AIP | The Journal of Chemical Physics

Theoretical Interpretation of Reactions Occurring in Photochlorination

Harold S. Johnston and Paul Goldfinger

Citation: The Journal of Chemical Physics **37**, 700 (1962); doi: 10.1063/1.1733150
View online: http://dx.doi.org/10.1063/1.1733150
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/37/4?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 37, NUMBER 4 AUGUST 15, 1962

Theoretical Interpretation of Reactions Occurring in Photochlorination*

HAROLD S. JOHNSTON† AND PAUL GOLDFINGER
Service de Chimie Physique I, Université Libre de Bruxelles, Bruxelles 5, Belgique

(Received April 5, 1962)

The Arrhenius A and E factors of over 60 elementary reactions in photochlorination systems have recently been evaluated experimentally in this and other laboratories. In this article a uniform treatment of most of these reactions is given by activated complex theories. Two parameters are fit to the data from two activation energies. The other activation energies follow the expected trend for reactions of chlorine atoms with hydrocarbons, but the reactions of chlorine atoms with chlorinated hydrocarbons do not follow the expected trends. For reactions with activation energy, the theory accounts very well for the magnitudes and trends of the Arrhenius A factors. For reactions with no activation energy, the activated complex theory as used by Gorin accounts for the order of magnitude of the rate constants of the group as a whole, but it fails to account for several pronounced trends in the data and is judged to be of no predictive value. For certain limited types of chemical reactions and over restricted ranges of experimental conditions, activated-complex theory is judged capable of predicting some kinetic factors. The range of predictions is small, but is not zero.

INTRODUCTION

In recent years a large amount of work has been done on the kinetics of chlorine-atom reactions, with several sequences of organic reactants. The results are summarized in convenient tables for saturated hydrocarbons[1] and for chloro-substituted methane, ethylene and ethane.[2] The first series[1] of reactants has been considered by means of activated-complex theory by the rather primitive method of regarding bonds in all the activated complex as "half bonds" and assigning the same bending and stretching force constants to the entire series. The second series of reactions has not been subjected to a theoretical treatment.

Use of the London–Polanyi–Eyring semiempirical method of deducing potential-energy surfaces for chemical reactions was thoroughly analyzed in the book by Glasstone, Laidler, and Eyring.[3] Potential-energy surfaces constructed by the model typically give a deep "well in the top of the pass." On more detailed theoretical treatment, it appears that the "well" is an "artifact of the approximation." Also detailed calculations of kinetic isotope effects using these surfaces give strong disagreement with experiment for a number of cases. Thus the use of potential-energy surfaces in interpretation of kinetic data has fallen more or less into disuse.

A modification of Eyring's semiempirical scheme has been proposed by Sato[4] and reviewed by Weston.[5] This potential-energy surface has all the conceptual flaws of Eyring's semiempirical surface, but as a practical computational device it has the status of a postulate that should be tested. An alternate approach has recently been proposed[6]; this method is frankly "100% empirical," but the empiricism is in the fields of molecular structure and molecular spectroscopy, external to the field of kinetics itself.

The methods discussed above are applicable only to reactions with activation energy. For reactions with zero activation energy, such as ion–molecule reactions[7] or recombination of radicals,[8] activated-complex theory calculates the rate of reaction as the rate of crossing the "rotational barriers."

The object of this article is to apply activated-complex theory in a uniform manner to chlorine-atom reactions of references 1 and 2. What is tested by this procedure? Is it a test of activated-complex theory itself; is it a test of the methods of finding a potential-energy surface; is it a test of the experimental data? One expects errors in all three. Perhaps it should be interpreted as an examination of the range of variation predicted by the theory and the potential-energy models, and a broad test of whether the magnitudes and trends of the data are reflected by the theory and the models.

THEORY AND MODELS

It will be recalled from the outset that activated-complex theory does not calculate the rate of reaction. It calculates the rate of crossing the top of a potential-energy barrier; and it provides an undetermined function κ, the transmission coefficient, which is the fraction of systems crossing the barrier that go on to form products. The function κ has been evaluated only for strictly one-dimensional reactions, and no chemical reaction from reactants to products is strictly one dimensional. In interpretation of experimental data the usual procedure is to set κ equal to unity, in absence of

---

* This research has been sponsored in part by the Office, Chief of Research and Development, U.S. Department of Army, through its European Office under Contract No. DA-91-591 EUC-1434.

