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Citation: [The Journal of Chemical Physics](#) **17**, 503 (1949); doi: 10.1063/1.1747304

View online: <http://dx.doi.org/10.1063/1.1747304>

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or polish layer, the vitreous, amorphous, or cold-worked state, etc.) Such "mixed" surfaces, although they may be largely crystalline, pick up activities commensurate with those acquired by highly polished surfaces (100–200 counts per min. per cm²), and give autoradiographs showing that this activity is largely confined to the crystalline areas. This means that crystalline silver, which by itself shows little tendency to exchange with ions in solution, receives a deposit of metal when it is mixed with non-crystalline silver. This must be the result of an electrolytic action in which ions enter the solution from the anodic worked areas and deposit from solution on the cathodic crystalline surface. However, many attempts to increase the activity take-up of an etched annealed foil by connecting it electrically with a polished foil in the same solution have been fruitless. It would seem that the potential differences involved are so small that they are effectively short-circuited by imperfections in the polish layer.

The fact that polished surfaces slowly acquire a partially removable activity and that considerable activity is picked up by the smooth anodic areas of a mixed surface suggests to the writers that two exchange mechanisms are involved. One of these, the electrochemical, discussed above, accounts for the greater part of the activity acquired by the crystalline areas of a mixed surface. The other, kinetic in nature, is responsible for the activity taken up by polished surfaces and the anodic non-crystalline areas of cold-worked specimens. The enhanced reactivity and solvent properties of metals brought about by polishing and cold-working are well known, and it is probable that such surfaces would take part in exchanges that are impossible for crystals. Preliminary experiments on the pre-treatment of surfaces in non-active solutions indicate that it is possible to separate these two effects. Other tracer experiments on corrosion of metals, the autoradiographic measurement of small potentials, and the phenomena of cold-working are in progress. Details are being published in the Canadian Journal of Research.

Financial assistance from the National Research Council of Canada is gratefully acknowledged.

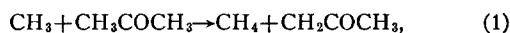
Note on Steric Factors for Some Reactions Involving Free Radicals*

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March 21, 1949

FOR purposes of possible comparison with experimental results from this Laboratory to be reported later, we have calculated steric factors for several reactions involving free radicals, using the theory of absolute reaction rates of Eyring and others.

I. An approximate calculation for the reaction,



leads to $P = 2 \times 10^{-4}$ (the accuracy is such that the possible range is about $6 \times 10^{-4} - 6 \times 10^{-5}$). It is probably not worth while to give the details of the calculation, but we might indicate the general features. We write, in the usual notation,

$$k = \kappa(kT/h)(F^\ddagger/F_A F_B) \exp(-E_0/kT), \quad (2)$$

$$= f(T) \exp(-E_0/kT). \quad (3)$$

We define the experimental activation energy E_{exp} by

$$E_{\text{exp}} = kT^2(d \ln k/dT) \quad (4a)$$

$$= E_0 + kT^2(d \ln f/dT). \quad (4b)$$

The steric factor P is not a fundamental quantity in the theory of absolute reaction rates. However, one can obtain a value

for P by comparing the collision theory expression

$$k = PZ \exp(-E/kT), \quad E = E_{\text{exp}} - \frac{1}{2}kT, \quad (5)$$

with Eq. (3), using Eq. (4b) for E_{exp} . This gives

$$P = \frac{f(T)e^{-1}}{Z \exp[-T(d \ln f/dT)]}. \quad (6)$$

Z is the collision number.

Thus P can be calculated, without knowing the activation energy (either E_0 or E), by an approximate treatment of the geometry, vibrational frequencies, moments of inertia, and internal rotations of the activated complex and the reactants. Because the individual factors in the vibrational partition functions are not much greater than unity, the calculation is fortunately not very sensitive to the vibrational assignment. We took $\kappa = \frac{1}{2}$ here because of the probability of the existence of a potential basin. Whether the mean molecular diameter in Z is taken from the estimated geometry of the activated complex or from an estimate of the kinetic theory, collision diameter turns out to make no appreciable difference in this case.

