

The Mechanism of Substitution Reactions

A. R. Olson

Citation: [The Journal of Chemical Physics](#) **1**, 418 (1933); doi: 10.1063/1.1749311

View online: <http://dx.doi.org/10.1063/1.1749311>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/1/6?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Precipitation mechanism of Alsubstituted tobermorite using hydrothermal reaction](#)

AIP Conf. Proc. **1251**, 300 (2010); 10.1063/1.3529306

[Rotational effects in complex-forming bimolecular substitution reactions: A quantum-mechanical approach](#)

J. Chem. Phys. **131**, 224303 (2009); 10.1063/1.3264684

[Substitution reactions of carbon nanotube template](#)

Appl. Phys. Lett. **88**, 223105 (2006); 10.1063/1.2208548

[Reactions of substituted aromatic hydrocarbons with the Si\(001\) surface](#)

J. Vac. Sci. Technol. A **18**, 1965 (2000); 10.1116/1.582455

[Theory of the simplest substitution reactions](#)

J. Chem. Phys. **58**, 3065 (1973); 10.1063/1.1679618



The Mechanism of Substitution Reactions

A. R. OLSON, *Department of Chemistry, University of California*

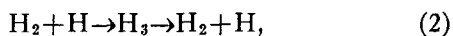
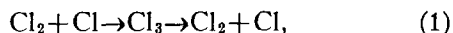
(Received April 15, 1933)

For many substitution reactions of the type $AB+C \rightarrow AC+B$, the strength of the bond between A and B is too great to account for the rate of the reaction. For such reactions addition or simultaneous addition and dissociations must occur. From the quantum mechanical conception of bonds, it is shown that a spatial inversion of A

occurs for every such substitution. This theory is applied in detail to some experiments on the Walden inversion, and a definite correlation between rotational and configurational changes is obtained. Its use in studying molecular rearrangements and cis-trans isomerization is sketched.

THE assumption that all substitution reactions, $AB+C \rightarrow AC+B$, can be divided into two mutually exclusive classes, i.e., (1) those in which dissociation of AB is the primary step, and (2) those in which the formation of the complex ABC is the primary step, is predicated on the postulate that each type of atom or molecule can be characterized by a definite size. However, dissociation and association are not instantaneous events, but are processes which require finite time, and therefore we must regard the above classes as limiting cases of a more inclusive group in which dissociation and association may be simultaneous phenomena.

The transition from the ordinary addition product to the simultaneous association and addition can be illustrated by the gaseous reactions



For all of these reactions, the heats of dissociation of the diatomic molecules is so large that in each case we can neglect primary dissociation.

Rollefson and Eyring¹ have applied the theory developed by London² to reaction (1). They found that 4.5 kilocalories activation energy was required to form the addition product, and 8.6 kilocalories was required to dissociate it. Further-

more the separation of the chlorine atoms in the original molecule increased only very slightly as the third atom approached. We would therefore be justified in assuming that in this case addition preceded dissociation.

For the hydrogen reaction Farkas³ found that atomic hydrogen was a catalyst for the conversion of para hydrogen into ortho hydrogen. London's theory was applied to this reaction by Eyring and Polanyi.⁴ They found that it required an activation energy of 11 kilocalories. They showed also that as the hydrogen atom approaches the molecule along the molecular axis, the atoms composing the original molecule begin to separate. The molecule H_3 needs about 1.5 kilocalories to decompose it, and so here again an addition compound could exist, but to a much more limited extent than in the chlorine case.

For the third reaction, the formation of an addition compound in the ordinary sense is impossible for the potential energy diagram of the reaction shows no region of stability for H_2Br . We are, therefore, dealing with simultaneous dissociation and addition. This evanescent addition product has this, however, in common with its more stable prototypes: The system requires much less activation energy if the bromine atom approaches the hydrogen molecule along the molecular axis than if it approaches it from any other direction.

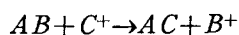
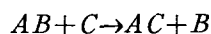
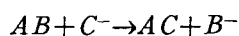
¹ G. K. Rollefson and H. Eyring, *J. Am. Chem. Soc.* **54**, 170 (1932).

² F. London, *Zeits. f. Elektrochemie* **35**, 552 (1929).

³ L. Farkas, *Zeits. f. physik. Chemie* **B10**, 419 (1930).

⁴ H. Eyring and M. Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931).

In the simple systems which we have considered, experimental proof of this statement cannot be obtained, but if the theory is extended to reactions such as



where A in particular may be a complex radical, we will be forced to certain conclusions, some of which can be subjected to experimental test. The strict application of London's theory to such complex systems is out of the question.

Not only are important data lacking, but the calculations involved in a quantitative solution of the problems are, at the present time, hopelessly burdensome. We can, however, get a qualitative picture from the type of potential energy diagram that would be expected for certain changes in the system. Thus let AB be the molecule $R_1R_2R_3CCl$ in which the bonds between the R 's and C are strong enough so that Cl can be identified with B . By plotting the energy of the system, ϵ , against the distance separating $R_1R_2R_3C$ from Cl (or between the corresponding ions) we obtain a curve of the type shown in Fig. 1, where r_0 is the equilibrium separation

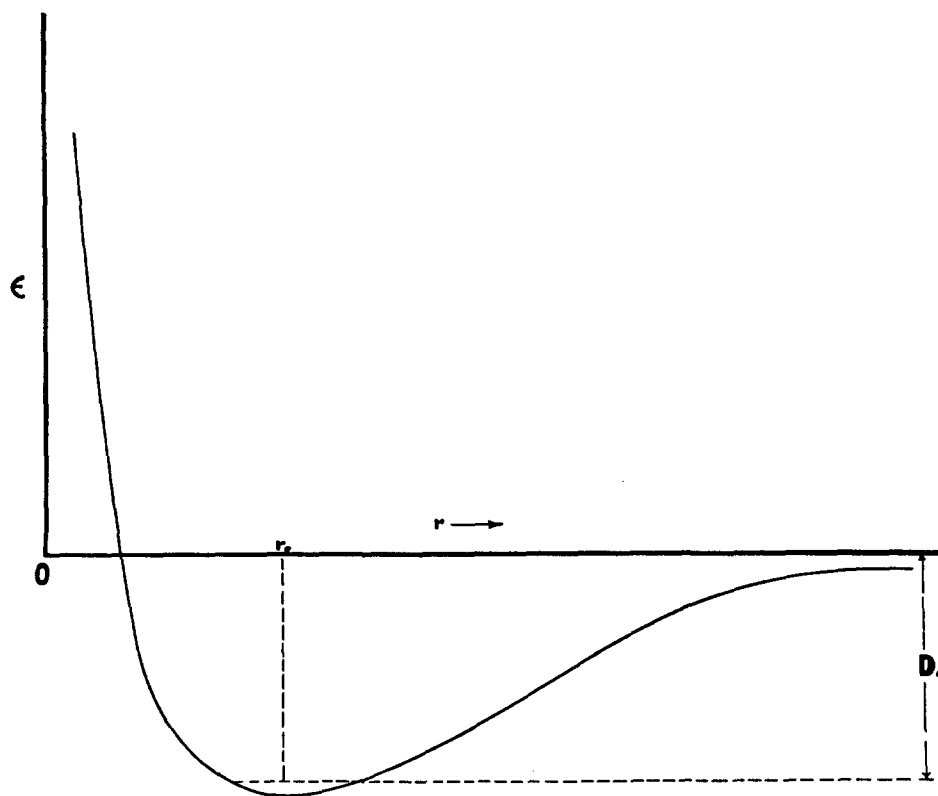


FIG. 1. Type of potential energy curve for the dissociation of $R_1R_2R_3CX$ into $R_1R_2R_3C$ and X , or into the corresponding ions.

According to Pauling⁵ the average value of D_0 for the carbon chlorine bond in substituted hydrocarbons is about 80 kilocalories per mol. This refers, however, to dissociation into a

⁵ L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

neutral atom and a radical. For dissociation into ions, D would be almost twice as much due to the difference between the ionizing potential of the radical and the electron affinity of chlorine. If the substance is in solution, cor-

rections for hydration and the dielectric constant of the solvent would have to be applied. This latter correction may be much smaller than is ordinarily supposed, for most of the work of separation is done at very small distance and here the effective dielectric constant seems to approach unity, as is shown by the fact that the frequencies of Raman lines are almost independent of the nature of the solvent. Fortunately for those substances which are to be discussed, we were able to obtain experimental⁶ proof of the assumption of a large value of the heat of dissociation into ions, not only for some chlorine compounds, but also for some bromine compounds. According to the Arrhenius equation, the speed of a reaction in which dissociation is a primary step is proportional to $e^{-D/RT}$. In our experiments aqueous solutions of *d*-chlor succinic acid, and of *l*-phenyl brom acetic acid were prepared. To the first solution sulfuric acid was added and to the second perchloric acid was added. This was done to repress not only hydroxide ion, but also the ions of the halogen acids so as to reduce either inter- or intra-ionic addition. Sulfate ion and perchlorate ion are much less prone to form addition complexes than other negative ions as was shown by Brönsted, Kilpatrick and Kilpatrick.⁷ This procedure does not eliminate all addition compounds for, as will be shown later, substances which have unbonded electron pairs can add. The chlor succinic acid solution was kept at 85°C for four hours and the phenyl brom acetic acid solution was kept at room temperature for five hours. In both cases the change in rotation was negligible, thus showing that primary dissociation does not occur to an appreciable extent. To this it might be objected that the free ions such as $C_6H_5C^+HCOOH$ retain their configurations, but were this the case, chloride and bromide ions could have no effect except to repress ionization. However, the racemizing action of these ions has been completely demonstrated not only in this laboratory, but also by Holmberg⁸ and by Kekule.⁹ The

⁶ The original experimental work mentioned in the various parts of this article will be published separately in collaboration with Miss M. J. Young and Mr. F. A. Long.

⁷ J. N. Brönsted, Mary Kilpatrick and Martin Kilpatrick, *J. Am. Chem. Soc.* **51**, 428 (1929).

⁸ B. Holmberg, *J. prakt. Chem.* **196**, 553 (1913).

⁹ Kekule, *Ann. Chem.* **130**, 21 (1864).

reaction of such compounds, therefore, cannot proceed by primary dissociation, and so we must assume an addition compound or simultaneous addition and dissociation.

The assumption of primary addition compounds in substitution reactions dates back at least to Kekule.⁹ Both Fischer¹⁰ and Werner¹¹ independently assumed addition reactions to explain the Walden inversion. Werner, furthermore, postulated simultaneous dissociation and addition. Both authors assumed that the entering group might or might not take the place of the dissociating group.

A more definite statement was made by Lewis.¹² "There seems to be but one possible way of accounting for this peculiar behavior (Walden inversion). Let us consider a carbon atom attached to the four radicals R_1 , R_2 , R_3 and R_4 , and let us assume that a fifth group, R_5 , becomes temporarily attached to the carbon atom near to the face of the tetrahedron which is opposite to R_1 . A slight shift of the kernel might make it now the center of a new tetrahedron with corners at R_2 , R_3 , R_4 and R_5 , while R_1 would become detached from the molecule. Then if the radical R_5 , in the new molecule were to be replaced by the radical R_1 , the resulting molecule would be the mirror image of the one with which we started. In this explanation it is not necessary to assume that the five radicals are attached to the carbon for any appreciable period of time, indeed it might be assumed that the R_1 leaves at the same instant that the R_5 becomes attached to the carbon atom."

Chemists and theoretical physicists agree that a molecule such as $R_1R_2R_3CCl$ should be represented as a tetrahedron. There is, however, this important difference; to most chemists the bond, i.e., the bond between carbon and chlorine, is thought of as extending between the carbon atom and the chlorine atom. But Pauling¹³ and Slater¹⁴ have shown by means of quantum mechanics that the carbon eigenfunction which is involved in the carbon chlorine bond extends beyond the

¹⁰ E. Fischer, *Ann.* **381**, 123 (1911).

¹¹ A. Werner, *Ber.* **44**, 873 (1911).

¹² G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, p. 113, Chemical Catalog Company, N. Y., 1923.

¹³ L. Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

¹⁴ J. C. Slater, *Phys. Rev.* **37**, 481 (1931).

carbon atom on the side away from the chlorine. The carbon atom, therefore, has a tendency to form a bond at each face of the tetrahedron. The stronger the bond is to the apex, the weaker the bond-forming power is to the opposite face since the strength of a bond is related to the amount that the eigenfunctions overlap. It must also be remembered that the chlorine in such a compound has, to some extent, the negative characteristics of chloride ion, as is shown, not only by its eventual ejection from the molecule as chloride ion, but also by dipole measurements, x-ray diffraction pictures of dichlor ethane, etc. A particle with unbonded electron pairs such as a chloride or a hydroxide ion will therefore require a smaller energy of activation to react with $R_1R_2R_3CCl$ if it approaches the carbon face directly opposite to the chlorine. It is immaterial whether there is addition or simultaneous addition and dissociation. The important point is that the group which is to be displaced determines a unique path for the entering group, such that the system requires less energy than it would for any other path. This, then, leads to complete inversion of configuration for a reaction which takes place in one step.

Experimentally the existence of this face centered bond is indicated by the work of

Menke.¹⁵ In order to interpret the x-ray diffraction pattern of liquid carbon tetrachloride, Menke assumed a structure in the liquid in which a chlorine from one molecule of carbon tetrachloride was face centered on the adjoining carbon tetrachloride tetrahedron.

The potential energy diagram of the system with the chloride ion added would be of the type shown in Fig. 2 where r_0 and ϵ_0 would depend on the distance AB separating the two chlorines. Some of these heats of activation for halogen acids and halide ions are now being measured in this laboratory. They are about 25 kilocalories per mol.

If there is more than one substance which can add we must consider sets of independent reactions. Thus in an aqueous solution of *l*-phenyl brom acetic acid, the initial reaction probably is



As the reaction proceeds the reaction



becomes increasingly important. If (5) is very fast compared to (4) a racemic mixture only can result. If (4) is very fast compared with (5), *l*-mandelic acid never could predominate. Nevertheless, such cases are known. Thus McKenzie and Clough¹⁶ report that when *l*-phenyl chlor acetic acid is treated with water or aqueous sodium hydroxide, *l*-mandelic acid results, but if it is treated with silver carbonate *d*-mandelic acid is secured. An explanation which suggested itself to us and which was in accord with the face centered addition theory, was that a third independent reaction was occurring which involved two inversions. Thus if the face of the asymmetric carbon atom opposite to the chlorine were absorbed on some surface, the carbon-chlorine bond would be weakened, causing the dissociation of chloride ion and inversion. Hydroxide ion could now add, again causing inversion and releasing the molecule from the

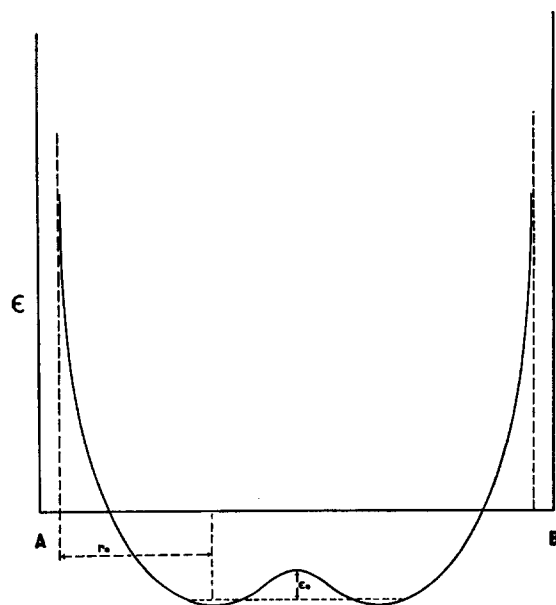
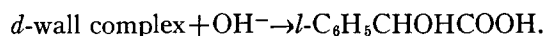
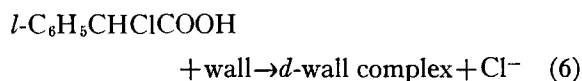


FIG. 2. Type of potential energy curve for the dissociation of $R_1R_2R_3CX$ into $R_1R_2R_3C$ and X , or into the corresponding ions in the presence of X or X ion.

¹⁵ H. Menke, Phys. Zeits. 33, 593 (1932).

¹⁶ Alex McKenzie and G. W. Clough, J. Chem. Soc. (London) 95, 777 (1909).

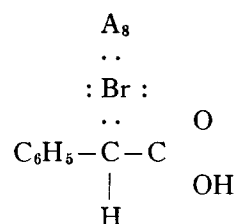
surface. The net result would be the production of *l*-mandelic acid from *l*-phenyl chlor acetic acid. Thus



No optically active phenyl chlor acetic acid was available to us but the corresponding brom compound was. This had been previously investigated by McKenzie and Walker,¹⁷ who found the action of silver carbonate on the brom compound to be similar to its action on the chlor compound. Water, however, produced a mandelic acid which was slightly dextro rotatory. Accordingly, we dissolved some phenyl brom acetic acid in water, divided the sample into two parts, and to one part added powdered silica. Both samples were then shaken in a thermostat kept at 25° for several days. The clear sample checked the observation of McKenzie and Walker, but that to which the silica had been added was levo rotatory.

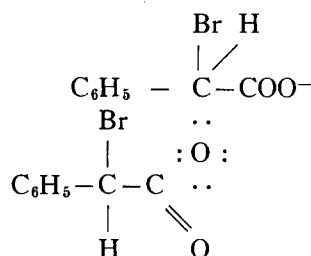
So far, there are then two ways in which a racemic mixture results; (a) reaction (5) is very fast compared to reactions (4) and (6); (b) reactions (4) and (6) have the same speed; in which case the velocity of reaction (5) is not critical. For phenyl brom acetic acid it is obvious that reaction (5) is slow enough so that we can determine that (4) is faster than (6). The addition of silica merely made (6) faster than (4). In the phenyl chlor acetic acid reaction (6) must be faster than (4).

We can now interpret the function of silver salts. The presence of silver ion will keep the halide ion concentration low and so prevent racemization by reaction (5). This can affect the magnitude of the final rotation but not the sign of the rotation—that is determined solely by the relative rates of (4) and (6). The addition of silver ion instead of reducing the surface will actually increase it due to the formation of silver chloride. Silver ion must therefore increase the speed of (4) more than (6). The formation of an addition compound such as



could accomplish this by decreasing the strength of the carbon bromine bond and thus increasing the speed of the homogeneous reaction.

In the above discussion we have neglected the possibility of ester and ring formation. If an ester such as



played a prominent part in this reaction, the rate law should contain the activity of this component to the second power which appears to be contrary to experiment.

The reactions of brom- and chlor-succinic acids are somewhat more complex than those of phenyl brom acetic acid. Walden¹⁸ obtained an *l*-malic acid from *l*-chlor succinic acid when silver oxide was present, and *d*-malic acid when potassium hydroxide was used. Holmberg⁸ and Bancroft and Davis¹⁹ showed that the rotation of the malic acid produced depended upon the amount of excess silver oxide. These observations can be explained if we assume that in the presence of a small amount of silver oxide the main effect is to reduce the speed of reaction (5). Malic acid and chlor succinic acid which have the same rotation must then have opposite configurations. In the presence of a large excess of silver oxide, not only is (5) slow, but reaction (6) is increased. This is in accord with a preliminary experiment in this laboratory on the effect of powdered silica on this reaction. Holmberg has also submitted evidence for the

¹⁷ Alex McKenzie and Nellie Walker, J. Chem. Soc. (London) 109, 1685 (1915).

¹⁸ P. Walden, Ber. 32, 1833 (1899).

¹⁹ W. D. Bancroft and H. L. Davis, J. Phys. Chem. 35, 1251 (1931).

formation of a lactone which may hydrolyze in two different ways, producing malic acids of opposite rotations. Formally, these hydrolysis reactions correspond to reactions (4) and (6) in that inversion of configuration is produced by one substitution on the asymmetric carbon atom, and the original configuration is the result of two successive substitutions, each of which is accompanied by inversion. Various authors have considered the possibility of the lack of configurational change as being due to an even number of inversions.

In the case of the Beckmann rearrangement this theory predicts the favorable experimental conditions. Thus, if in benzophenone oxime the nitrogen oxygen bond is strong enough so that primary dissociation does not take place, it will be necessary for a substance with an unbonded electron pair, such as chloride ion, to approach the nitrogen face opposite to the apex to which the hydroxide is bonded, i.e., X in Fig. 3. However, because of the free electron pair on the nitrogen, such an ion would be subjected to a large coulombic repulsion. In a strong acid solution hydrogen ion will add to the free pair, and reduce this repulsion considerably. This is just the condition which Lachman²⁰ found was necessary for the rearrangement.

As a further application, consider the thermal isomerization of *cis* dibrom ethylene catalyzed by bromine. The usual explanation of this reaction is the addition of bromine at the double bond followed by a dissociation. Such an

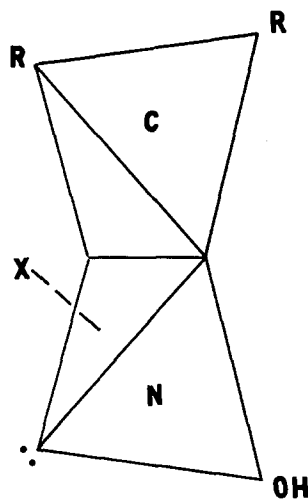


FIG. 3.

explanation cannot be correct for tetrabrom ethane is rather stable. But if bromine adds to the face of the carbon opposite to the apex at which a bromine is bound, a reaction corresponding to a Walden inversion of one of the carbons results. The new compound will be *trans* dibrom ethylene. This is the exact analogue of reaction (5) which has been experimentally demonstrated.

It is thus seen that this theory of chemical reactions, which is based on the energy relations involved, and on the quantum mechanical character of bonds, does satisfactorily explain the results of experiments. In its application to the experiments on the Walden inversion it leads to a direct correlation between rotation and configuration.

²⁰ A. Lachman, J. Am. Chem. Soc. **46**, 1477 (1924).