† On sabbatical leave from the Department of Chemistry, University of California, Berkeley 4, California; Guggenheim Fellow, 1961.

[1] G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, Can. J. Chem. **38**, 1643 (1960). See also J. H. Knox, Trans. Faraday Soc. **58**, 275 (1962).

[2] R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens, L. Meyers, and S. Smoes, Chem. Ber. **93**, 3014 (1960).

[3] S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[4] S. Sato, J. Chem. Phys. **23**, 592, 2465 (1955).

[5] R. Weston, J. Chem. Phys. **31**, 892 (1959).

[6] H. S. Johnston, Advances in Chem. Phys. **3**, 131 (1960).

[7] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, J. Chem. Phys. **4**, 499 (1936).

[8] E. Gorin, Acta Physicochim. U.R.S.S. **6**, 691 (1938).

better information. Recently Eyring[9] has pointed out that the job for theoretical kineticists of this generation is to understand and evaluate the "transmission coefficient."

Reactions with Activation Energy

The London–Polanyi–Eyring–Sato (LPES) model of potential-energy surface requires so much computation that it is practicable only for those who have access to a high-speed electronic computer. The bond-energy–bond-order (BEBO) method recently proposed and here somewhat modified and extended (Appendix A) is very much simpler and is in fact the sort of thing a chemist can readily carry out on the back of an envelope with aid of a slide rule (log-log scales on the slide rule further facilitate the computations). For this study a high-speed computer was used to compute a Sato potential-energy surface for a series of models C—H—Cl with various values of bond energy for the reactant C—H; the parameter Δ was adjusted to the observed activation energy for the CH_4+Cl reaction and held constant for the series. Similarly the BEBO method was used for the same series, and the index p was adjusted to the same observed activation energy. These computations involve successive approximations as corrections must be made for zero point and other energies which are not known until after the surface is constructed. Thus the activation energies for CH_4+Cl are not exactly the same by the two models nor either exactly that deduced from experiment, but the differences are within experimental error and are of no consequence to computed A factors and kinetic isotope effects.

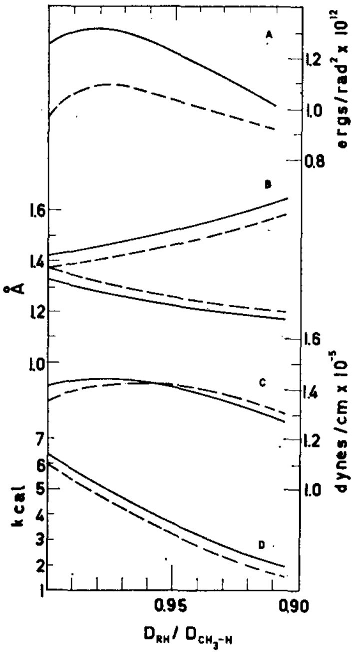


FIG. 1. Comparison of properties of activated complex as deduced by London – Polanyi – Eyring–Sato method (dotted line) and by bond - energy - bond-order method (solid line): A, bending force constant; B, bond length of activated complex; C, interaction force constant F_{12}; D, potential energy of activation. Sato's $\Delta=0.25$; index $p=1.07$.

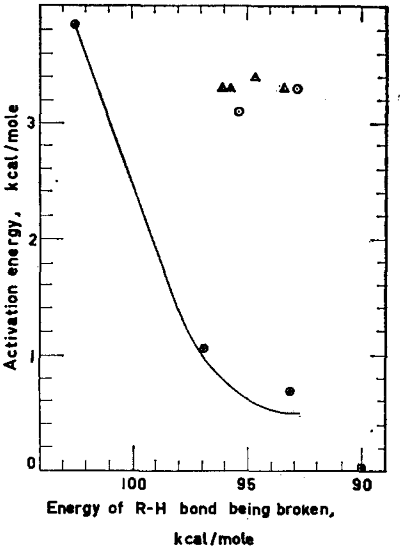


FIG. 2. Hydrogen-atom abstraction by chlorine atoms. Calculated and observed trends of activation energy with bond-dissociation energy: ⊕ saturated hydrocarbons+Cl (reference 1); ⊙ CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3+Cl$; △ C_2H_5Cl, $C_2H_4Cl_2$, $C_2H_3Cl_3$, C_2HCl_5+Cl (reference 2). The line is calculated from $p=1.07$ by the bond-energy–bond-order method.