This type of calculation was suggested by the discussions of Glasstone, Laidler, and Eyring¹ (pp. 16–25) and Kistiakowsky and Ransom.²

II. Eyring, Gorin, and co-workers have given a treatment³ of free radical and atomic association reactions (e.g., $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$) in which a crucial role is played by the rotational energy in determining the activated complex. In this treatment the activated complex turns out to correspond to relatively large interatomic or inter-radical distances. This allows, to a good approximation, considerable cancellation in and simplification of the expression for the absolute reaction rate. The rather general results for any reaction of this type is

$$k = \frac{\kappa 2^{11/6} \pi^{\frac{1}{2}} \Gamma(\frac{3}{2}) \beta^{\frac{1}{2}} (kT)^{1/6}}{\sigma \mu^{\frac{1}{2}}}, \quad (7)$$

where σ is the symmetry number, and μ is the reduced mass of the activated complex considered as a diatomic molecule. The potential of intermolecular force is assumed to have the form $-\beta/r^6$, which should be adequate for the large values of r of interest here.

One way to test Eq. (7) is to deduce a steric factor for comparison with experiment. Using Eqs. (4a), (5), and (7), together with

$$Z = D^2/\sigma(8\pi kT/\mu)^{\frac{1}{2}}, \quad (8)$$

where D is the mean molecular diameter, one finds

$$P = \frac{\kappa \Gamma(\frac{3}{2}) \left(\frac{2\beta}{ekT}\right)^{\frac{1}{2}}}{D^2}. \quad (9)$$

In comparing P from Eq. (9) with P deduced from experimental data, one should use the same value of D in both cases.⁴

For the association of two methyl radicals, we estimate⁵ $\beta = 1.475 \times 10^{-13}$ erg-cm,⁶ and for the kinetic theory collision diameter,⁶ $D = 3.5\text{\AA}$ (at 120°C). At 120°C, this gives, from Eq. (9), $P = 1.39\kappa$.

As has been pointed out,³ the neglected hindered rotation of the two methyl radicals in the activated complex, owing to their interaction, will reduce the above values of P by a factor of perhaps two or three.

In the expression $P = 1.39\kappa$, it is quite possible that κ is much less than unity. If deactivation of the associated molecule by collision occurs in every case before redissociation, $\kappa = 1$. A high foreign gas pressure and a long lifetime of the associated molecule tend to make $\kappa \rightarrow 1$. There has already been some discussion (but no definite conclusions) using classical mechanics,^{7,8} of the increase in lifetime to be expected as a result of the possibility of distributing the energy originally belonging to the reaction coordinate among the various vibrational modes. This effect might well lead to $\kappa \approx 1$ for sufficiently complicated cases (e.g., $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$), but of

course is not involved in the simplest cases (e.g., H+H). The case CH_3+CH_3 would appear to be of an intermediate nature.

The present model introduces another factor to be considered in the above connection. The (mean) activated state, in CH_3+CH_3 , comes at⁴ 5.90A. Ignoring the distribution of vibrational energy among other vibrational degrees of freedom, the lifetime of the associated molecule should be increased by virtue of this relatively large distance. We have calculated, using classical mechanics, the time necessary for two methyl radicals to go from $r=5.90\text{A}$ to $r=r_0$ (see below) and back to $r=5.90\text{A}$ for an average case. The location of the activated complex, $r=r^*$, depends on the value of $J(J+1)$. For the average case calculated, we have chosen that value of $J(J+1)$ which gives $r^{*2}=(5.90)^2$. The rotational energy U_R is then

