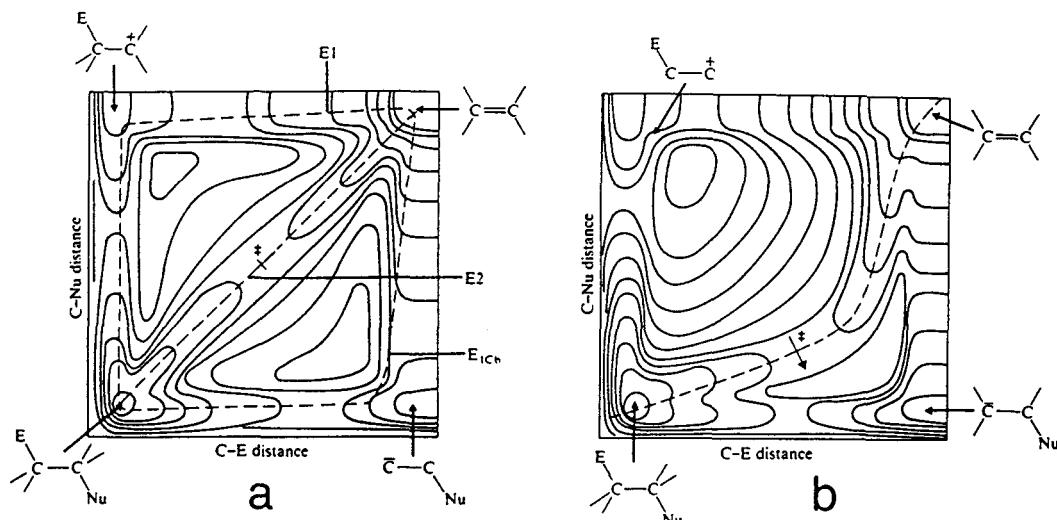


Figure. More O'Ferrall-Jencks diagrams of energy contours for β -elimination reactions as a function of lengths of the two bonds broken. Reaction coordinates follow the dotted lines. **a:** E_2 mechanism with "central" character, simultaneous fission of C_a -Nu and C_b -H bonds. **b:** The result of stabilization of the carbanion, Nu-C-C; a continuation of this trend would result in a switch to the $E1_{cb}$ mechanism (Reproduced from N. S. ISAACS, "Physical Organic Chemistry", Longman Scientific, Essex, UK, (1987), with permission of Longman Scientific).

Structural changes influencing vibrational modes of the transition states cause changes in transition state geometry. Changes in the direction of the reaction coordinate (reactant or product stabilizing- or destabilizing factors) cause changes according to the *Hammond principle*. Structural changes perpendicular to the reaction coordinate (anti-Hammond effects, perpendicular effects) cause changes opposite to the Hammond behaviour, i.e., the easier the process related to the structural change, the more advanced it will be at the transition state.

See WINEY and THORNTON (1975).

multi-centre bond

Representation of some *molecular entities* solely by localized two-electron two-centre bonds appears to be unsatisfactory. Instead, multi-centre bonds have to be considered in which electron pairs occupy orbitals encompassing three or more atomic centres. Examples include the three-centre bonds in diborane, the delocalized π -bonding of benzene, and *bridged carbocations*.

+ multi-centre reaction

A synonym for *pericyclic reaction*. The number of "centres" is the number of atoms not bonded initially, between which single bonds are breaking or new bonds are formed in the transition state. This number does not necessarily correspond to the ring size of the transition state for the pericyclic reaction. Thus, a Diels-Alder reaction is a "four-centre reaction". This terminology has largely been superseded by the more detailed one developed for the various pericyclic reactions.

See *cycloaddition*, *sigmatropic rearrangement*.

multident

See *ambident*.

μ (μ u) and $\underline{\mu}$

Notation for a ligand (prefix) that bridges two or more metal centres. The symbol μ is used for dipole moments.

+ narcissistic reaction

A *chemical reaction* that can be described as the conversion of a reactant into its mirror image, without rotation or translation of the product, so that the product enantiomer actually coincides with the mirror image of the reactant molecule. Examples of such reactions are cited under the entries *fluxional* and *degenerate rearrangement*.

SALEM (1971).

neighbouring group participation

The direct interaction of the reaction centre (usually, but not necessarily, an incipient carbenium centre) with a lone pair of electrons of an atom or with the electrons of a σ - or π -bond contained within the parent molecule but not conjugated with the reaction centre. A distinction is sometimes made between n-, σ - and π -participation.

A rate increase due to neighbouring group participation is known as "anchimeric assistance". "Synartetic acceleration" is the special case of anchimeric assistance ascribed to participation by electrons binding a substituent to a carbon atom in a β -position relative to the leaving group attached to the α -carbon atom. According to the underlying model, these electrons then provide a three-centre bond (or "bridge") "fastening together" (as the word "synartetic" is intended to suggest) the α - and β -carbon atoms between which the charge is divided in the intermediate *bridged ion* formed (and in the transition state preceding its formation). The term synartetic acceleration is not widely used.

See also *intramolecular catalysis, multi-centre bond*.

NHOMO

See *subadjacent orbital*.

NIH shift

The *intramolecular hydrogen migration* which can be observed in enzymatic and chemical hydroxylations of aromatic rings. It is evidenced by appropriate deuterium labelling, i.e.



In enzymatic reactions the NIH shift is generally thought to derive from the rearrangement of arene oxide intermediates, but other pathways have been suggested.

(NIH stands for National Institutes of Health where the shift was discovered.)

HANZLIK, HOGBERG and JUDSON (1984).

nitrene

Generic name for HN_2 and substitution derivatives thereof, containing an electrically neutral univalent nitrogen atom with four non-bonding electrons. Two of these are paired; the other two may have parallel spins (triplet state) or antiparallel spins (singlet state). The name is the strict analogue of carbene and, as a generic name, it is preferred to a number of alternatives proposed ("imene", "imine radical", "azene", "azylene", "azacarbene", "imin", "imidogen").

See LWOWSKI (1970).

nitrenium ion

The cation H_2N^+ and its N-hydrocarbyl derivatives R_2N^+ , in which the nitrogen has a positive charge, and two unshared electrons. A synonymous term is aminylum ion.

IUPAC CLASS NAMES (1993).

no-bond resonance

See *hyperconjugation*.

nonclassical carbocation

A carbocation the ground state of which has delocalized (bridged) bonding π - or σ -electrons. (N.B.: Allylic and benzylic carbocations are not considered nonclassical.)

BARTLETT (1965).

normal kinetic isotope effect

See *isotope effect*.

nucleofuge

A leaving group that carries away the bonding electron pair. For example, in the *hydrolysis* of an alkyl chloride, Cl^- is the nucleofuge. The tendency of atoms or groups to depart with the bonding electron pair is called nucleofugality.

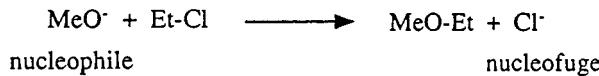
The adjective is nucleofugal.

See also *electrofuge, nucleophile*.

nucleophile, nucleophilic

A nucleophile (or nucleophilic reagent) is a reagent that forms a bond to its reaction partner (the *electrophile*) by donating both bonding electrons.

A "nucleophilic substitution reaction" is a *heterolytic* reaction in which the reagent supplying the entering group acts as a nucleophile. For example

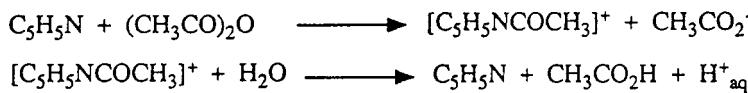


The term "nucleophilic" is also used to designate the apparent polar character of certain *radicals*, as inferred from their higher relative reactivity with reaction sites of lower electron density.

Nucleophilic reagents are *Lewis bases*.

nucleophilic catalysis

Catalysis by a *Lewis base*, involving formation of a *Lewis adduct* as a *reaction intermediate*. For example, the hydrolysis of acetic anhydride in aqueous solution catalysed by pyridine:

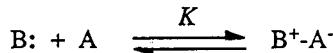


See also *electrophilic, nucleophilicity*.

nucleophilicity

(1) The property of being *nucleophilic*.

(2) The relative reactivity of a *nucleophilic* reagent. (It is also sometimes referred to as "nucleophilic power".) Qualitatively, the concept is related to Lewis basicity. However, whereas Lewis basicity is measured by relative equilibrium constants,



nucleophilicity of a Lewis base is measured by relative *rate constants* of different nucleophilic reagents towards a common *substrate*, most commonly involving formation of a bond to carbon,



See also *electrophilicity, Ritchie equation, Swain-Scott equation*.

 $n-\sigma^*$ delocalization (or $n-\sigma^*$ no bond resonance)

Delocalization of a free electron pair (*n*) into an antibonding σ -orbital (σ^*).

See *hyperconjugation, resonance*.

onium ion

(1) A cation (with its counterion) derived by addition of a hydron to a mononuclear parent hydride of the nitrogen, chalcogen and halogen family, e.g. H_4N^+ ammonium ion.

(2) Derivatives formed by substitution of the above parent ions by univalent groups, e.g. $(\text{CH}_3)_2\text{S}^+\text{H}$ dimethylsulfonium, $(\text{CH}_3\text{CH}_2)_4\text{N}^+$ tetraethylammonium.

(3) Derivatives formed by substitution of the above parent ions by groups having two or three free valencies on the same atom. Such derivatives are, whenever possible, designated by a specific class name. E.g. $\text{R}_2\text{C}=\text{NH}_2^+$ iminium ion.

IUPAC CLASS NAMES (1993).

See also *carbenium ion, carbonium ion*.

opposing reactions

See *composite reactions*.

optical yield

In a *chemical reaction* involving chiral reactants and products, the ratio of the optical purity of the product to that of the precursor, reactant or catalyst. This should not be confused with "enantiomeric excess". The optical yield is in no way related to the chemical yield of the reaction.

IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

See *stereoselectivity*.

orbital

See *atomic orbital, molecular orbital*.

orbital steering

A concept expressing that the stereochemistry of approach of two reacting species is governed by the most favourable overlap of their appropriate *orbitals*.

orbital symmetry

The behaviour of an atomic or localized *molecular orbital* under molecular symmetry operations characterizes its orbital symmetry. For example, under a reflection in an appropriate symmetry plane, the phase of the orbital may be unchanged (symmetric), or it may change sign (antisymmetric), i.e. the positive and negative lobes are interchanged.

A principal context for the use of orbital symmetry is the discussion of chemical changes that involve "conservation of orbital symmetry". If a certain symmetry element (e.g. the reflection plane) is retained along a reaction pathway, that pathway is "allowed" by orbital symmetry conservation if each of the occupied orbitals of the reactant(s) is of the same symmetry type as a similarly (e.g. singly or doubly) occupied orbital of the product(s). This principle permits the qualitative construction of correlation diagrams to show how molecular orbitals transform (and how their energies change) during idealized chemical changes (e.g. *cycloadditions*).

An idealized single bond is a σ -bond, i.e., it has cylindrical symmetry, whereas a p-orbital or π -bond orbital has π -symmetry, i.e. it is antisymmetric with respect to reflection in a plane passing through the atomic centres with which it is associated. In ethene, the π -bonding orbital is symmetric with respect to reflection in a plane perpendicular to and bisecting the C-C bond, whereas the π^* -antibonding orbital is antisymmetric with respect to this operation.

Considerations of orbital symmetry are frequently grossly simplified in that, for example, the p-orbitals of a carbonyl group would be treated as having the same symmetry as those of ethene, and the fact that the carbonyl group in, for example, camphor, unlike that in formaldehyde, has no mirror planes would be ignored. These simplified considerations nevertheless afford the basis of one approach to the understanding of the rules which indicate whether *pericyclic reactions* are likely to occur under thermal or photochemical conditions.

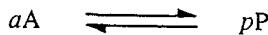
WOODWARD and HOFFMANN (1969); HALEVI (1992).