A comparison of some computed quantities (potential energy of activation, interaction force constant, bond distance in the activated complex, and bending force constants) as a function of bond-dissociation energy for a series of C—H—Cl complexes is given by Fig. 1. For a 10-kcal variation in C—H bond energy, the two models give almost identical properties of the activated complex. For larger variations in bond energy the two methods give divergent predictions, and this difference is the subject of further study by one of the authors. Over the range of reactions given by references 1 and 2, the methods agree. Thus all detailed computations were carried out by use of the simple, flexible BEBO method. Also all work on other reactions, such as R+Cl—Cl, were done by the simple method.

Any theoretical rate expression[10] takes the form

$$k(\text{theory})=B(T)\exp(-V_a/RT), \tag{1}$$

where V_a, the potential energy of activation, is independent of temperature. Kineticists report data in the form of

$$k(\text{exp})=A\exp(-E_a/RT), \tag{2}$$

where A and E are evaluated as if constant over a more or less narrow range of temperature. The relations between these terms are

$$E_a=V_a+\theta RT, \tag{3}$$

$$A=B\exp\theta, \tag{4}$$

where θ is a correction function for temperature

---

[9] H. Eyring, recent lectures.

[10] D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. E. Powell, J. Chem. Phys. **25**, 736 (1956).

TABLE I. Hydrogen-transfer reactions for chlorinated methanes. Properties of reactants and activated complex. Computed and observed rate parameters at 400°K. Electronic partition functions are 4 for Cl and 2 for the complexes. B_σ is 4, 3, 2 and 1 for the four cases. Tunneling corrections for methane as reactant are: Γ^* (500°K), 1.60; Γ^* (400°K), 1.92; Γ^* (300°K), 2.65.

	CH_3—H+Cl	CH_2Cl—H+Cl	$CHCl_2$—H+Cl	CCl_3—H+Cl
D_e, R—H, kcal	108.7	104.8	101.4	98.9
ω_{str}, cm^{-1}	2968	3004	3016	3030
ω_{bend}, cm^{-1}	1526	1355	1266	1217
$F_{str}\times10^{-5}$	4.79	4.91	4.95	5.00
$F_{bend}\times10^{-5}$	0.70	0.96	0.89	0.84
$n_{C-H}^{(\ddagger)}$	0.42	0.55	0.66	0.73
$n_{H-Cl}^{(\ddagger)}$	0.58	0.45	0.34	0.27
R_{C-H}, A	1.32	1.25	1.20	1.17
R_{H-Cl}, A	1.42	1.50	1.56	1.62
F_{CH}, $F_{11}\times10^{-5}$	0.65	1.40	2.28	2.98
F_{HCl}, $F_{22}\times^{10-5}$	1.61	0.81	0.36	0.18
$F_{12}\times10^{-5}$	1.42	1.44	1.33	1.16
$F_\phi\times10^{11}$(R—C—H)	0.28	0.53	0.59	0.62
$F_\phi\times10^{11}$(C—H—Cl)	0.124	0.127	0.115	0.100
ω_{str} cm^{-1}	539	511	856	1404
$\omega_{r.c.}$	$1051i$	$1103i$	$647i$	$367i$
$1000w$	$968i$	$924i$	$1061i$	$1211i$
ω_b cm^{-1}	1036	1108	1140	1139
ω_b cm^{-1}	457	233	187	159
V_{act}, kcal/mole	6.5	4.3	2.9	2.1
θRT at 400°K, kcal/mole	−2.9	−2.7	−2.0	−1.3
E_{act}, calc, kcal/mole	3.6	1.6	0.9	0.8
E, obs, kcal/mole	3.9	3.1	3.1	3.3
$B(T)\times10^{-14}$(cc/mole-sec)[a]	13.6	7.22	1.72	0.31
exp θ	0.0242	0.035	0.076	0.21
log A, calc	13.5	13.4	13.1	12.8
log A, obs	13.7	13.5	13.4	13.2

[a] Parameter of Eqs. (1), (4), and (5).

variation

$$\theta=d\ln B/d\ln T. \tag{5}$$

For reactions of low activation energy such as this series, the term θRT is fully as important as the potential-energy barrier height.