$$U_R = [h^2 J(J+1)/8\pi^2 \mu r^2]. \quad (10)$$

For the interaction energy U_I we have used $U_I = -\beta/r^6$ for $r > 4\text{A}$ and a Morse curve (giving $r_e = 1.54\text{A}$, $\nu_{\text{C-C}} = 993\text{ cm}^{-1}$ and $D_{\text{C-C}} = 79.1\text{ kcal./mole}$) for $r < 2.5\text{A}$. A smooth, arbitrary transition curve was used in the range $2.5\text{A} < r < 4\text{A}$. The time for a classical particle of average energy $\frac{3}{2}kT$ (rotation plus vibration) and mass μ to go from $r=5.90\text{A}$ to $r=r_0$ and back to $r=5.90\text{A}$ in the potential field $U = U_R + U_I$ was then computed by numerical integration, where $U(r_0) = \frac{3}{2}kT$ ($r_0 = 1.20\text{A}$); also, the potential barrier at $r=5.90\text{A}$ turns out to be 101 cal./mole . For 120°C , this time was found to be $5.4 \times 10^{-13}\text{ sec.}$ The corresponding time for a harmonic oscillator of frequency $\nu = 993\text{ cm}^{-1}$ is $0.34 \times 10^{-13}\text{ sec.}$, which is smaller by a factor of 16.

However, in the presence of acetone at 117.4 mm pressure ,^{6,9} the mean interval between collisions of such an associated molecule with acetone molecules is $6.75 \times 10^{-10}\text{ sec.}$ Hence, in the lifetime $5.4 \times 10^{-13}\text{ sec.}$, the probability of deactivation by collision (assuming every collision is effective) is 8.0×10^{-4} . This value can probably be considered a lower limit for κ (at this pressure and temperature), as the effect studied by Kimball⁷ and Kassel⁸ will of course tend to increase κ .

The author is indebted to Professor W. A. Noyes, Jr., for suggesting this problem and to Professor Noyes, Professor W. D. Walters, and Dr. L. M. Dorfman for helpful discussions.

* This work was carried out with the support of the ONR.

¹ Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

² Kistiakowsky and Ransom, *J. Chem. Phys.* **7**, 725 (1939).

³ Summarized on pp. 127-133, 260-261 of reference 1.

⁴ The mean square inter-radical distance in the activated complex, using k_J as a weighting function in computing the average, where k_J is the rate of the reaction for an activated complex with rotational quantum number J , turns out to be $2\Gamma(\frac{1}{2})/(\beta/kT)^{1/2}/\Gamma(\frac{1}{2})$. Using this for D^2 in Eq. (9) gives $P = \kappa[\Gamma(\frac{1}{2})]^2/\Gamma(\frac{1}{2})^2 = 0.49\kappa$ for any reaction of this type. For the combination of two methyl radicals at 120°C , and using the β mentioned, the root-mean-square inter-radical distance in the activated complex is 5.90A .

⁵ T. L. Hill, *J. Chem. Phys.* **16**, 399 (1948).

⁶ T. L. Hill, *J. Chem. Phys.* (to be submitted).

⁷ G. E. Kimball, *J. Chem. Phys.* **5**, 310 (1937).

⁸ L. S. Kassel, *J. Chem. Phys.* **5**, 922 (1937).

⁹ Estimating kinetic theory collision diameters of 4.95A for acetone and 5.1A for a rather expanded ethane.

Symmetry Species of Overtones of Degenerate Vibrational Fundamentals

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March 17, 1949

THE symmetry species of overtones of degenerate vibrational fundamentals have been derived by Tisza,¹ whose calculation of the characters of such levels involved essentially a recursion relation between the characters of successive overtones. It is the purpose of this note to describe several closed expressions for such characters; the expressions are limited to the cases of double and triple degeneracy of the fundamental.

By choosing polar normal coordinates, defined in terms of the "cartesian" normal coordinates, Q_a , Q_b , and Q_c , the (unnormalized) wave functions assume the following forms:

(i) Doubly degenerate case:
 $\psi_{vi} = \exp(-\gamma\rho^2/2)F_{vi}(\gamma^{\frac{1}{2}}\rho)\exp(i\ell\phi). \quad (1)$

(ii) Triply degenerate case:

$$\psi_{vlm} = \exp(-\gamma r^2/2)G_{vl}(\gamma^{\frac{1}{2}}r)P_l^{|m|}(\cos\theta)\exp(im\phi). \quad (2)$$