See also *sigma, pi*.

order of reaction, n (SI unit: 1)

If the macroscopic (observed, empirical or phenomenological) *rate of reaction* (v) for any reaction can be expressed by an empirical differential rate equation (or *rate law*) which contains a factor of the form $k [A]^\alpha[B]^\beta\dots$ (expressing in full the dependence of the rate of reaction on the concentrations [A], [B]...) where α, β are constant exponents (independent of concentration and time) and k is independent of [A] and [B] etc. (rate constant, rate coefficient), then the reaction is said to be of order α with respect to A, of order β with respect to B,..., and of (total or overall) order $n = \alpha+\beta+\dots$. The exponents α, β, \dots can be positive or negative integral or rational nonintegral numbers. They are the reaction orders with respect to A, B,... and are sometimes called "partial orders of reaction". Orders of reaction deduced from the dependence of initial rates of reaction on concentration are called "orders of reaction with respect to concentration"; orders of reaction deduced from the dependence of the rate of reaction on time of reaction are called "orders of reaction with respect to time".

The concept of order of reaction is also applicable to chemical rate processes occurring in systems for which concentration changes (and hence the rate of reaction) are not themselves measurable, provided it is possible to measure a *chemical flux*. For example, if there is a dynamic equilibrium according to the equation



and if a chemical flux is experimentally found, (e.g. by NMR *line shape analysis*) to be related to concentrations by the equation

$$\varphi_A/a = k[A]^\alpha[L]^\lambda.$$

then the corresponding reaction is of order α with respect to A... and of total (or overall) order n ($= \alpha + \lambda + \dots$).

The proportionality factor k above is called the (n th order) "rate coefficient".

Rate coefficients referring to (or believed to refer to) *elementary reactions* are called "rate constants" or, more appropriately "microscopic" (hypothetical, mechanistic) rate constants.

The (overall) order of a reaction cannot be deduced from measurements of a "rate of appearance" or "rate of disappearance" at a single value of the concentration of a species whose concentration is constant (or effectively constant) during the course of the reaction. If the overall rate of reaction is, for example, given by

$$v = k[A]^\alpha[B]^\beta$$

but $[B]$ stays constant, then the order of the reaction (with respect to time), as observed from the concentration change of A with time, will be α , and the rate of disappearance of A can be expressed in the form

$$v_A = k_{\text{obs}}[A]^\alpha$$

The proportionality factor k_{obs} deduced from such an experiment is called the "observed rate coefficient" and it is related to the $(\alpha + \beta)$ th order rate coefficient k by the equation

$$k_{\text{obs}} = k[B]^\beta$$

For the common case when $\alpha = 1$, k_{obs} is often referred to as a "pseudo-first order rate coefficient" (k_p).

For a simple (elementary) reactions a partial order of reaction is the same as the stoichiometric number of the reactant concerned and must therefore be a positive integer (see *rate of reaction*). The overall order is then the same as the *molecularity*. For stepwise reactions there is no general connection between stoichiometric numbers and partial orders. Such reactions may have more complex rate laws, so that an apparent order of reaction may vary with the concentrations of the *chemical species* involved and with the progress of the reaction: in such cases it is not useful to speak of orders of reaction, although apparent orders of reaction may be deducible from initial rates.

In a *stepwise reaction*, orders of reaction may in principle always be assigned to the elementary steps.

See also *kinetic equivalence*.

outer-sphere (electron transfer)

An outer-sphere electron transfer is a reaction in which the electron transfer takes place with no or very weak ($4 - 16 \text{ kJ mol}^{-1}$) electronic interaction between the reactants in the transition state. If instead the donor and the acceptor exhibit a strong electronic coupling, the reaction is described as inner-sphere electron transfer. The two terms derive from studies concerning metal complexes and it has been suggested that for organic reactions the term "nonbonded" and "bonded" electron transfer should be used.

See also *inner-sphere electron transfer*.

EBERSON (1987); LITTLER (1970).

oxidation

(1) The complete, net removal of one or more electrons from a *molecular entity* (also called "de-electronation").

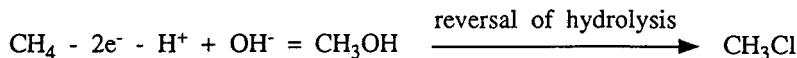
(2) an increase in the *oxidation number* of any atom within any *substrate* (see HENDRICKSON, CRAM and HAMMOND (1970)).

(3) Gain of oxygen and/or loss of hydrogen of an organic *substrate*.

All oxidations meet criteria (1) and (2), and many meet criterion (3), but this is not always easy to demonstrate.

Alternatively, an oxidation can be described as a *transformation* of an organic substrate that can be rationally dissected into steps or *primitive changes*. The latter consist in removal of one or several electrons from the substrate followed or preceded by gain or loss of water and/or hydrons or hydroxide ions, or by *nucleophilic substitution* by water or its reverse and/or by an *intramolecular molecular rearrangement*.

This formal definition allows the original idea of oxidation (combination with oxygen), together with its extension to removal of hydrogen, as well as processes closely akin to this type of transformation (and generally regarded in current usage of the term in organic chemistry to be oxidations and to be effected by "oxidizing agents") to be descriptively related to definition (1). For example the oxidation of methane to chloromethane may be considered as follows:



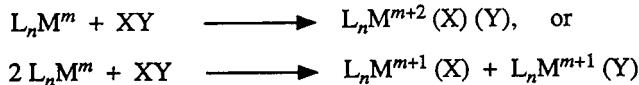
oxidation number

See IUPAC INORGANIC RULES (1970), Rule 0.1; IUPAC INORGANIC NOMENCLATURE (1990), Rules I-5.5.2 and I-10.2.7.

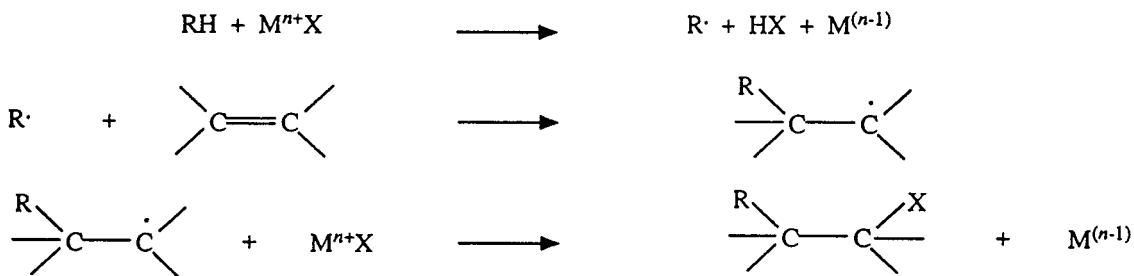
See also *oxidation*.

oxidative addition

The *insertion* of a metal or a metal complex into a covalent bond involving formally an overall two-electron loss on one metal or a one-electron loss on each of two metals, i.e.,

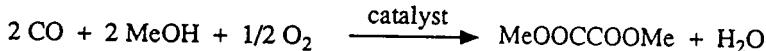


In free-radical chemistry, the term is used to indicate a free radical addition to a carbon-carbon double bond, under oxidative conditions. For example:



oxidative coupling

The coupling of two *molecular entities* through an oxidative process, usually catalysed by a transition metal compound and involving dioxygen as the oxidant; e.g.,



parallel reaction

See *composite reaction*.

paramagnetic

Substances having a magnetic susceptibility greater than 0 are paramagnetic. They are drawn into a magnetic field.

See also *diamagnetic*.

partial rate factor

The rate of substitution at one specific site in an *aromatic* compound relative to the rate of substitution at *one* position in benzene. For example, the partial rate factor f_p^Z for *para*-substitution in a monosubstituted benzene C_6H_5Z is related to the rate constants $k(C_6H_5Z)$ and $k(C_6H_6)$ for the total reaction (i.e. at all positions) of C_6H_5Z and benzene, respectively, and % *para* (the percentage *para*-substitution in the total product formed from C_6H_5Z) by the relation

$$f_p^Z = \frac{6k(C_6H_5Z)}{k(C_6H_6)} \frac{\% \text{ para}}{100}$$

Similarly for *meta*-substitution:

$$f_m^Z = \frac{6k(C_6H_5Z)}{2k(C_6H_6)} \frac{\% \text{ meta}}{100}$$

(The symbols p_f^Z , m_f^Z , o_f^Z are also in use.) The term applies equally to the *ipso* position, and it can be extended to other substituted substrates undergoing parallel reactions at different sites with the same reagent according to the same rate law.

INGOLD (1953); STOCK and BROWN (1963).

See also *selectivity*.

pericyclic reaction

A chemical reaction in which concerted reorganization of bonding takes place throughout a cyclic array of continuously bonded atoms. It may be viewed as a reaction proceeding through a fully conjugated cyclic transition state. The number of atoms in the cyclic array is usually six, but other numbers are also possible. The term embraces a variety of processes, including *cycloadditions*, *cheletropic reactions*, *electrocyclic reactions* and *sigmatropic rearrangements*, etc. (provided they are concerted).

See also *multi-centre reaction*.

periselectivity

The differentiation between two symmetry-allowed processes, for example the [2+4] *vs.* [4+6] *cycloaddition* of cyclopentadiene to tropone.

perpendicular effect

See *More O'Ferrall-Jencks diagram*.

persistent

The term *persistent* is used to characterize *radicals* which have lifetimes of several minutes or greater in dilute solution in inert solvents. Persistence is a kinetic or reactivity property. In contrast, *radical stability*, which is a thermodynamic property, is expressed in terms of the C-H bond strength of the appropriate hydrocarbon. The lifetime of a radical is profoundly influenced by steric shielding of the radical centre by bulky substituents.

GRILLER and INGOLD (1976).

See also *transient*.

pH-rate profile

A plot of observed rate coefficient, or more usually its decadic logarithm, against pH of solution, other variables being kept constant.

phase-transfer catalysis

The phenomenon of rate enhancement of a reaction between *chemical species* located in different phases (immiscible liquids or solid and liquid) by addition of a small quantity of an agent (called the "phase-transfer catalyst") that extracts one of the reactants, most commonly an anion, across the interface into the other phase so that reaction can proceed. These catalysts are salts of "*onium ions*" (e.g. tetraalkylammonium salts) or agents that complex inorganic cations (e.g. crown ethers). The catalyst cation is not consumed in the reaction although an anion exchange does occur.

phenonium ion

See *bridged carbocation*.

photolysis

The cleavage of one or more covalent bonds in a *molecular entity* resulting from absorption of light, or a photochemical process in which such cleavage is an essential part. For example:



The term is used incorrectly to describe irradiation of a sample, although in the combination flash photolysis this usage is accepted.

IUPAC PHOTOCHEMICAL GLOSSARY (1992).

+ polar aprotic solvent

See *dipolar aprotic*.

polar effect

For a reactant molecule RY, the polar effect of the group R comprises all the processes whereby a substituent may modify the electrostatic forces operating at the reaction centre Y, relative to the standard R^0Y . These forces may be governed by charge separations arising from differences in the *electronegativity* of atoms (leading to the presence of dipoles), the presence of

unipoles, or electron *delocalization*. It is synonymous with *electronic effect* or "electrical effect" of a substituent as distinguished from other substituent effects, e.g. *steric effects*.

Sometimes, however, the term "polar effect" is taken to refer to the influence, other than steric, that non-conjugated substituents exert on reaction rates, i.e. effects connected with electron delocalization between a substituent and the molecular framework to which it is attached are excluded. Polar effect is then not synonymous with electronic effect.

See also *field effect*, *inductive effect*, *mesomeric effect*.

polar solvent

See *polarity*.

polarity

When applied to solvents, this rather ill-defined term covers their overall solvation capability (solvation power) for solutes (i.e. in chemical equilibria: reactants and products; in reaction rates: reactants and *activated complex*; in light absorptions: ions or molecules in the ground and excited state), which in turn depends on the action of all possible, nonspecific and specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute. Occasionally, the term solvent polarity is restricted to nonspecific solute/solvent interactions only (i.e. to *van der Waals forces*).

See also *Dimroth-Reichardt E_T parameter*, *Grunwald-Winstein equation*, *ionizing power*, *Kamlet-Taft solvent parameters*, *van der Waals forces*, *Z-value*.