The potential energy of activation V_a as found from a potential-energy surface, was corrected for zero-point energy and other terms in θ, to give the calculated activation energy for a series of model reactants in which the reactant C—H bond energy changed from 102.5 to 93 kcal/mole. This range covers the variations CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, chloro-ethanes, and also saturated hydrocarbons CH_4, C_2H_6, and $(CH_3)_2CH$—H; the reactant $(CH_3)_3C$—H lies just outside this range. The calculated activation energy as a function of bond energy is given by Fig. 2. The activation energies observed for the saturated hydrocarbons follow this curve very well indeed. The chlorinated methanes and ethanes all lie very high above the curve. Especially for the substituted ethanes, these data follow a trend contrary to the Polanyi relation of decreasing activation energy with decreasing bond energy.

From the potential-energy surfaces, the saddle points were found, curvatures through the saddle points give the force constants F_{11}, F_{22}, F_{12}, and F_ϕ, from which one obtains vibration frequencies. Model calculations were carried out for the entire series of reactions. Detailed calculations, taking into consideration different vibration frequencies and other properties of the reactants with a full vibrational analysis of the complex, were done only for 8 reactions: hydrogen-atom transfer for CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$; free-radical attack on Cl_2 by CH_3, CH_2Cl, $CHCl_2$, and CCl_3. For the hydrogen-atom transfer the models are linear reactant and complex

$$\begin{array}{ccc}
\text{X—C—H+Cl} & \to & \text{X—C}\cdots\text{H}\cdots\text{Cl} \\
R_0\ \ R_1 & & R_0\ \ R_1\ \ R_2 \\
F_0\ \ F_1 & & F_0\ \ F_{11}\ \ F_{22}\ . \\
F_\phi & & F_{12} \\
 & & F_{\phi1}\ \ F_{\phi2}
\end{array} \tag{6}$$

For the reactant the mass of X was taken as the average of the three atoms not being attacked; the length R_0 was taken as the average of the three bonds and was assumed not to change during reaction; the force constant F_0 was taken to be very low and unchanged during reaction; R_1 was taken to be the normal bond length; F_1 and F_ϕ were evaluated from the observed frequencies of the molecule and the linear model here chosen. For the complex the distances, force constants, and frequencies were evaluated by the method of reference 6 as here modified by Appendix B.

The properties of reactants and complex are entered in Table I for hydrogen-transfer reactions. The activation energies and Arrhenius A factors are calculated and listed in the table, along with observed values of the same quantities. For the model given by (6), in terms of the recently derived method that emphasizes local properties[11,12] the rate constant is

$$k=B_eB_\sigma 4.62\times10^{11}(F_1/F_{11}\ddagger)^{\frac{1}{2}}(F_{\phi1}/F_{\phi1}\ddagger)(R_1\ddagger/R_1)^2$$
$$\times\frac{(T/1000)^{\frac{3}{2}}(\omega^*/1000w)}{(F_{22}\ddagger)^{\frac{1}{2}}F_\phi}R_2^2\frac{\Gamma^*\Pi\Gamma\ddagger}{\Pi\Gamma}\exp(-V_a/RT) \quad (7)$$

in units of cc/mole-sec, where B_e is the product of electronic partition functions, B_σ is the product of rotational-symmetry numbers or the number of equivalent reaction sites, ω^* is the imaginary frequency of the reaction coordinate in cm^{-1}, w is $(1-F_{12}^2/F_{11}F_{22})^{\frac{1}{2}}$, Γ is $(\frac{1}{2}u)/\sinh(\frac{1}{2}u)$ for the real vibrations where u is $h\nu/kT$, and Γ^* is the quantum correction or "tunneling factor" for the reaction coordinate. The temperature coefficient of B is

$$\theta=\tfrac{3}{2}+\sum_{\substack{\text{str}\\ 4\text{ bend}}}\ddagger(\tfrac{1}{2}u\coth\tfrac{1}{2}u-1)+\theta^*-\sum_{\substack{\text{str}\\ 2\text{ bend}}}(\tfrac{1}{2}u\coth\tfrac{1}{2}u-1), \quad (8)$$

where θ^* is $d\ln\Gamma^*/d\ln T$. For small values of u, the expression [$(\frac{1}{2}u\coth\frac{1}{2}u-1)$ approaches zero; for large values of u it approaches $\frac{1}{2}u-1$. For hydrogen-transfer reactions between 300°–500°K, the dominant term in (8) is $(\frac{1}{2}u\coth\frac{1}{2}u-1)$ for the reactant; thus the activation energy, Eq. (3), is less than the potential energy of activation for these cases. The tunneling correction is believed to be small for CH_4+Cl or CD_4+Cl and virtually zero for the other cases, because the zero-point energy for C—H stretch of the reactant exceeds the height of the potential-energy barrier in all cases except methane. Tunneling corrections[12] for methane were found from unsymmetrical Eckart functions fitted from zero-point energy for stretch from reactant, to barrier height, to zero-point energy of product, and with u^* for the Eckart function the same as u^* found from normal mode analysis.

The reaction of free radicals with chlorine molecules requires a different model

$$\begin{array}{ccccc} \text{Cl—Cl}+\text{C—X}\rightarrow & \text{Cl}\cdots & \text{Cl}\cdots & \text{C—X} & \\ R_1 \qquad R_0 & R_1 & R_2 & R_0 & \\ F_1 \qquad F_0 & F_{11} & F_{22} & F_0 & . \\ & F_{\phi1} & F_{\phi2} & & \\ & F_{12} & & & \end{array} \quad (9)$$

The mass of X, and R_0 and F_0 are the same for this series as for the first. In this model two new pairs of bending force constants appear in the activated complex and a different rate expression obtains

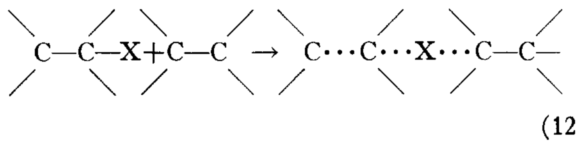
$$k=B_eB_\sigma 3.20\times10^9(F_1/F_{11}\ddagger)^{1/2}(R_1\ddagger/R_1)^2$$
$$\times\frac{(T/1000)^{5/2}(\omega^*/1000w)}{(F_{22}\ddagger)^{1/2}F_{\phi1}F_{\phi2}}R_2^2\frac{\Gamma^*\Pi\Gamma\ddagger}{\Pi\Gamma}\exp(-V_a/RT), \quad (10)$$

$$\theta=\tfrac{5}{2}+\sum_{\substack{\text{str}\\ 4\text{ bend}}}\ddagger(\tfrac{1}{2}u\coth\tfrac{1}{2}u-1)+\theta^*-(\tfrac{1}{2}u\coth\tfrac{1}{2}u-1)_{\text{str}}. \quad (11)$$

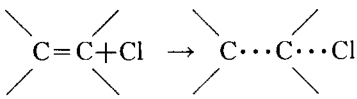
For this case all frequencies are so low that the terms in $(\frac{1}{2}u\coth\frac{1}{2}u-1)$ are very small, and the term $\frac{5}{2}$ dominates. Thus, (3), the activation energy exceeds the potential energy of activation by about $2.5RT$ or about 2 kcal at 400°K. The properties of the reactants and activated complexes are given in Table II. From the frequencies, values of θ are computed and activation energies as well as potential energy of activation are given.

This table is based on a value of 1.20 for the index p in the BEBO method. This gives agreement of activation energy in the center of the range. The observed activation energies cover a wider range than the calculated values for the series as a whole. The Arrhenius A factors are evaluated, and these agree very well both in value and sense of trend with observed values.

In treating the reactions above, two parameters were fitted to observed activation energies, $p=1.07$ for C···H···Cl and $p=1.20$ for C···Cl···Cl. Previous studies[6] found $p=1.20$ for C···H···C. Thus one should be able to predict the order of magnitude of activation energy for free-radical dismutations


(12)

and chlorine-atom addition to the double bond


(13)

where X in (12) is H or Cl. From bond energies,[13]

---

[11] D. R. Herschbach, H. S. Johnston, and D. Rapp, J. Chem. Phys. **31**, 1652 (1959).

[12] H. S. Johnston and D. Rapp, J. Am. Chem. Soc. **183**, 1 (1961).

[13] T. L. Cottrell, *The Strength of Chemical Bonds* (Butterworths Scientific Publications, Ltd., London, 1958), 2nd ed., p. 273.

TABLE II. Chlorine-atom-transfer reactions for chlorinated methanes. Properties of reactants and activated complex. Computed and observed rate parameters. Electronic partition functions are 2 for radical and 2 for complex. B_σ is 2 in all cases.

	Cl—Cl	CH_3+Cl—Cl	CH_2Cl+Cl—Cl	$CHCl_2$+Cl—Cl	CCl_3+Cl—Cl
D_e, R—Cl, kcal	58.1	81.8	72.2	76.2	72.6
ω_{str}, cm^{-1}	565				
$F_{\mathrm{str}}\times10^{-5}$	3.27				
$n_{\mathrm{C-Cl}}{}^{(\ddagger)}$		0.15	0.19	0.20	0.25
$n_{\mathrm{Cl-Cl}}{}^{(\ddagger)}$		0.85	0.81	0.80	0.75
$R_{\mathrm{C-Cl}}$, A		2.27	2.21	2.19	2.14
$R_{\mathrm{Cl-Cl}}$, A		2.03	2.05	2.05	2.06
$F_{\mathrm{C-Cl}}$, $F_2\times10^{-5}$		−.15	−.16	−.15	−.14
$F_{\mathrm{Cl-Cl}}$, $F_1\times10^{-5}$		2.60	2.37	2.31	2.06
$F_{12}\times10^{-5}$		0.514	0.645	0.683	0.803
F_ϕ(C—Cl—Cl)$\times10^{11}$		0.077	0.092	0.092	0.11
F_ϕ(R—C—Cl)$\times10^{11}$		0.107	0.170	0.191	0.257
ω_{str}, cm^{-1}		466	423	410	371
$\omega_{\mathrm{r.c.}}$		$359i$	$319i$	$307i$	$285i$
$1000w$		1295	1455	1520	1810
ω_{b}, cm^{-1}		426	(Interpolated)		226
$\dot{\omega}_{\mathrm{b}}$, cm^{-1}		107	(Interpolated)		59
V_{act}, kcal/mole		1.9	2.4	2.6	3.2
θRT at 400°K, kcal/mole		2.2	2.1	2.0	1.9
E_{act}, calc, kcal/mole.		4.1	4.5	4.6	5.1
E_{act}, obs, kcal/mole.		2.3	3.0	4	6
$B(T)\times10^{-11}$(cc/mole-sec)[a]		6.7	2.8	2.2	1.2
exp θ		16.1	14.2	12.2	10.5
log$A$, calc		13.0	12.6	12.4	12.1
log$A$, obs		12.9	12.6	12.0	11.7

[a] Parameter of Eqs. (1), (4), and (5).

145.8 for double and 82.6 for single carbon–carbon bonds, the index p is about 0.82 for carbon–carbon, between first and second order. For this rough calculation, one ignores the difference in D_0 and D_e. The energy of (12) relative to zero for reactants is

$$V=D_{\mathrm{C-C}}+D_{\mathrm{C-X}}-[D_{\mathrm{C-C}}(1+n)^{0.82}+D_{\mathrm{C-X}}(1-n)^{1.20}+D_{\mathrm{C-X}}n^{1.20}], \quad (14)$$

where n is order of the new bond formed. Differentiation with respect to n and setting to zero as a condition for a maximum gives

$$0.82D_{\mathrm{CC}}/1.20D_{\mathrm{CX}}=(1+n)^{0.18}[(1-n)^{0.20}-n^{0.20}]. \quad (15)$$

When X is hydrogen the left-hand side of (15) is 0.554, and when X is chlorine it is 0.73 to 0.78. The order formally deduced is 0.018 for hydrogen-atom transfer and 0.001 for chlorine-atom transfer. The activation energy is computed to be 0.3 kcal/mole for hydrogen-atom transfer by disproportionation and 0.006 kcal/mole for chlorine-atom transfer. Thus, this model indicates about zero activation energy.

For reaction (13) a single bond is formed and a double bond is reduced to a single bond; in the sense then it is analogous to an atom-transfer reaction in which one bond is formed as another is broken. The energy relative to zero for reactants is

$$V=D_{\mathrm{C-C}}(2)^{0.82}-D_{\mathrm{C-C}}(2-n)^{0.82}-D_{\mathrm{C-Cl}}(n)^{1.20}, \quad (16)$$

where n is the order of the C—Cl bond being formed. Differentiating to find the maximum of V with respect to n, one finds

$$0.82D_{\mathrm{CC}}/1.20D_{\mathrm{CCl}}=(2-n)^{0.18}n^{0.20}. \quad (17)$$

The order of the complex is found to be 0.12, and the activation energy is calculated to be 1.2 kcal. In four cases out of five in reference 2 the observed activation energy was 0±1.5 kcal, and in one case it was 1.6±1.5 kcal.

Relative to (15) it was noted that the computed order of one bond in the complex was 0.018 in one case and 0.001 in another. The conclusion that the model predicts a zero activation energy is valid enough, but a strong warning must be issued about the nature of the activated complex in this case. The most revealing quantity to evaluate is the classical angular-vibrational amplitude

$$l_\phi=(2\pi kT/F_\phi)^{\frac{1}{2}}\ \text{rad}; \tag{18}$$

when the order is 0.01 the bending force constant is computed to be about 0.005×10^{-11} erg/rad^2, and the vibrational amplitude is approximately equal to π or 180° at 500°K. The rate expression for activated complex theory is based on separability of energy and small vibrations. The activated complex is "like an ordinary molecule except for one degree of freedom ..." only when vibrational amplitudes are small. The bending normal modes of the complex arise more or less directly from the rotational normal modes of the separate reactants. When the "bending vibrational amplitude is 180°," the two reactants are still rotating rather freely and have not yet interacted strongly enough to convert rotations to bending vibrations. This model has been recognized for a long time as appropriate for combination of radicals,[3,8] but it must be invoked for atom transfer and other reactions if the bending force constants are imputed to be below 0.01×10^{-11}.

Reactions with Zero Activation Energy

The model upon which activated-complex theory calculates the rate of radical recombinations and other reactions with zero activation energy is given by Fig. 3. The angular momentum of the complex as a whole is quantized and its magnitude is given by the quantum number J. For a fixed value of the angular momentum, conserved in spite of expansion or contraction of the intermolecular distance R, and for inverse R^6 potential-energy function $V=-a/R^6$, there is only one internuclear distance R_c at which attractive and centrifugal forces are balanced. At larger separations the complex spirals apart. At shorter separations the complex spirals inward, and the radicals or molecules undergo a close encounter. Activated-complex theory calculates the rate at which complexes cross into a spherical shell of diameter R_c for a given value of J, and then sums over all values of J. It is assumed that the distance R_c is so great that the radicals in the complex have about the same vibrational and rotational energy levels as for the free reactants. For this condition to be relaxed, one must have a detailed potential energy expression as a function of angle of rotation of the radicals.

The magnitude of the angular momentum is M,

$$M^2=J(J+1)\hbar^2. \tag{19}$$

The multiplicity of the quantum number J is $2J+1$. If the intermolecular attraction is given by $-a/R^6$, the critical diameter is

$$R_c=(6a\mu/M^2)^{\frac{1}{4}}, \tag{20}$$

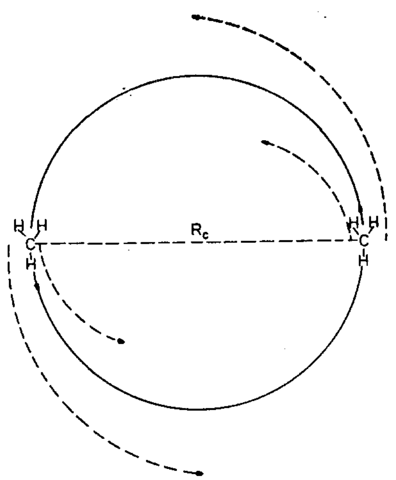


FIG. 3. Model upon which activated-complex theory derives rate constant expression for bimolecular reactions with zero activation energy. The radicals are assumed to rotate and vibrate as for separated reactants, and the forces between the radicals are assumed to be central and spherically symmetrical.

where μ is the reduced mass. The potential energy at this distance is

$$V(R_c)=2M^3/(6\mu)^{\frac{3}{2}}a^{\frac{1}{2}}; \tag{21}$$

the relative rate from one rotational state to another is given by

$$\beta(J)=(2J+1)\ \exp\{-2[J(J+1)\hbar^2]^{\frac{3}{2}}/(6\mu)^{\frac{3}{2}}a^{\frac{1}{2}}kT\}. \tag{22}$$

The integration of (22) over all states gives rise to the gamma function of $\frac{2}{3}$. The final rate expression[8] is

$$k=\kappa B_{\text{int}}\left(\frac{f\ddagger}{f_Af_B}\right)_e\frac{2^{1/6}\pi^{1/2}a^{1/3}(kT)^{1/6}\Gamma(\frac{2}{3})}{\sigma\mu^{1/2}}. \tag{23}$$