The polar coordinates, ρ and ϕ ; r , θ , and ϕ , are defined by

$$(i) \quad Q_a = \rho \cos\phi \quad Q_b = \rho \sin\phi, \quad (3)$$

$$(ii) \quad Q_a = r \sin\theta \cos\phi \quad Q_b = r \sin\theta \sin\phi \quad Q_c = r \cos\theta. \quad (4)$$

The quantum numbers assume the following values: (i) $v=0, 1, 2, \dots$; $l=0, \pm 2, \pm 4, \dots \pm v$ if v even, $l=\pm 1, \pm 3, \pm 5, \dots \pm v$ if v odd; (ii) $v=0, 1, 2, \dots$; $l=0, 2, 4, \dots v$ if v even, $l=1, 3, 5, \dots v$ if v odd; $m=0, \pm 1, \pm 2, \dots \pm l$.

In order to determine the characters of overtones ($v=2, 3, \dots$) it is necessary to determine from a character table two properties of the doubly or triply degenerate fundamental species corresponding to $v=1$. These are: (a) whether the (irreducible) representation matrix has a positive or negative determinant; (b) an angle, α_R , such that

$$\chi_R^{(1)} = 2 \cos \alpha_R \quad (\text{doubly degenerate case}), \quad (5)$$

$$\chi_R^{(1)} = \pm 1 + 2 \cos \alpha_R \quad (\text{triply degenerate case}). \quad (6)$$

In (5) and (6), $\chi_R^{(1)}$ is the character of a group operation, R , for a doubly or triply degenerate species which corresponds with the fundamental level ($v=1$) in question. It is unnecessary to solve (5) if the matrix has a negative determinant; the choice of signs in (6) corresponds precisely to positive or negative determinants.

The criteria for the signs of the determinant are:

(i) Doubly degenerate case:

The sign is negative if $\chi_R^{(1)}=0$ and $\chi_R^{(1)}=+2$; otherwise positive.

(ii) Triply degenerate case:

The sign is positive if $\chi_R^{(1)} = (\chi_R^{(1)})^2 - 2\chi_R^{(1)}$ when $\chi_R^{(1)} \neq 0$, or if $\chi_R^{(1)} = +3$ when $\chi_R^{(1)} = 0$; otherwise negative.

In the above expressions, $\chi_R^{(1)}$ means the character of the n th power of the group operation, R .

The following character formulas can then be shown to hold (R^+ mean a group operation whose matrix in the given irreducible representation has a positive determinant, R^- a negative determinant):

(i) Doubly degenerate case:

$$\chi_{R^+}^{(v)} = \frac{\sin(v+1)\alpha_R^+}{\sin\alpha_R^+}, \quad (7)$$

$$\chi_{R^-}^{(v)} = \begin{cases} 0, & v \text{ odd} \\ 1, & v \text{ even} \end{cases}. \quad (8)$$

(ii) Triply degenerate case:

$$\chi_{R^+}^{(v)} = \frac{\{\sin[(v+1)\alpha_R^+/2]\} \{\sin[(v+2)\alpha_R^+/2]\}}{[\sin(\alpha_R^+/2)][\sin\alpha_R^+]}, \quad (9)$$

$$v \text{ odd} \quad \chi_{R^-}^{(v)} = \frac{\{\sin[(v+1)\alpha_R^-/2]\} \{\cos[(v+2)\alpha_R^-/2]\}}{[\cos(\alpha_R^-/2)][\sin\alpha_R^-]}, \quad (10)$$

$$v \text{ even} \quad \chi_{R^-}^{(v)} = \frac{\{\cos[(v+1)\alpha_R^-/2]\} \{\sin[(v+2)\alpha_R^-/2]\}}{[\cos(\alpha_R^-/2)][\sin\alpha_R^-]}. \quad (11)$$

It is also possible to give character formulas for the sub-levels of a given v , which will be useful particularly in studying the splitting of degeneracies when anharmonic potential terms and vibration-rotation interaction energies are included in the general molecular problem. Thus, in the doubly degenerate case, it is possible to express $\chi_R^{(v)}$ in the form: