

A Possible Contributing Mechanism of Catalysis

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alter the molecular complexity, and in the dissolved state, combination between the solute and the solvent may take place. The method proposed in the present paper is being extensively tested by the writer.

¹ M. S. Telang, *J. Chem. Phys.* **15**, 525 (1947).

² The theoretical basis of this derivation will be the subject of a future paper by the writer.

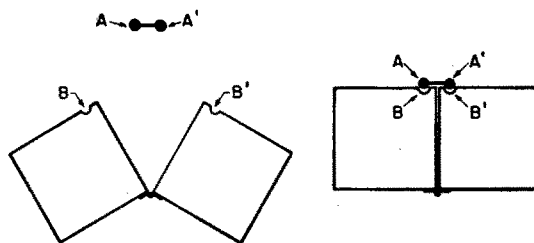


FIG. 1.

A Possible Contributing Mechanism of Catalysis

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IT seems remarkable that organic catalysts, and most inorganic ones, have a large mass, often much larger than that of their substrate. For example, catalase is about 10,000 times heavier than H_2O_2 . It may, therefore, be worth while to consider types of mechanism in which the mass of the catalyst could play a role.

It is generally assumed that the effect of a catalyst is to establish some course for the reaction to follow which does not involve as high an energy of activation as the uncatalyzed reaction. A catalytic effect would also be afforded, however, by establishing a course in which the reaction is accompanied by a large increase in the entropy of the catalyst.

Calling S the substrate and S' the product of the reaction catalyzed by C , the reaction might involve the following steps:

(1) $S + C \rightarrow SC$ accompanied by a moderate release of energy and a large loss of entropy.

(2) $SC \rightarrow S'C$ requiring a large activation energy E but accompanied by a regain of the entropy lost in (1).

(3) $S'C \rightarrow S' + C$ accompanied by a moderate uptake of energy.

If, for example, the loss of entropy Δs in (1) were equal to $E/2T$, the rates of reaction of (1) and (2) would be both moderately slow, being proportional, respectively, to $\exp(-\Delta s/R) = \exp(-E/2RT)$ and to $\exp[(\Delta s/R) - (E/RT)] = \exp(-E/2RT)$, but far higher than the rate of the uncatalyzed reaction.

Consider now the possible influence of the mass of a catalyst on this type of reaction, for example, in a case where $S = A-A'$, $S' = A+A'$. Step (1) of the reaction might be further resolved into:

(1a) $A-A' + C \rightarrow CA-A'$ accompanied by a moderate release of energy and no loss of entropy.

(1b) $CA-A' \rightarrow CA-A'$ accompanied by a further moderate release of energy and a large loss of entropy. As a concrete model, S might be a particle suspended in water and consisting of two blocks hinged together carrying specific receptor spots B and B' (for A and A') at the positions indicated on the sketch. Step (1a) may then occur according to the usual picture, step (1b) when the blocks happen to come in the right configuration; the absorption of A' onto B' then locks the blocks together, preventing their free rotation. This entails a loss of entropy of the

order of $R \log(IkT/\hbar^2)^{1/2}$, where I is the rotational moment of inertia of the hinged blocks and R , k , T , and \hbar have their usual meaning. The quantity in parentheses is of the order of magnitude of 100 for diatomic molecules and may be taken as 10^7 for an enzyme of molecular weight between 10^4 and 10^5 . The resulting entropy change affects the free energy by about 5000 calories, an amount which is not large but yet is significant. From an atomistic standpoint it may be said that Brownian fluctuations of the pressure of water molecules on the large faces of the blocks tend to tear the bond between A and A' .

In general, a catalyst of this type might be described as a particle so constructed that: (a) a very low zero-point energy corresponds to some of its internal degrees of freedom (this can happen only if the mass of the particle is large), and (b) those degrees of freedom can be nearly frozen in a particular configuration by specific absorption of a substrate molecule, so that their zero-point energy is thereby raised very much. For comparison it is recalled that the entropy increase in the reversible denaturation of proteins is equivalent to more than 50,000 calories.

Dr. J. E. Mayer, to whom I am also indebted for other suggestions, pointed out that step (2) in the reaction above would have a high temperature coefficient corresponding to the full activation energy E while its rate is determined by the lower free energy change $E - T\Delta s$. In fact, the temperature coefficient of enzymatic reactions is rather low.

This discrepancy and the result of the numerical calculation above make it unlikely that the mechanism suggested here is the main factor of catalysis. It may, however, be one among several concurrent factors of comparable importance.

The Dependence of Quenching Efficiency on Temperature

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October 13, 1947

A SMALL cross section for the process in which electronically excited atoms are quenched by other molecules may be theoretically associated with a small temperature coefficient if the non-adiabatic step or entropy of activation is the principal factor restricting the occurrence

of quenching, or with an appreciable temperature coefficient if an energy of activation is the principal restrictive factor.

In continuation of work instigated by Professor R. G. W. Norrish on the factors influencing degradation of electronic excitation energy to thermal energy, we have investigated a quenching process of small cross section; the quenching of excited sodium by methane. Norrish and Smith¹ found that the cross section for the quenching of sodium atoms in the 3^2P state by methane is approximately 0.11×10^{-18} cm² at 130°C. We have carried out measurements at 585°C and at 615°C, using the method developed by Terenin² and by Winans³ in which sodium atoms excited to the 3^2P state are produced by photo-dissociation of sodium iodide, the energy absorbed in excess of that required to produce dissociation going into kinetic energy of the sodium and iodine atoms. Nickel and cadmium condensed sparks have been used as sources of the radiation producing photolysis. The details of our experimental method resembled those of Winans.

Methane proved to be weakly quenching under our experimental conditions and in consequence cross sections have been calculated on the assumption that, before suffering quenching, sodium atoms attain velocities characteristic of the temperature of the quenching gas. The values for the cross sections evaluated in this manner are 0.19×10^{-16} cm² for 585°C and 0.16×10^{-16} cm² for 615°C. (There was no significant dependence of quenching ratio on the nature of the spark.) Because of the difficulties in photometry associated with the presence of a perceptible background of radiation and the low intensities of the radiation from the sodium, and because of the small extent of the quenching, these values are probably not significantly different and cannot be considered alone to indicate the magnitude of the temperature coefficient. However, taken in conjunction with the value 0.11×10^{-18} cm² obtained by Norrish and Smith by the resonance method at 130°C, they do indicate that the temperature coefficient for quenching by methane is very small.

If the only restrictions on the occurrence of quenching are the approach of the centers of the sodium atom and methane molecule to within about 4×10^{-8} cm and an activation energy (localized in two square terms), then a change in temperature of the system from 130°C to 585°C should be accompanied by a change in cross section from 0.11×10^{-18} cm² to approximately 4.5×10^{-16} cm². Our results consequently indicate that an activation energy is not the important restrictive factor.⁴ They do not, however, allow separate evaluation of the factors which lead to the small cross section.

The methane was prepared by the action of a zinc copper couple on a solution of methyl iodide, and was purified by passage through fuming sulfuric acid, over heated copper oxide, and by several distillations in vacuum. A portion of the gas subjected to a second purification showed no significant change in quenching properties.

¹ Norrish and Smith, *Proc. Roy. Soc. London* **A176**, 295 (1940).

² Terenin, *Zeits. f. Physik* **37**, 98 (1926).

³ Winans, *Zeits. f. Physik* **60**, 631 (1930).

⁴ K. J. Laidler, *J. Chem. Phys.* **10**, 34 (1942).

On the Structure of Ozone

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July 8, 1947

THE shape of the ozone molecule is still a subject for controversy. Adel and Dennison,¹ from investigations of the rotational fine structure of the infra-red bands, considered that they had obtained conclusive evidence for an acute-angled structure, and this seemed supported by the bond-energy calculations of Glockler and Matlack.² More recently Eberhardt³ has shown that the bond energies can equally well be interpreted on the basis of a wide-angled model with dimensions given by the electron-diffraction investigations.⁴ It is the purpose of the present note to indicate that the interpretation of the infra-red bands given by Adel and Dennison is not unique, and that their experimental data are not incompatible with a wide-angled structure.

Adel and Dennison suggest: (a) that the strong band at 705 cm⁻¹ is near perpendicular in type, with a coarse rotational spacing ~ 5.7 cm⁻¹ and subsidiary fine structure, so that the change in electric moment for this vibration must be along the middle axis of inertia; (b) that since both the strong bands at 1043 and 2108 cm⁻¹ have *Q* branches and a rotational spacing of ~ 1 cm⁻¹, and since their appearance is very different from that of the 705-cm⁻¹ band, they must both be near parallel bands with change in electric moment along the least axis of inertia.

Taken together, these arguments indicate that if the three strongest regions of absorption correspond to the three fundamental frequencies, that since 1043 and 2108 cm⁻¹ are near parallel bands and 705 cm⁻¹ is near perpendicular, the assignment to ν_1 , ν_2 , and ν_3 , respectively, follows; moreover, the molecule must be acute-angled, the least axis of inertia coinciding with the symmetry axis. The moments of inertia may then be calculated from the observed rotational spacings, and the apical angle so derived (34°) is in good agreement with that obtained from the fundamental frequencies (39°) using a central force field.⁵

From the published curves for the bands at 1043 cm⁻¹ and 2108 cm⁻¹,^{6,7} it is seen that the latter has a pronounced *Q* branch, while the former, at least under low dispersion, has none. The dissimilarity of the contours is striking. It should also be noted that the published curves were not obtained under ideal conditions, the band at 1043 cm⁻¹ is overlaid with carbon dioxide absorption, that at 2108 cm⁻¹ was observed using a specimen admittedly contaminated with nitrogen pentoxide, a substance which absorbs in the same region.⁸ The fine structure observed, therefore, cannot be due entirely to ozone. There is thus some justification in criticizing Adel and Dennison's conclusion that both 1043 and 2108 cm⁻¹ are near parallel bands. Further, unless *both* are near parallel bands, the molecule is not necessarily acute-angled and their interpretation of the rotational fine structure is not unique.

For the wide-angled model, the middle axis of inertia coincides with the symmetry axis. *A*₁ bands (e.g., ν_1 , ν_2) have a doublet structure, *B*₁ bands (e.g., ν_3) a *Q* branch. For this