REICHARDT (1965, 1988).

polarizability

The ease of distortion of the electron cloud of a *molecular entity* by an electric field (such as that due to the proximity of a charged reagent). It is experimentally measured as the ratio of induced dipole moment (μ_{ind}) to the field E which induces it:

$$\alpha = \mu_{\text{ind}}/E$$

The units of α are $C^2 m^2 V^{-1}$. In ordinary usage the term refers to the "mean polarizability", i.e., the average over three rectilinear axes of the molecule. Polarizabilities in different directions (e.g. along the bond in Cl_2 , called "longitudinal polarizability", and in the direction perpendicular to the bond, called "transverse polarizability") can be distinguished, at least in principle. Polarizability along the bond joining a substituent to the rest of the molecule is seen in certain modern theoretical approaches as a factor influencing chemical *reactivity*, etc., and parametrization thereof has been proposed.

See INGOLD (1953); TAFT and TOPSOM (1987).

polydent

See *ambident*.

potential-energy profile

A curve describing the variation of the potential energy of the system of atoms that make up the reactants and products of a reaction as a function of one geometric coordinate, and corresponding to the "energetically easiest passage" from reactants to products (i.e. along the line produced by joining the paths of steepest descent from the *transition state* to the reactants and to the products). For an *elementary reaction* the relevant geometric coordinate is the *reaction coordinate*; for a *stepwise reaction* it is the succession of reaction coordinates for the successive individual reaction steps. (The reaction coordinate is sometimes approximated by a quasi-chemical index of reaction progress, such as "degree of atom transfer" or *bond order* of some specified bond.)

See also *potential-energy (reaction) surface*, *Gibbs energy diagram*.

potential-energy (reaction) surface

A geometric hypersurface on which the potential energy of a set of reactants is plotted as a function of the coordinates representing the molecular geometries of the system.

For simple systems two such coordinates (characterizing two variables that change during the progress from reactants to products) can be selected, and the potential energy plotted as a contour map.

For simple *elementary reactions*, e.g. $A-B + C \rightarrow A + B-C$, the surface can show the potential energy for all values of the A, B, C geometry, providing that the ABC angle is fixed.

For more complicated reactions a different choice of two coordinates is sometimes preferred, e.g. the *bond orders* of two different bonds. Such a diagram is often arranged so that reactants are located at the bottom left corner and products at the top right. If the trace of the

representative point characterizing the route from reactants to products follows two adjacent edges of the diagram, the changes represented by the two coordinates take place in distinct succession; if the trace leaves the edges and crosses the interior of the diagram, the two changes are *concerted*. In many qualitative applications it is convenient (although not strictly equivalent) for the third coordinate to represent the standard Gibbs energy rather than potential energy.

Using bond orders is, however, an oversimplification, since these are not well-defined, even for the transition state. (Some reservations concerning the diagrammatic use of Gibbs energies are noted under *Gibbs energy diagram*.)

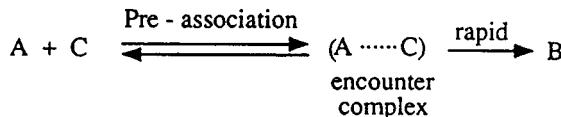
The energetically easiest route from reactants to products on the potential-energy contour map defines the *potential-energy profile*.

ALBERY (1967); MORE O'FERRALL (1970); JENCKS (1972, 1985).

See also *reaction coordinate*.

pre-association

A step on the *reaction path* of some *stepwise reactions* in which the *molecular entity C* is already present in an *encounter pair* or *encounter complex* with A during the formation of B from A, e.g.



In this mechanism the *chemical species C* may but does not necessarily assist the formation of B from A, which may itself be a *bimolecular reaction* with some other reagent.

Pre-association is important when B is too short-lived to permit B and C to come together by diffusion.

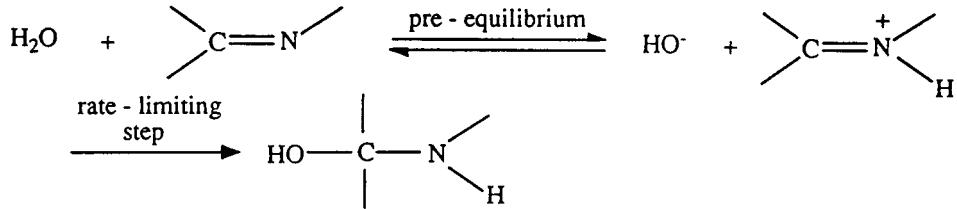
See also *microscopic diffusion control, spectator mechanism*.

precursor complex

See *encounter complex*.

pre-equilibrium (or prior equilibrium)

A rapidly reversible step preceding the *rate-limiting step* in a *stepwise reaction*. For example



See also *kinetic equivalence*.

pre-exponential factor

See *energy of activation, entropy of activation*.

primary kinetic electrolyte effect

See *kinetic electrolyte effect*.

primary kinetic isotope effect

See *isotope effect*.

primitive change

One of the conceptually simpler molecular changes into which an *elementary reaction* can be notionally dissected. Such changes include *bond rupture*, *bond formation*, *internal rotation*, *change of bond length* or *bond angle*, *bond migration*, *redistribution of charge*, etc.

The concept of primitive changes is helpful in the detailed verbal description of elementary reactions, but a primitive change does not represent a process that is by itself necessarily observable as a component of an elementary reaction.

IUPAC REACTION MECHANISMS (1989).

prior equilibrium

See *pre-equilibrium*.

that reaction and also to be consumed during the process. The acid or base is then not a *catalyst* and the phenomenon cannot be called *catalysis* according to the well-established meaning of these terms in chemical kinetics, although the *mechanism* of such a process is often intimately related to that of a catalysed reaction. It is recommended that the term *pseudo-catalysis* be used in these and analogous cases (not necessarily involving acids or bases). For example, if a *Brønsted acid* accelerates the hydrolysis of an ester to a carboxylic acid and an alcohol, this is properly called acid catalysis, whereas the acceleration, by the same acid, of hydrolysis of an amide should be described as pseudo-catalysis by the acid: the "acid pseudo-catalyst" is consumed during the reaction through formation of an ammonium ion. The terms "general acid pseudo-catalysis" and "general base pseudo-catalysis" may be used as the analogues of *general acid catalysis* and *general base catalysis*.

The term "base-promoted", "base-accelerated, or "base-induced" is sometimes used for reactions that are pseudo-catalysed by bases. However, the term "promotion" also has a different meaning in other chemical contexts.

pseudo-first order rate coefficient

See *order of reaction*.

+ pseudomolecular rearrangement

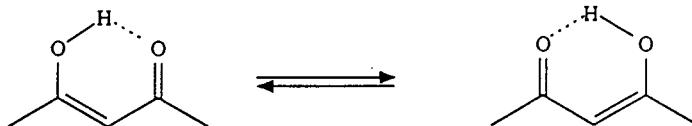
The use of this awkwardly formed term is discouraged. It is synonymous with "intermolecular rearrangement".

See *molecular rearrangement*.

pseudopericyclic

A concerted transformation is pseudopericyclic if the primary changes in bonding occur within a cyclic array of atoms at one (or more) of which nonbonding and bonding atomic orbitals interchange roles.

A formal example is the enol → enol prototropy of pentane-2,4-dione (acetylacetone).



Because the π - and σ -atomic orbitals that interchange roles are orthogonal, such a reaction does not proceed through a fully conjugated transition state and is thus not a pericyclic reaction and therefore not governed by the rules that express orbital symmetry restrictions applicable to pericyclic reactions.

ROSS, SEIDERS and LEMAL (1976).

+ pseudo-unimolecular

A term sometimes used as synonymous with pseudo-first order, but is inherently meaningless.

See *molecularity, order of reaction*.

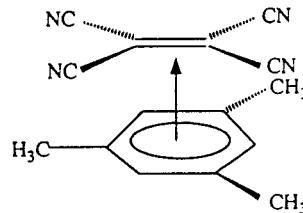
pyrolysis

Thermolysis, usually associated with exposure to a high temperature.

See also *flash vacuum pyrolysis*.

π -adduct (pi-adduct)

An *adduct* formed by electron-pair donation from a π -orbital into a σ -orbital, or from a σ -orbital into a π -orbital, or from a π -orbital into a π -orbital. For example:



Such an adduct has commonly been known as a "pi-complex", but, as the bonding is not necessarily weak, it is better to avoid the term *complex*, in accordance with the recommendations in this Glossary.

See also *coordination*.

π -bond (pi bond)

See *sigma, pi*.

+ π -complex

See *π -adduct*.

 π -electron acceptor, π -electron donor group

A substituent capable of a +R (e.g. NO₂) or -R (e.g. OCH₃) effect, respectively.

See *electronic effect, polar effect, σ -constant*.

 π -orbital

See *sigma, pi*.

quantitative structure-activity relationships (QSAR)

The building of structure-biological activity models by using regression analysis with physicochemical constants, indicator variables or theoretical calculations. The term has been extended by some authors to include chemical reactivity, i.e. activity is regarded as synonymous with reactivity. This extension is, however, discouraged.

See CHARTON (1989).

See also *correlation analysis*.

quantum yield

The number of defined events which occur per photon absorbed by the system. The integral quantum yield is

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

For a photochemical reaction,

$$\phi = \frac{\text{moles of reactant consumed or product formed}}{\text{moles of photons absorbed}}$$

The differential quantum yield is

$$\phi = \frac{d[x]/dt}{n}$$

where d[x]/dt is the rate of change of the amount of (substance) concentration of a measurable quantity, and n the amount of photons (mol or its equivalent *einstins*) absorbed per unit time. ϕ can be used for photophysical processes or photochemical reactions.

IUPAC PHOTOCHEMICAL GLOSSARY (1992).

radical (or free radical)

A molecular entity such as ·CH₃, ·SnH₃, Cl· possessing an unpaired electron. (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals. However, in the "isovalent analogy" (see HOFFMANN (1982)), the similarity between certain paramagnetic metal ions and radicals becomes apparent.

At least in the context of physical organic chemistry, it seems desirable to cease using the adjective "free" in the general name of this type of *chemical species* and *molecular entity*, so that the term "free radical" may in future be restricted to those radicals which do not form parts of radical pairs.

Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centred radicals. If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed σ - or π -radicals.

In the past, the term "radical" was used to designate a *substituent group* bound to a *molecular entity*, as opposed to "free radical", which nowadays is simply called radical. The bound entities may be called *groups* or *substituents*, but should no longer be called radicals.

IUPAC NOMENCLATURE GUIDE (1993).

See also *biradical*.

radical anion

See *radical ion*.

radical centre(s)

The atom (or group of atoms) in a polyatomic radical on which an unpaired electron is largely localized. Attachment of a monovalent atom to a radical centre gives a molecule for which it is possible to write a *Lewis formula* in which the normal stable valencies are assigned to all atoms.

radical combination

See *colligation*.

radical ion

A radical that carries an electric charge. A positively charged radical is called a "radical cation" (e.g., the benzene radical cation $C_6H_6^+$); a negatively charged radical is called a "radical anion" (e.g., the benzene radical anion $C_6H_6^-$ or the benzophenone radical anion Ph_2C-O^-). Commonly, but not necessarily, the odd electron and the charge are associated with the same atom.

Unless the positions of unpaired spin and charge can be associated with specific atoms, superscript dot and charge designations should be placed in the order .+ or .- suggested by the name "radical ion", (e.g. $C_3H_6^+$).

Note: In the previous edition of the Glossary, it was recommended to place the charge designation directly above the centrally placed dot. However, this format is now discouraged because of the difficulty of extending it to ions bearing more than one charge, and/or more than one unpaired electron.

In mass spectroscopic usage the symbol for the charge precedes the dot representing the unpaired electron.

IUPAC MASS SPECTROMETRY (1991).

radical pair (or geminate pair)

The term is used to identify two *radicals* in close proximity in solution, within a solvent cage. They may be formed simultaneously by some *unimolecular* process, e.g., peroxide decomposition, or they may have come together by diffusion. While the radicals are together, correlation of the unpaired electron spins of the two species cannot be ignored: this correlation is responsible for the CIDNP phenomenon.

See also *geminate recombination*.

radiolysis

The cleavage of one or several bonds resulting from exposure to high-energy radiation. The term is also often used loosely to specify the method of irradiation ("pulse radiolysis") used in any radiochemical reaction, not necessarily one involving bond cleavage.

rate coefficient

See *order of reaction, kinetic equivalence*.

rate-controlling step

A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite reaction sequence is an *elementary reaction* the rate constant for which exerts a strong effect - stronger than that of any other rate constant - on the overall rate. It is recommended that the expressions *rate-controlling*, *rate-determining* and *rate-limiting* be regarded as synonymous, but some special meanings sometimes given to the last two expressions are considered under a separate heading.

A rate-controlling step can be formally defined on the basis of a control function (or control factor) CF, identified for an elementary reaction having a rate constant k_i by

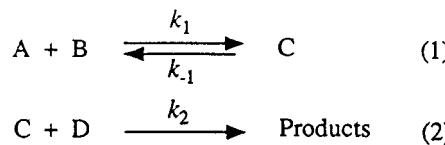
$$CF = \frac{\partial \ln v / \partial \ln k_i}{K_j, k_j}$$

where v is the overall rate of reaction. In performing the partial differentiation all equilibrium constants K_j and all rate constants except k_i are held constant. The elementary reaction having the largest control factor exerts the strongest influence on the rate v , and a step having a CF much larger than any other step may be said to be rate-controlling.

A rate-controlling step defined in the way recommended here has the advantage that it is directly related to the interpretation of *kinetic isotope effects*.

IUPAC CHEMICAL KINETICS (1991)

As formulated this implies that all rate constants are of the same dimensionality. Consider however the reaction of A and B to give an intermediate C, which then reacts further with D to give products:



Assuming that C reaches a *steady state*, then the observed rate is given by

$$v = \frac{k_1 k_2 [A] [B] [D]}{k_{-1} + k_2 [D]}$$

Considering $k_2[D]$ a pseudo-first order rate constant, then $k_2[D] \gg k_{-1}$, and the observed rate $v = k_1[A][B]$ and $k_{\text{obs}} = k_1$

Step (1) is said to be the rate-controlling step.

If $k_2[D] \ll k_{-1}$, then the observed rate

$$\begin{aligned} v &= \frac{k_1 k_2}{k_{-1}} [A] [B] [D] \\ &= K k_2 [A] [B] [D] \end{aligned}$$

where K is the equilibrium constant for the pre-equilibrium (1) and is equal to k_1/k_{-1} , and $k_{\text{obs}} = K k_2$.

Step (2) is said to be the rate-controlling step.

See also *Gibbs energy diagram*, *microscopic diffusion control*, *mixing control*, *rate-determining step*, *rate-limiting step*.

rate constant, k (SI unit: $\text{s}^{-1} (\text{dm}^3 \text{ mol}^{-1})^{n-1}$)

See *order of reaction*.

rate-determining step, rate-limiting step

These terms are best regarded as synonymous with *rate-controlling step*. However, other meanings that have been given to them should be mentioned, as it is necessary to be aware of them in order to avoid confusion:

Sometimes the term *rate-determining* is used as a special case of *rate-controlling*, being assigned only to an initial slow step which is followed by rapid steps. Such a step imposes an upper limit on the rate, and has also been called *rate-limiting*.

In view of the considerable danger of confusion when special meanings are applied to *rate-determining* and *rate-limiting*, it is recommended that they be regarded as synonymous, with the meaning explained under the entry *rate-controlling step*. See *Michaelis-Menten kinetics*.

IUPAC CHEMICAL KINETICS (1991).

rate law (or empirical differential rate equation)

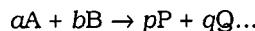
An expression for the *rate of reaction* of a particular reaction in terms of concentrations of *chemical species* and constant parameters (normally *rate coefficients* and partial *orders of reaction*) only. For examples of rate laws see equations (1) to (3) under *kinetic equivalence*, and (1) under *steady state*.

rate of appearance

See *rate of reaction*.

rate of reaction

For the general *chemical reaction*



occurring under constant-volume conditions, without an appreciable build-up of reaction *intermediates*, the rate of reaction v is defined as

$$v = - \frac{1}{a} \frac{d[A]}{dt} = - \frac{1}{b} \frac{d[B]}{dt} = + \frac{1}{p} \frac{d[P]}{dt} = + \frac{1}{q} \frac{d[Q]}{dt}$$

where symbols placed inside square brackets denote amount (or amount of substance) concentrations (conventionally expressed in units of mol dm^{-3}). The symbols R and r are also commonly used in place of v . It is recommended that the unit of time should always be the second.

In such a case the rate of reaction differs from the rate of increase of concentration of a product P by a constant factor (the reciprocal of its coefficient in the stoichiometric equation, p) and from the rate of decrease of concentration of the reactant A by 1/a. [It should be noted that all coefficients in the stoichiometric equation are positive; those for products (p, q...) will therefore differ in sign from the stoichiometric numbers defined in IUPAC MANUAL (1979).]

The quantity

$$\dot{\xi} = \frac{d\xi}{dt}$$

defined by the equation

$$\dot{\xi} = -\frac{1}{a} \frac{dn_A}{dt} = -\frac{1}{b} \frac{dn_B}{dt} = +\frac{1}{p} \frac{dn_P}{dt} = +\frac{1}{q} \frac{dn_Q}{dt}$$

(where n_A designates the amount of substance A, conventionally expressed in units of mole) may be called the "rate of conversion" and is appropriate when the use of concentrations is inconvenient, e.g. under conditions of varying volume. In a system of constant volume, the rate of reaction is equal to the rate of conversion per unit volume throughout the reaction.

For a *stepwise reaction* this definition of "rate of reaction" (and "extent of reaction", ξ) will apply only if there is no accumulation of intermediate or formation of side products. It is therefore recommended that the term "rate of reaction" be used only in cases where it is experimentally established that these conditions apply. More generally, it is recommended that, instead, the terms "rate of disappearance" or "rate of consumption" of A (i.e. $-d[A]/dt$, the rate of decrease of concentration of A) or "rate of appearance" of P (i.e. $d[P]/dt$, the rate of increase of concentration of product P) be used, depending on the concentration change of the particular *chemical species* that is actually observed. In some cases reference to the *chemical flux* observed may be more appropriate.

The symbol v (without lettered subscript) should be used only for rate of reaction; v with a lettered subscript (e.g. v_A) refers to a rate of appearance or rate of disappearance (e.g. of the chemical species A).

N.B. This definition is consistent with CODATA (1974) recommendations and with IUPAC MANUAL APPENDIX V (1981), but differs from the unconventional terminology in the earlier IUPAC MANUAL (1979).

See also *chemical relaxation, lifetime, order of reaction*.

reacting bond rules

(1) For an internal motion of a *molecular entity* corresponding to progress over a *transition state* (energy maximum), any change that makes the motion more difficult will lead to a new molecular geometry at the energy maximum, in which the motion has proceeded further. Changes that make the motion less difficult will have the opposite effect. (This rule corresponds to the *Hammond principle*.)

(2) For an internal motion of a *molecular entity* that corresponds to a vibration, any change that tends to modify the equilibrium point of the vibration in a particular direction will actually shift the equilibrium in that direction.

(3) Effects on reacting bonds (bonds made or broken in the reaction) are the most significant. The bonds nearest the site of structural change are those most strongly affected.

THORNTON (1967).

See also *More O'Ferrall-Jencks diagram*.

reaction

See *chemical reaction*.

reaction coordinate

A geometric parameter that changes during the conversion of one (or more) reactant *molecular entities* into one (or more) product molecular entities and whose value can be taken for a measure of the progress of an *elementary reaction* (for example, a bond length or bond angle or a combination of bond lengths and/or bond angles; it is sometimes approximated by a non-geometric parameter, such as the *bond order* of some specified bond).

In the formalism of "*transition-state theory*", the reaction coordinate is that coordinate in a set of curvilinear coordinates obtained from the conventional ones for the reactants which, for each reaction step, leads smoothly from the configuration of the reactants through that of the transition state to the configuration of the products. The reaction coordinate is typically chosen to follow the path along the gradient (path of shallowest ascent/deepest descent) of potential energy from reactants to products.

The term has also been used interchangeably with the term transition coordinate, applicable to the coordinate in the immediate vicinity of the potential energy maximum. Being more specific, the name transition coordinate is to be preferred in that context.

MARCUS (1966).

See also *potential-energy profile*, *potential-energy reaction surface*.

reaction mechanism

See *mechanism*.

reaction path

- (1) A synonym for *mechanism*.
- (2) A trajectory on the *potential-energy surface*.
- (3) A sequence of synthetic steps.

reaction stage

A set of one or more (possibly experimentally inseparable) *reaction steps* leading to and/or from a detectable or presumed reaction *intermediate*.

reaction step

An *elementary reaction*, constituting one of the stages of a *stepwise reaction* in which a reaction *intermediate* (or, for the first step, the reactants) is converted into the next reaction intermediate (or, for the last step, the products) in the sequence of intermediates between reactants and products.

See also *rate-limiting step*, *reaction stage*.

reactive, reactivity

As applied to a *chemical species*, the term expresses a kinetic property. A species is said to be more reactive or to have a higher reactivity in some given context than some other (reference) species if it has a larger rate constant for a specified *elementary reaction*. The term has meaning only by reference to some explicitly stated or implicitly assumed set of conditions. It is not to be used for reactions or reaction patterns of compounds in general.

The term is also more loosely used as a phenomenological description not restricted to elementary reactions. When applied in this sense the property under consideration may reflect not only rate, but also equilibrium, constants.

See also *stable*, *unreactive*, *unstable*.

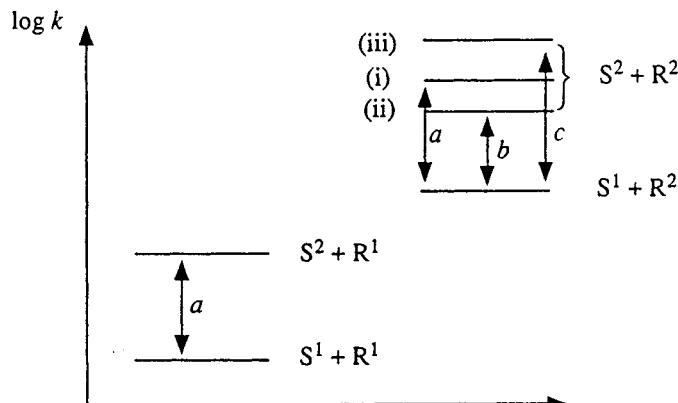
reactivity index

Any numerical index derived from quantum mechanical model calculations that permits the prediction of relative reactivities of different molecular sites. Many indices are in use, based on a variety of theories and relating to various types of reaction. The more successful applications have been to the *substitution reactions* of *conjugated systems* where relative reactivities are determined largely by changes of π -electron energy.

reactivity-selectivity principle (RSP)

This idea may be expressed loosely as: the more *reactive* a reagent is, the less selective it is.

Consider two substrates S^1 and S^2 undergoing the same type of reaction with two reagents R^1 and R^2 , S^2 being more reactive than S^1 , and R^2 more reactive than R^1 in the given type of reaction. The relative reactivities (in log units, see *selectivity*) for the four possible reactions may notionally be represented as follows:



With the positions of $(S^1 + R^1)$, $(S^2 + R^1)$, and $(S^1 + R^2)$ fixed, there are three types of positions for $(S^2 + R^2)$:

In position (i) the selectivity of R^2 for the two substrates, measured by a is the same as the selectivity of R^1 for the two substrates, also a .

In position (ii) the selectivity of R^2 for the two substrates, measured by b , is less than the selectivity of R^1 for the two substrates, i.e. $b < a$. It is this situation which is in accord with the RSP.

In position (iii) the selectivity of R^2 for the two substrates, measured by c , is greater than the selectivity of R^1 for the two substrates, i.e. $c > a$. This situation may be described as anti-RSP.

There are many examples in which the RSP is followed, but there are also many examples corresponding to situations (i) and (iii). The RSP is in accord with intuitive feeling and certainly holds in the limiting case when reactivity is controlled by diffusion. However, the validity of the RSP is a matter of great controversy "...and diverse opinions have been expressed, from declaring the reactivity-selectivity principle as a universal law up to 'virtually useless in practice as a general rule'." [EXNER (1988)].

ARGILE, CAREY, FUKATA, HARCOURT, MORE O'FERRAL AND MURPHY (1985); BUNCEL and WILSON (1987); JOHNSON (1975); STOCK and BROWN (1963).

rearrangement

See *degenerate rearrangement*, *molecular rearrangement*, *sigmatropic rearrangement*.

rearrangement stage

The *elementary reaction* or *reaction stage* (of a *molecular rearrangement*) in which there is both making and breaking of bonds between atoms common to a reactant and a reaction product or a reaction *intermediate*. If the rearrangement stage consists of a single elementary reaction, this is a "rearrangement step".

reduction

The complete transfer of one or more electrons to a *molecular entity* (also called "electronation"), and, more generally, the reverse of the processes described under *oxidation* (2), (3).

reductive elimination

The reverse of *oxidative addition*.

regioselectivity, regioselective

A regioselective reaction is one in which one direction of bond making or breaking occurs preferentially over all other possible directions. Reactions are termed completely (100 %) regioselective if the discrimination is complete, or partially ($x \%$), if the product of reaction at one site predominates over the product of reaction at other sites. The discrimination may also semi-quantitatively be referred to as high or low regioselectivity.

(Originally the term was restricted to addition reactions of unsymmetrical reagents to unsymmetrical alkenes.)

In the past, the term "regiospecificity" was proposed for 100 % regioselectivity. This terminology is not recommended owing to inconsistency with the terms *stereoselectivity* and *stereospecificity*.

See ADAMS (1992); HASSNER (1968).

See also *chemoselectivity*.

relaxation

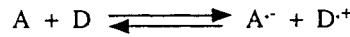
Passage of an excited or otherwise perturbed system towards or into thermal equilibrium with its environment.

IUPAC PHOTOCHEMICAL GLOSSARY (1988).

See also *chemical relaxation*.

reorganization energy

In a one-electron transfer reaction



the reorganization energy λ is the energy required for all structural adjustments (in the reactants and in the surrounding solvent molecules) which are needed in order that A and D assume the configuration required for the transfer of the electron.

See *intrinsic barrier*, *Marcus equation*.

resonance

In the context of chemistry, the term refers to the representation of the electronic structure of a *molecular entity* in terms of *contributing structures*. Resonance among contributing structures means that the wavefunction is represented by "mixing" the wavefunctions of the contributing structures. The concept is the basis of the quantum mechanical valence bond methods. The resulting stabilization is linked to the quantum mechanical concept of "resonance energy". The term resonance is also used to refer to the delocalization phenomenon itself.

See ATKINS (1974).

See also *mesomerism*.

resonance effect

This is the term most commonly used to describe the influence (on reactivity, spectra, etc.) of a *substituent* through electron *delocalization* into or from the substituent. The use of the term obviates the need to attempt to distinguish between the operation of the *mesomeric effect* and the *electromeric effect*. (An alternative term with essentially the same meaning is "conjugative effect". At one time "tautomeric effect" was also used, but was abandoned because *tautomerism* implies reorganization of the atomic nuclei.) The effect is symbolized by R.

resonance energy

The difference in potential energy between the actual *molecular entity* and the *contributing structure* of lowest potential energy. The resonance energy cannot be measured, but only estimated, since contributing structures are not observable *molecular entities*.

See *resonance*.

+ retroaddition

See *cycloelimination*.

+ retrocycloaddition

See *cycloelimination*.

retro-ene reaction

See *ene reaction*.

reverse micelle (or reversed micelle)

See *inverted micelle*.

Ritchie equation

The *linear free energy relation*

$$\log k_N = \log k_0 + N_+$$

applied to the reactions between nucleophiles and certain large and relatively stable organic cations, e.g. arenediazonium, triarylmethyl, and aryltropylium cations in various solvents. k_N is the rate constant for reaction of a given cation with a given nucleophilic system (i.e. given nucleophile in a given solvent). k_0 is the rate constant for the same cation with water in water, and N_+ is a parameter which is characteristic of the nucleophilic system and independent of the cation. A surprising feature of the equation is the absence of a coefficient of N_+ , characteristic of the substrate (cf. the s in the *Swain-Scott equation*), even though values of N_+ vary over 13 log units. The equation thus involves a gigantic breakdown of the *reactivity-selectivity principle*. The equation has been extended both in form and in range of application.

RITCHIE (1972, 1978, 1986).

See also CHAPMAN and SHORTER (1978).

 ρ -value (rho-value)

A measure of the susceptibility to the influence of *substituent* groups on the rate constant or equilibrium constant of a particular organic reaction involving a family of related *substrates*. Defined by Hammett for the effect of ring substituents in *meta*- and *para*-positions of aromatic side-chain reactions by the empirical " $\rho\sigma$ -equation" of the general form

$$\log(k_X/k_H) = \rho\sigma_X$$

in which σ_X is a constant characteristic of the substituent X and of its position in the reactant molecule.

More generally (and not only for aromatic series), ρ -values (modified with appropriate subscripts and superscripts) are used to designate the susceptibility of reaction series for

families of various organic compounds to any substituent effects, as given by the modified set of σ -constants in an empirical $\rho\sigma$ -correlation.

Reactions with a positive ρ -value are accelerated (or the equilibrium constants of analogous equilibria are increased) by substituents with positive σ -constants. Since the sign of σ was defined so that substituents with a positive σ increase the acidity of benzoic acid, such substituents are generally described as attracting electrons away from the aromatic ring. It follows that reactions with a positive ρ -value are considered to involve a transition state (or reaction product) so that the difference in energy between this state and the reactants is decreased by a reduction in electron density at the reactive site of the substrate.

See also *Hammett equation*, σ -constant, *Taft equation*.

$\rho\sigma$ -equation (rho-sigma equation)

See *Hammett equation*, ρ -value, σ -constant, *Taft equation*.

sacrificial hyperconjugation

See *hyperconjugation*.

+ salt effect

See *kinetic electrolyte effect*.

saturation transfer

A term used in nuclear magnetic resonance. When a nucleus is strongly irradiated, its spin population may partly be transferred to another nucleus by an exchange process.

See *magnetization transfer*.

Saytzeff rule

Dehydrohalogenation of secondary- and tertiary-alkyl halides proceeds by the preferential removal of the β -hydrogen from the carbon that has the smallest number of hydrogens. Originally formulated by A. Saytzeff (Zaitsev) to generalize the orientation in β -elimination reactions of alkyl halides, this rule has been extended and modified, as follows: When two or more olefins can be produced in an elimination reaction, the thermodynamically most stable alkene will predominate. Exceptions to the Saytzeff rule are exemplified by the *Hofmann rule*.

SAYTZEFF (1875).

See also *Markownikoff rule*.

scavenger

A substance that reacts with (or otherwise removes) a trace component (as in the scavenging of trace metal ions) or traps a reactive reaction intermediate.

IUPAC COMPENDIUM (1987).

See also *inhibition*.

scrambling

See *isotopic scrambling*.

secondary kinetic electrolyte effect

See *kinetic electrolyte effect*.

secondary kinetic isotope effect

See *isotope effect*.

selectivity

The discrimination shown by a reagent in competitive attack on two or more substrates or on two or more positions in the same substrate. It is quantitatively expressed by ratios of rate constants of the competing reactions, or by the decadic logarithms of such ratios.

See also *isoselective relationship*, *partial rate factor*, *regioselectivity*, *selectivity factor*, *stereoselectivity*.

selectivity factor

A quantitative representation of selectivity in aromatic substitution reactions (usually *electrophilic*, for monosubstituted benzene derivatives). If the partial rate factor, f , expresses the reactivity of a specified position in the aromatic compound PhX relative to that of a single position in benzene, then the selectivity factor S_f (expressing discrimination between *p*- and *m*-positions in PhX) is defined as

$$S_f = \log (f_p^X/f_m^X).$$

STOCK and BROWN (1963).

shielding

In the context of NMR spectroscopy shielding is the effect of the electron shells of the observed and the neighbouring nuclei on the external magnetic field. The external field induces circulations in the electron cloud. The resulting magnetic moment is oriented in the opposite direction to the external field, so that the local field at the central nucleus is weakened, although it may be strengthened at other nuclei (deshielding).

The phenomenon is the origin of the structural dependence of the resonance frequencies of the nuclei.

See also *chemical shift*.

sigma, pi (σ , π)

The terms are symmetry designations, π molecular orbitals being antisymmetric with respect to a defining plane containing at least one atom (e.g. the molecular plane of ethene), and σ molecular orbitals symmetric with respect to the same plane. In practice the terms are used both in this rigorous sense (for orbitals encompassing the entire molecule) and also for localized two-centre orbitals or bonds, and it is necessary to make a clear distinction between the two usages.

In the case of two-centre bonds, a π -bond has a nodal plane that includes the internuclear bond axis, whereas a σ -bond has no such nodal plane. (A δ -bond in organometallic or inorganic molecular species has two nodes.) *Radicals* are classified by analogy into σ - and π -radicals.

Such two-centre orbitals may take part in molecular orbitals of σ - or π -symmetry. For example, the methyl group in propene contains three C-H bonds, each of which is of local σ -symmetry (i.e. without a nodal plane including the internuclear axis), but these three " σ -bonds" can in turn be combined to form a set of group orbitals one of which has π -symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of π -symmetry (π -bond) of the double-bonded carbon atoms, to form a molecular orbital of π -symmetry.

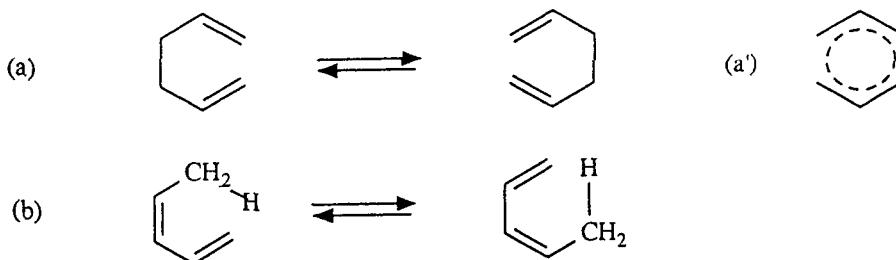
Such an interaction between the CH_3 group and the double bond is an example of what is called *hyperconjugation*. This cannot rigorously be described as " σ - π conjugation" since σ and π here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

See also JORGENSEN and SALEM (1973).

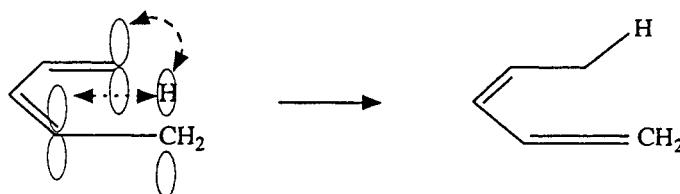
sigmatropic rearrangement

A molecular rearrangement that involves both the creation of a new σ -bond between atoms previously not directly linked and the breaking of an existing σ -bond. There is normally a concurrent relocation of π -bonds in the molecule concerned, but the total number of π - and σ -bonds does not change. The term was originally restricted to *intramolecular pericyclic reactions*, and many authors use it with this connotation. It is, however, also applied in a more general, purely structural, sense.

If such reactions are *intramolecular*, their *transition state* may be visualized as an *association* of two fragments connected at their termini by two partial σ -bonds, one being broken and the other being formed as, for example, the two allyl fragments in (a'). Considering only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the numbers of these in the two fragments are designated i and j , then the rearrangement is said to be a sigmatropic change of order $[i:j]$ (conventionally $[i] \leq [j]$). Thus the rearrangement (a) is of order [3,3], whilst reaction (b) is a [1,5]sigmatropic shift of hydrogen. (N.B.: By convention square brackets [...] here refer to numbers of atoms, in contrast with current usage in the context of cycloaddition.)



The descriptors *a* and *s* (*antarafacial* and *suprafacial*) may also be annexed to the numbers *i* and *j*; (b) is then described as a [1s,5s] sigmatropic rearrangement, since it is suprafacial with respect both to the hydrogen atom and to the pentadienyl system:



The prefix "homo" (meaning one extra atom, interrupting *conjugation* - cf. "*homoaromaticity*") has frequently been applied to sigmatropic rearrangements, but is misleading.

See also *cycloaddition*, *tautomerism*.

silylene

(1) Generic name for H_2Si : and substitution derivatives thereof, containing an electrically neutral bivalent silicon atom with two non-bonding electrons. (The definition is analogous to that given for *carbene*.)

(2) The silanediyl group (H_2Si), analogous to the methylene group (H_2C).

single-electron transfer mechanism (SET)

A reaction *mechanism* characterized by the transfer of a single electron between the species occurring on the *reaction coordinate* of one of the *elementary steps*.

single-step reaction

A reaction that proceeds through a single *transition state*.

Slater-type orbital

An approximate atomic orbital that attempts to allow for electron-electron repulsion by scaling the nuclear charge for each orbital.

soft acid

See *hard acid*.

soft base

See *hard base*.

solvation

Any stabilizing interaction of a solute (or solute *moiety*) and the solvent or a similar interaction of solvent with groups of an insoluble material (i.e., the ionic groups of an ion-exchange resin). Such interactions generally involve electrostatic forces and *van der Waals forces*, as well as chemically more specific effects such as *hydrogen bond* formation.

See also *cybotactic region*.

solvatochromic relationship

A linear free-energy relationship based on *solvatochromism*.

See also *Kamlet-Taft solvent parameters*.

solvatochromism

The (pronounced) change in position and sometimes intensity of an electronic absorption or emission band, accompanying a change in the polarity of the medium. Negative (positive) solvatochromism corresponds to a *hypsochromic* (*bathochromic*) shift with increasing solvent polarity.

BUNCEL and RAJAGOPAL (1990); REICHARDT (1988).

See also *Dimroth-Reichardt E_T parameter*, *Z-value*.

solvent isotope effect

See *isotope effect*.

solvent parameter

Quantitative measures of the capability of solvents for interaction with solutes. Such parameters have been based on numerous different physico-chemical quantities, e.g. *rate constants*, solvatochromic shifts in ultraviolet/visible spectra, solvent-induced shifts in infrared

frequencies, etc. Some solvent parameters are purely empirical in nature, i.e. they are based directly on some experimental measurement. It may be possible to interpret such a parameter as measuring some particular aspect of solvent-solute interaction or it may be regarded simply as a measure of solvent *polarity*. Other solvent parameters are based on analysing experimental results. Such a parameter is considered to quantify some particular aspect of solvent capability for interaction with solutes.

See REICHARDT (1965).

See also Dimroth-Reichardt E_T parameter, Grunwald-Winstein equation, Kamlet-Taft solvent parameters, Koppel-Palm solvent parameters, solvophobicity parameter, Z-value.

solvent polarity

See polarity.

solvent-separated ion pair

See ion pair.

solvolysis

Generally, reaction with a solvent, or with a *lyonium ion* or *lyate ion*, involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for *substitution*, *elimination* and *fragmentation reactions* in which a solvent species is the *nucleophile* ("alcoholysis" if the solvent is an alcohol, etc.).

solvophobicity parameter

A solvent parameter defined by

$$Sp = 1 - M/M(\text{hexadecane})$$

derived from the Gibbs energy of transfer ($\Delta_t G^\ominus$) of a series of solutes from water to numerous aqueous-organic mixtures and to pure solvents:

$$\Delta_f G^\circ(\text{to solvent}) = MR_T + D$$

where R_T is a solute parameter, and M and D characterize the solvent. The M values are used to define a solvent solvophobic effect so that Sp values are scaled from unity (water) to zero (hexadecane).

ABRAHAM, GRELLIER, and MCGILL (1988).

SOMO

A Singly Occupied Molecular Orbital (such as the half-filled *HOMO* of a radical). See also *frontier orbitals*.

sonication

Irradiation with (often ultra)sound waves, e.g. to increase the rate of a reaction or to prepare vesicles in mixtures of surfactants and water.

special salt effect

The initial steep rate increase observed in the *kinetic electrolyte effect* on certain solvolysis reactions, upon addition of some non-common ion salts, especially LiClO₄.

species

See chemical species.

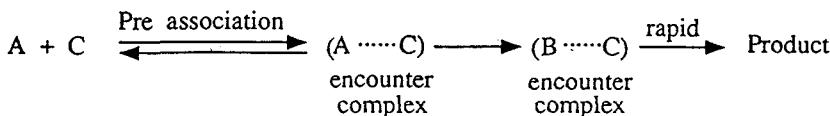
specific catalysis

The acceleration of a reaction by a unique *catalyst*, rather than by a family of related substances. The term is most commonly used in connection with specific hydrogen-ion or hydroxide-ion (*lyonium ion* or *lyate ion*) catalysis.

See also general acid catalysis, general base catalysis, pseudo-catalysis.

spectator mechanism

A pre-association mechanism in which one of the molecular entities, C, is already present in an encounter pair with A during formation of B from A, but does not assist the formation of B, e.g.



The formation of B from A may itself be a bimolecular reaction with some other reagent. Since C does not assist the formation of A, it is described as being present as a spectator, and hence such a mechanism is sometimes referred to as a spectator mechanism.

See also *microscopic diffusion control*.

spin adduct

See *spin trapping*.

spin counting

See *spin trapping*.

spin density

The unpaired *electron density* at a position of interest, usually at carbon, in a *radical*. It is often measured experimentally by electron paramagnetic resonance (EPR, ESR (electron spin resonance)) spectroscopy through hyperfine coupling constants of the atom or an attached hydrogen.

See also *radical centre*.

spin label

A *stable paramagnetic group* (typically a nitryl radical) that is attached to a part of a *molecular entity* whose microscopic environment is of interest and may be revealed by the electron spin resonance (ESR) spectrum of the spin label.

When a simple paramagnetic molecular entity is used in this way without covalent attachment to the molecular entity of interest it is frequently referred to as a "spin probe".

spin trapping

In certain reactions in solution a *transient radical* will interact with a diamagnetic reagent to form a more *persistent radical*. The product radical accumulates to a concentration where detection and, frequently, identification are possible by EPR/ESR spectroscopy. The key reaction is usually one of *attachment*; the diamagnetic reagent is said to be a "spin trap", and the persistent product radical is then the "spin adduct". The procedure is referred to as *spin trapping*, and is used for monitoring reactions involving the intermediacy of *reactive radicals* at concentrations too low for direct observation. Typical spin traps are C-nitroso compounds and nitrones, to which *reactive radicals* will rapidly add to form nitryl radicals. A quantitative development, in which essentially all reactive radicals generated in a particular system are intercepted, has been referred to as "spin counting". Spin trapping has also been adapted to the interception of radicals generated in both gaseous and solid phases. In these cases the spin adduct is in practice transferred to a liquid solution for observation in order to facilitate interpretation of the EPR/ESR spectra of the radicals obtained.

stable

As applied to *chemical species*, the term expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies. A chemical species A is more stable than its isomer B if $\Delta_f G^\circ > 0$ for the (real or hypothetical) reaction $A \rightarrow B$, under standard conditions. If for the two reactions



$\Delta_f G_1^\circ > \Delta_f G_2^\circ$, P is more stable relative to the product Y than is Q relative to Z. Both in qualitative and quantitative usage the term *stable* is therefore always used in reference to some explicitly stated or implicitly assumed standard.

The term should not be used as a synonym for *unreactive* or "less reactive" since this confuses thermodynamics and kinetics. A relatively more stable chemical species may be more *reactive* than some reference species towards a given reaction partner.

See also *inert, unstable*.

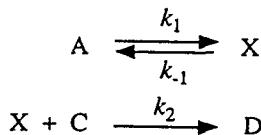
stationary state

- (1) In quantum mechanics: A state that does not evolve with time.
- (2) In kinetics: See *steady state*.

steady state (or stationary state)

(1) In a kinetic analysis of a complex reaction involving *unstable* intermediates in low concentration, the rate of change of each such *intermediate* is set equal to zero, so that the *rate equation* can be expressed as a function of the concentrations of *chemical species* present in

macroscopic amounts. For example, assume that X is an unstable intermediate in the reaction sequence:



Conservation of mass requires that:

$$[A] + [X] + [D] = [A]_0$$

which, since $[A]_0$ is constant, implies:

$$-d[X]/dt = d[A]/dt + d[D]/dt.$$

Since $[X]$ is negligibly small, the rate of formation of D is essentially equal to the rate of disappearance of A, and the rate of change of $[X]$ can be set equal to zero. Applying the steady state approximation ($d[X]/dt = 0$) allows the elimination of $[X]$ from the kinetic equations, whereupon the rate of reaction is expressed:

$$\frac{d[D]/dt}{d[A]/dt} = - \frac{k_1 k_2 [A] [C]}{k_1 + k_2 [C]}$$

Note: The steady-state approximation does not imply that $[X]$ is even approximately constant, only that its absolute rate of change is very much smaller than that of $[A]$ and $[D]$. Since according to the reaction scheme $d[D]/dt = k_2[X][C]$, the assumption that $[X]$ is constant would lead, for the case in which C is in large excess, to the absurd conclusion that formation of the product D will continue at a constant rate even after the reactant A has been consumed.

(2) In a stirred flow reactor a steady state implies a regime so that all concentrations are independent of time.

stepwise reaction

A chemical reaction with at least one reaction *intermediate* and involving at least two consecutive elementary reactions.

See also *composite reaction*.

stereoelectronic

Pertaining to the dependence of the properties (especially the energy) of a *molecular entity* in a particular electronic state (or of a *transition state*) on relative nuclear geometry. The electronic ground state is usually considered, but the term can apply to excited states as well. Stereoelectronic effects are ascribed to the different alignment of electronic orbitals in different arrangements of nuclear geometry.

stereoelectronic control

Control of the nature of the products of a chemical reaction (or of its rate) by stereoelectronic factors. The term is usually applied in the framework of an orbital approximation. The variations of *molecular orbital* energies with relative nuclear geometry (along a *reaction coordinate*) are then seen as consequences of variations in basis-orbital overlaps.

stereoselectivity, stereoselective

Stereoselectivity is the preferential formation in a chemical reaction of one stereoisomer over another. When the stereoisomers are enantiomers, the phenomenon is called enantioselectivity and is quantitatively expressed by the enantiomer excess; when they are diastereoisomers, it is called diastereoselectivity and is quantitatively expressed by the diastereomer excess. Reactions are termed (100%) stereoselective if the discrimination is complete or partially ($x\%$) stereoselective if one product predominates. The discrimination may also be referred to semiquantitatively as high or low stereoselectivity.

ELIEL (1962); IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

stereospecificity, stereospecific

(1) A reaction is termed stereospecific if starting materials differing only in their configuration are converted into stereoisomeric products. According to this definition, a stereospecific process is necessarily stereoselective but not all stereoselective processes are stereospecific. Stereospecificity may be total (100%) or partial. The term is also applied to

situations where reaction can be performed with only one stereoisomer. For example the exclusive formation of *trans*-1,2-dibromocyclohexane upon bromination of cyclohexene is a stereospecific process, although the analogous reaction with (*E*)-cyclohexene has not been performed.

(2) The term has also been applied to describe a reaction of very high stereoselectivity, but this usage is unnecessary and is discouraged.

ELIEL (1962).

[For the use of the term "stereospecific polymerization" see IUPAC POLYMERS (1981)]

steric-approach control

Control of stereoselectivity of a reaction by steric hindrance towards attack of the reagent, which is directed to the less hindered face of the molecule. Partial bond making is strong enough at the *transition state* for steric control to take place. This suggests that the transition state should not be close to products.

See also *product development control*.

steric effect

The effect on a chemical or physical property (structure, rate or equilibrium constant) upon introduction of substituents having different steric requirements. The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a *transition state*, (or products). A steric effect on a rate process may result in a rate increase ("steric acceleration") or a decrease ("steric retardation"). (The adjective "steric" is not to be confused with *stereochemical*.)

Steric effects arise from contributions ascribed to *strain* as the sum of (1) non-bonded repulsions, (2) bond angle strain, and (3) bond stretches or compressions.

For the purpose of *correlation analysis* or *linear free-energy relations* various scales of steric parameters have been proposed, notably *A values*, Taft's E_s and Charton's v scales.

In a reactant molecule RY and an appropriate reference molecule R^oY , the "primary steric effect" of R is the direct result of differences in compressions which occur because R differs from R^o in the vicinity of the reaction centre Y . A "secondary steric effect" involves the differential moderation of electron delocalization by non-bonded compressions.

Some authors make a distinction between "steric" effects attributed to van der Waals repulsions alone, and "strain" effects, attributed to deviations of bond angles from "ideal" values.

CHARTON (1987).

See *Taft equation*, *van der Waals forces*.

steric isotope effect

See *isotope effect*, *steric*.

steric hindrance

The original term for a *steric effect* arising from crowding of substituents.

stoichiometric number

See *rate of reaction*.

stopped flow

A technique for following the kinetics of reactions in solution (usually in the millisecond time range) in which two reactant solutions are rapidly mixed by being forced through a mixing chamber. The flow of the mixed solution along a uniform tube is then suddenly arrested. At a fixed position along the tube the solution is monitored (as a function of time following the stoppage of the flow) by some method with a rapid response (e.g. photometry).

See *mixing control*.

strain

Strain is present in a *molecular entity* or *transition structure* if the energy is enhanced because of unfavourable bond lengths, bond angles, or dihedral angles ("torsional strain") relative to a standard.

It is quantitatively defined as the standard enthalpy of a structure relative to a strainless structure (real or hypothetical) made up from the same atoms with the same types of bonding. (The enthalpy of formation of cyclopropane is 53.6 kJ mol⁻¹, whereas the enthalpy of formation based on three "normal" methylene groups, from acyclic models, is -62 kJ mol⁻¹. On this basis cyclopropane is destabilized by ca. 115 kJ mol⁻¹ of strain energy.)

See *molecular mechanics calculation*.

subjacent orbital

The Next-to-Highest Occupied Molecular Orbital ("NHOMO", also called "HOMO⁻") and the Second Lowest Unoccupied Molecular Orbital (SLUMO). Subjacent orbitals are sometimes found to play an important role in the interpretation of molecular interactions according to the *frontier orbital* approach.

BERSON (1972).

substituent electronegativity

See *electronegativity*.

substituent

An atom or *group* of bonded atoms that can be considered to have replaced a hydrogen atom (or two hydrogen atoms in the special case of bivalent groups) in a parent *molecular entity* (real or hypothetical).

substitution reaction

A *reaction*, *elementary* or *stepwise*, in which one atom or *group* in a *molecular entity* is replaced by another atom or group. For example,

**substrate**

A *chemical species*, the reaction of which with some other chemical reagent is under observation (e.g., a compound that is transformed under the influence of a *catalyst*). The term should be used with care. Either the context or a specific statement should always make it clear which chemical species in a reaction is regarded as the substrate.

See also *transformation*.

successor complex

The radical ion pair which forms by the transfer of an electron from the donor D to the acceptor A after these species have diffused together to form the *precursor* or *encounter complex*.

**suicide inhibition**

See *mechanism-based inhibition*.

superacid

A medium having a high *acidity*, generally greater than that of 100 wt.-% sulfuric acid. The common superacids are made by dissolving a powerful Lewis acid (e.g. SbF₅) in a suitable *Bronsted acid*, such as HF or HSO₃F. (An equimolar mixture of HSO₃F and SbF₅ is known by the trade name "magic acid".)

In a biochemical context "superacid catalysis" is sometimes used to denote catalysis by metal ions analogous to catalysis by hydrogen ions.

By analogy, a compound having a very high *basicity*, such as lithium diisopropylamide, is called a "superbase".

GILLESPIE (1968); OLAH (1985); OLAH and OLAH (1970).

superbase

See *superacid*.

suprafacial

See *antarafacial*.

supramolecule

A system of two or more *molecular entities* held together and organized by means of intermolecular (noncovalent) binding interactions.

LEHN (1993).

Swain-Scott equation

The *linear free-energy relation* of the form

$$\lg(k/k_0) = sn$$

applied to the variation of *reactivity* of a given *electrophilic substrate* towards a series of nucleophilic reagents. n is characteristic of the reagent (i.e. a measure of its *nucleophilicity*) and s is characteristic of the substrate (i.e. a measure of its sensitivity to the nucleophilicity of the reagent). A scale of n values is based on the rate coefficients k for the reaction of methyl bromide with nucleophiles in water at 25 °C, s being defined as 1.00 for these reactions and n being defined as 0.00 for the hydrolysis of methyl bromide. (Other scales have been devised.)

SWAIN and SCOTT (1953).

Swain-Lupton equation

A dual parameter approach to the correlation analysis of substituent effects, which involves a field constant (F) and a resonance constant (R). The original treatment was modified later.

SWAIN and LUPTON (1968); SWAIN, UNGER, ROSENQUIST and SWAIN (1983).

The procedure has been considerably applied, but also much criticized (see REYNOLDS and TOPSOM (1984); HOEFNAGEL, OSTERBEEK and WEPSTER (1984); CHARTON (1984); SWAIN (1984); HANSCH, LEO, and TAFT (1991)).

symbiosis

The term was originally applied to describe the maximum flocking of either hard or soft ligands in the same complexes. For hydrocarbon molecules, symbiosis implies that those containing a maximum number of C-H bonds (e.g. CH_4) or C-C bonds (e.g. Me_4C) are the most stable.

HO (1977).

symporation

Synonymous with *comproportionation*.

syn

See *anti*.

synartetic acceleration

See *neighbouring group participation*.

synchronization (principle of nonperfect synchronization)

This principle applies to reactions in which there is a lack of synchronization between bond formation or bond rupture and other *primitive changes* that affect the stability of products and reactants, such as *resonance*, *solvation*, *electrostatic*, *hydrogen bonding* and *polarizability* effects. The principle states that a product-stabilizing factor whose development lags behind bond changes at the *transition state*, or a reactant-stabilizing factor whose loss is ahead of bond changes at the *transition state*, increases the *intrinsic barrier* and decreases the "intrinsic rate constant" of a reaction. For a product-stabilizing factor whose development is ahead of bond changes, or reactant factors whose loss lags behind bond changes, the opposite relations hold. The reverse effects are observable for factors that destabilize a reactant or product.

BERNASCONI (1992).

See also *imbalance*, *synchronous*.

synchronous

A concerted process in which the *primitive changes* concerned (generally bond rupture and bond formation) have progressed to the same extent at the *transition state* is said to be synchronous. The term figuratively implies a more or less synchronized progress of the changes. However, the progress of the bonding change (or other primitive change) has not been defined quantitatively in terms of a single parameter applicable to different bonds or different bonding changes. The concept is therefore in general only qualitatively descriptive and does not admit an exact definition except in the case of concerted processes involving changes in two identical bonds.

See also *imbalance*.

σ-adduct (sigma adduct)

The product formed by the attachment of an *electrophilic* or *nucleophilic entering group* or of a *radical* to a ring carbon of an aromatic species so that a new σ -bond is formed and the original *conjugation* is disrupted. (This has generally been called a " σ -complex", but adduct is more appropriate than complex according to the definitions given.) The term may also be used for analogous adducts to unsaturated (and conjugated) systems in general.

See also *Meisenheimer adduct*.

σ -bond (sigma bond)

See *sigma, pi*.

 σ -constant (sigma constant)

Specifically the substituent constant for *meta*- and for *para*-substituents in benzene derivatives as defined by Hammett on the basis of the ionization constant of a substituted benzoic acid in water at 25°C, i.e. $\log(K_a/K_a^0)$, where K_a is the ionization constant of a *m*- or *p*-substituted benzoic acid and K_a^0 that of benzoic acid itself.

The term is also used as a collective description for related electronic substituent constants based on other standard reaction series, of which, σ^+ , σ and σ° are typical; also constants which represent dissected electronic effects such as σ_I and σ_R . For this purpose it might be better always to spell out the term in full, i.e. as "Hammett sigma constant", and restrict σ -constants to the scale of substituent constants which is based on benzoic acid.

A large positive σ -value implies high electron-withdrawing power by inductive and/or resonance effect, relative to H; a large negative σ -value implies high electron-releasing power relative to H.

CHAPMAN and SHORTER (1972, 1978); JOHNSON (1973); SHORTER (1973).

See also *Hammett equation, p-value, Taft equation*.

 σ -orbital (sigma orbital)

See *sigma, pi*.

T-jump

See *chemical relaxation*.

Taft equation

Various equations are associated with R.W. Taft, but the term is most often used to designate the family of equations that emerged from Taft's analysis of the reactivities of aliphatic esters, and which involved the polar substituent constant σ^* and the steric substituent constant E_s

$$\log k = \log k_0 + \rho^* \sigma^* + \delta E_s$$

or the one-parameter forms applicable when the role of either the polar term or the steric term may be neglected. Nowadays σ^* is usually replaced by the related constant σ_I .

TAFT (1952, 1953).

See also *Hammett equation, p-value, σ -constant*.

+ tautomeric effect

See *electromeric effect*.

tautomerism

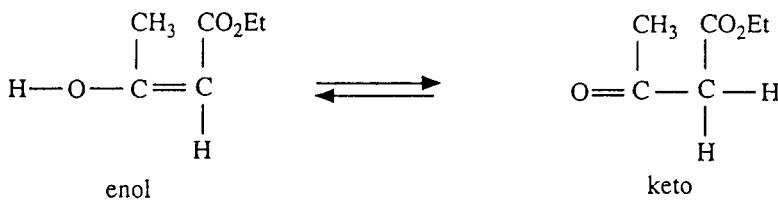
Isomerism of the general form



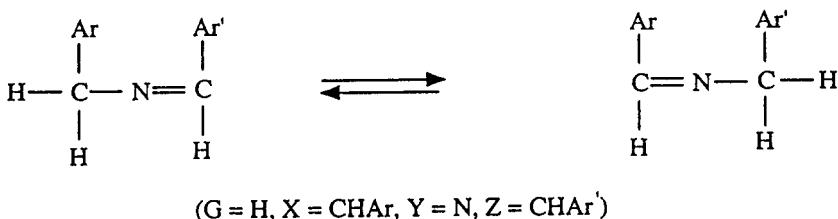
where the isomers (called tautomers) are readily interconvertible; the atoms connecting the groups X,Y,Z are typically any of C, H, O, or S, and G is a group which becomes an *electrofuge* or *nucleofuge* during isomerization. The commonest case, when the electrofuge is H^+ , is also known as "prototropy".

Examples, written so as to illustrate the general pattern given above, include:

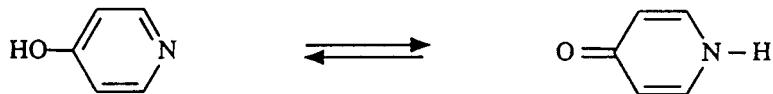
Keto-enol tautomerism, such as



(G = H, X = O, Y = CCH₃, Z = CHCO₂Et)

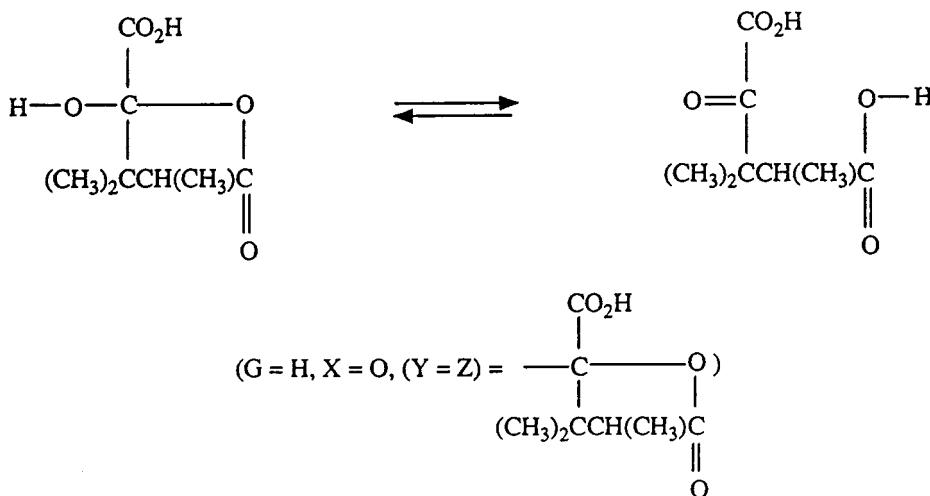


The grouping Y may itself be a three-atom (or five-atom) chain extending the conjugation, as in



$(G = H, X = O, Y = \text{C}-\text{CH}=\text{CH}, Z = N)$

The double bond between Y and Z may be replaced by a ring, when the phenomenon is called ring-chain tautomerism, as in



INGOLD (1953).

See also *ambident*, *sigmatropic rearrangement*, *tautomerization*, *valence tautomerization*.

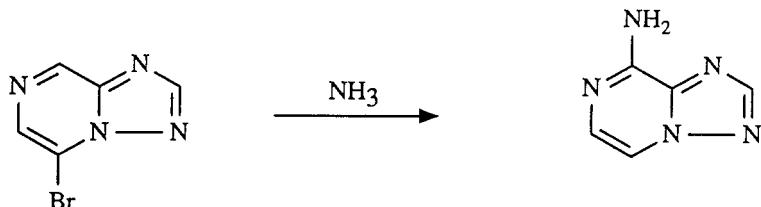
tautomerization

The *isomerization* by which tautomers are interconverted. It is a *heterolytic molecular rearrangement* and is frequently very rapid.

See *tautomerism*.

tele-substitution

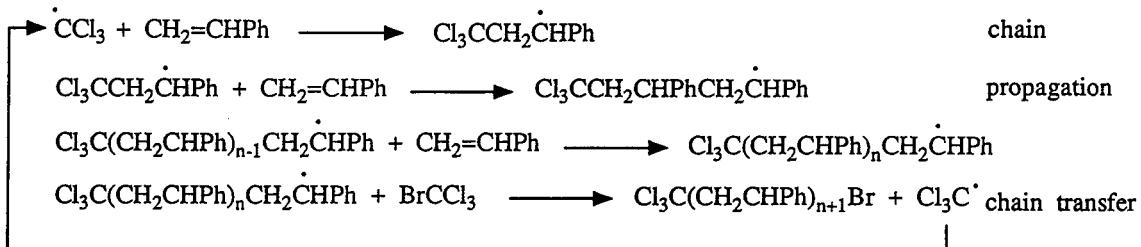
A *substitution reaction* in which the *entering group* takes up a position more than one atom away from the atom to which the *leaving group* was attached.



See also *cine-substitution*.

telomerization

The formation of an *addition* oligomer, having uniform end groups X'...X", by a *chain reaction* in which a *chain transfer* limits the length of the polymer ("telomer") produced. An example is the polymerization of styrene in bromotrichloromethane solution ($X' = \text{CCl}_3$, $X'' = \text{Br}$), where $\text{Cl}_3\text{C}\cdot$ radicals are formed in the initiation step to produce $\text{Cl}_3\text{C}[\text{CH}_2\text{CHPh}]_n\text{Br}$, with n greater than 1 and often less than ca. 10:



termination

The steps in a *chain reaction* in which reactive *intermediates* are destroyed or rendered inactive, thus ending the chain.

tetrahedral intermediate

A reaction *intermediate* in which the bond arrangement around an initially double-bonded carbon atom (typically a carbonyl carbon atom) has been transformed from trigonal to tetrahedral. For example, aldol in the *condensation reaction* of acetaldehyde (but most tetrahedral intermediates have a more fleeting existence).

thermodynamic control (of product composition)

The term characterizes conditions that lead to reaction products in a proportion governed by the equilibrium constant for their interconversion and/or for the interconversion of reaction *intermediates* formed in or after the *rate-limiting step*. (Some workers prefer to describe this phenomenon as "equilibrium control".)

See also *kinetic control*.

thermolysis

The uncatalysed cleavage of one or more covalent *bonds* resulting from exposure of a compound to a raised temperature, or a process in which such cleavage is an essential part.

See also *pyrolysis*.

tight-ion pair

See *ion pair*.

torquoselectivity

The term refers to the preference for "inward" or "outward" rotation of substituents in conrotatory or disrotatory electrocyclic ring opening reactions.

JEFFORD, BERNARDINELLI, WANG, SPELLMEYER, BUDA, and HOUK (1992).

transferability

Transferability assumes invariance of properties, associated conceptually with an atom or a fragment present in a variety of molecules. The property, such as *electronegativity*, nucleophilicity, NMR *chemical shift*, etc. is held as retaining a similar value in all these occurrences.

transformation

The conversion of a *substrate* into a particular product, irrespective of reagents or *mechanisms* involved. For example, the transformation of aniline ($\text{C}_6\text{H}_5\text{NH}_2$) into *N*-phenylacetamide ($\text{C}_6\text{H}_5\text{NHCOCCH}_3$) may be effected by use of acetyl chloride or acetic anhydride or ketene. A transformation is distinct from a reaction, the full description of which would state or imply all the reactants and all the products.

For nomenclature of transformations see IUPAC TERMINOLOGY FOR TRANSFORMATIONS (1989).

transient (chemical) species

Relating to a short-lived reaction *intermediate*. It can be defined only in relation to a time scale fixed by the experimental conditions and the limitations of the technique employed in the detection of the intermediate. The term is a relative one.

Transient species are sometimes also said to be "metastable". However, this latter term should be avoided, because it relates a thermodynamic term to a kinetic property, although most transients are also thermodynamically *unstable* with respect to reactants and products.

See also *persistent*.

transition coordinate

The *reaction coordinate* at the *transition state* corresponding to a vibration with an imaginary frequency. Motion along it in the two opposite senses leads towards the reactants or towards the products.

See also *reaction coordinate*, *transition state*.

transition state

In theories describing *elementary reactions* it is usually assumed that there is a transition state of more positive molar Gibbs energy between the reactants and the products through which an assembly of atoms (initially composing the *molecular entities* of the reactants) must pass on going from reactants to products in either direction. In the formalism of "transition state theory" the transition state of an elementary reaction is that set of states (each characterized by its own geometry and energy) which an assembly of atoms, when randomly placed there, would have an equal probability of forming the reactants or of forming the products of that elementary reaction. The transition state is characterized by one and only one imaginary frequency. The assembly of atoms at the transition state has been called an *activated complex*. (It is not a *complex* according to the definition in this Glossary.)

It may be noted that the calculations of reaction rates by the transition state method and based on calculated *potential-energy surfaces* refer to the potential energy maximum at the saddle point, as this is the only point for which the requisite separability of transition state coordinates may be assumed. The ratio of the number of assemblies of atoms that pass through to the products to the number of those that reach the saddle point from the reactants can be less than unity, and this fraction is the "transmission coefficient" κ . (There are also reactions, such as the gas-phase *colligation* of simple *radicals*, that do not require "activation" and which therefore do not involve a transition state.)

See also *Gibbs energy of activation*, *Hammond principle*, *potential energy profile*, *transition structure*.

transition state analogue

A substrate designed to mimic the properties or the geometry of the *transition state* of reaction.

transition structure

A saddle point on a *potential-energy surface*. It has one negative force constant in the harmonic force constant matrix.

See also *activated complex*, *transition state*.

transmission coefficient

See *transition state*.

transport control

See *microscopic diffusion control*.

trapping

The interception of a *reactive molecule* or reaction *intermediate* so that it is removed from the system or converted into a more *stable* form for study or identification.

See also *scavenger*.

tunnelling

The process by which a particle or a set of particles crosses a barrier on its potential energy surface without having the energy required to surmount this barrier. Since the rate of tunnelling decreases with increasing reduced mass, it is significant in the context of *isotope effects* of hydrogen isotopes.

umpolung

Any process by which the normal alternating donor and acceptor reactivity pattern of a chain, which is due to the presence of O or N heteroatoms, is interchanged. Reactivity

umpolung is most often achieved by temporary exchange of heteroatoms (N, O) by others, such as P, S, and Se.

The original meaning of the term has been extended to the reversal of any commonly accepted reactivity pattern. For example, reaction of R-C≡CX (X = halide) as a synthon for "R-C≡C⁺ (i.e. *electrophilic* acetylene) is an umpolung of the normal more common acetylidc, R-C≡C⁻ (i.e. *nucleophilic*) reactivity.

SEEBACH (1979).

unimolecular

See *molecularity*.

unreactive

Failing to react with a specified *chemical species* under specified conditions. The term should not be used in place of *stable*, since a relatively more stable species may nevertheless be more *reactive* than some reference species towards a given reaction partner.

unstable

The opposite of *stable*, i.e. the *chemical species* concerned has a higher molar Gibbs energy than some assumed standard. The term should not be used in place of *reactive* or *transient*, although more reactive or transient species are frequently also more unstable.

(Very unstable chemical species tend to undergo exothermic *unimolecular* decompositions. Variations in the structure of the related chemical species of this kind generally affect the energy of the *transition states* for these decompositions less than they affect the stability of the decomposing chemical species. Low stability may therefore parallel a relatively high rate of unimolecular decomposition.)

upfield

See *chemical shift*.

valence

The maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted.

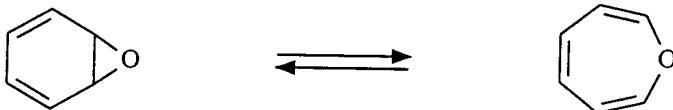
valence isomer

A constitutional isomer interrelated with another by *pericyclic reactions*. For example, Dewar benzene, prismane and benzvalene are valence isomers of benzene.

See *tautomerism*.

valence tautomerization

The term describes simple reversible and generally rapid *isomerizations* or *degenerate rearrangements* involving the formation and rupture of single and/or double bonds, without migration of atoms or groups; e.g.



TISLER (1973)

See also *fluxional, tautomerism*.

van der Waals forces

The attractive or repulsive forces between *molecular entities* (or between groups within the same molecular entity) other than those due to *bond formation* or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. The term includes: *dipole-dipole*, *dipole-induced dipole* and *London* (instantaneous induced dipole-induced dipole) *forces*.

The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces.

volume of activation, $\Delta^{\ddagger}V$

A quantity derived from the pressure dependence of the *rate constant* of a reaction (mainly used for reactions in solution), defined by the equation

$$\Delta^{\ddagger}V = -RT(\partial \ln k / \partial p)_T$$

providing that the rate constants of all reactions (except first-order reactions) are expressed in pressure-independent concentration units, such as mol dm⁻³ at a fixed temperature and pressure.

The volume of activation is interpreted, according to *transition state* theory as the difference between the partial molar volumes of the transition state ($\ddagger V$) and the sums of the partial volumes of the reactants at the same temperature and pressure, i.e.,

$$\Delta \ddagger V = \ddagger V - \Sigma(rV_R)$$

where r is the order in the reactant R and V_R its partial molar volume.

Wheland intermediate

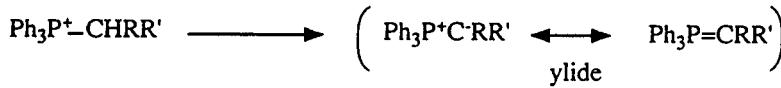
See *Meisenheimer adduct*, σ -adduct.

Woodward-Hoffmann rules

See *orbital symmetry*.

Ylide

A chemical species produced (actually or notationally) by loss of a *hydron* from an atom directly attached to the central atom of an "onium" ion, e.g.



Yukawa-Tsuno equation

A multiparameter extension of the *Hammett equation* to quantify the role of *enhanced resonance effects* on the reactivity of *meta*- and *para*-substituted benzene derivatives, e.g.

$$\lg k = \lg k_0 + \rho[\sigma + r(\sigma^+ - \sigma)]$$

The parameter r gives the enhanced resonance effect on the scale ($\sigma^+ - \sigma$), or ($\sigma^- - \sigma$), respectively.

See also ρ -value, σ -constant.

See YUKAWA and TSUNO (1959); SHORTER (1973).

Z-value

An index of the *ionizing power* of a solvent based on the frequency of the longest wavelength electronic absorption maximum of 1-ethyl-4-methoxycarbonylpyridinium iodide in the solvent. The Z-value is defined by

$$Z = 2.859 \times 10^4 / \lambda$$

where Z is in kcal mol⁻¹ and λ is in nm.

KOSOWER (1958).

See also *Dimroth-Reichardt E_T parameter*, *Grunwald-Winstein equation*.

Zaitsev rule

See *Saytzeff rule*.

zwitterionic compound

A neutral compound having electrical charges of opposite sign, delocalized or not on adjacent or nonadjacent atoms. Zwitterionic compounds have no uncharged canonical representations. Sometimes referred to as inner salts, ampholytes, dipolar ions (a misnomer).

For example: H₃N⁺CH₂C(=O)O⁻, glycine.

See also *ylide*.

Zucker-Hammett hypothesis

This hypothesis states that, if in an acid catalyzed reaction, $\lg k_1$ (first-order rate constant of the reaction) is linear in H_o (Hammett *acidity function*), water is not involved in the *transition state* of the *rate-controlling step*. However, if $\log k_1$ is linear in $\log[H^+]$, then water is involved. This has been shown to be incorrect by Hammett himself (see HAMMETT (1970)).

LONG and PAUL (1957).

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