Expressing a in units of 10^{-60} erg-cm^6 and μ in atomic mass units, one obtains

$$k=2.47\times10^{14}\kappa B_{\text{int}}B_{\text{el}}\frac{a^{1/3}}{\sigma\mu^{1/2}}\left(\frac{T}{400}\right)^{1/6}\ \text{cc/mole-sec.} \tag{24}$$

B_{int} is the ratio of internal partition function of the radicals in the complex and radicals far removed; usually this factor is regarded as unity. B_{el} is the product of electronic partition functions, $(f\ddagger/f_Af_B)_{\text{el}}\sigma$ is 2 or 1 depending on whether the reactants are identical or different, and the attractive constant a may be estimated[14] from polarizabilities α[15] and effective number of electrons N by

$$a=\frac{3e\hbar}{2m_e^{\frac{1}{2}}}\frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{\frac{1}{2}}+(\alpha_2/N_2)^{\frac{1}{2}}}. \tag{25}$$

The numerical values are

$$a=\frac{25.0\alpha_1\alpha_2}{(\alpha_1/N_1)^{\frac{1}{2}}+(\alpha_2/N_2)^{\frac{1}{2}}}\times10^{-60} \tag{26}$$

---

[14] K. S. Pitzer, J. Am. Chem. Soc. **78**, 4565 (1956).

[15] J. A. A. Ketelaar, *Chemical Constitution* (Elsevier Publishing Company, Amsterdam and Houston, 1953), p. 93.

TABLE III. Bimolecular reactions with zero activation energy. Rate constants calculated by method of Gorin.

R_1	R_2	α_1[a]	α_2[a]	N_1	N_2	B_e^{-1}	B_σ^{-1}	log$k$[b] calc	log$k$[c] obs
CH_3	CH_3	2.2	2.2	7	7	4	2	13.8	13.5
CH_2Cl	CH_2Cl	4.0	4.0	16	16	4	2	13.7	12.6
$CHCl_2$	$CHCl_2$	5.9	5.9	25	25	4	2	13.7	12.4
CCl_3	CCl_3	7.8	7.8	34	34	4	2	13.7	11.8
C_2H_5	C_2H_5	4.0	4.0	13	13	4	2	13.8	13.5
C_2H_4Cl	C_2H_4Cl	5.8	5.8	22	22	4	2	13.7	13.1
$C_2H_3Cl_2$	$C_2H_3Cl_2$	7.7	7.7	31	31	4	2	13.7	13
$C_2H_2Cl_3$	$C_2H_2Cl_3$	9.5	9.5	40	40	4	2	13.7	13
C_2Cl_5	C_2Cl_5	13.3	13.3	58	58	4	2	13.7	11.7
CH_3	Cl	2.2	2.3	12	10	8	1	13.7	14.6
CH_2Cl	Cl	4.0	2.3	16	10	8	1	13.6	14.4
$CHCl_2$	Cl	5.9	2.3	25	10	8	1	13.6	14.4
CCl_3	Cl	7.8	2.3	34	10	8	1	13.7	14.4
C_2H_5	Cl	4.0	2.3	13	10	8	1	13.7	14.3
C_2H_4Cl	Cl	5.8	2.3	22	10	8	1	13.7	14.3
$C_2H_3Cl_2$	Cl	7.7	2.3	31	10	8	1	13.7	14.3
$C_2H_2Cl_3$	Cl	9.5	2.3	40	10	8	1	13.7	14.3
C_2HCl_4	Cl	11.4	2.3	49	10	8	1	13.7	14.2
C_2Cl_5	Cl	13.3	2.3	58	10	8	1	13.7	14.3
C_2H_4	Cl	4.1	2.3	12	10	2	1	14.3	13.2
C_2H_3Cl	Cl	6.0	2.3	21	10	2	1	14.2	13.2
C_2HCl_3	Cl	9.7	2.3	39	10	2	1	14.3	13
C_2Cl_4	Cl	10.6	2.3	48	10	2	1	14.3	12.6

[a] In units of 10^{-24} cm³.

[b]

$$k=(B_{\mathrm{int}}\,\kappa)B_eB_\sigma\frac{7.23\times10^{14}}{\mu^{\frac{1}{2}}}\left[\frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{\frac{1}{2}}+(\alpha_2/N_2)^{\frac{1}{2}}}\right]^{1/3}\ \text{cc/mole-sec}$$

with μ, reduced mass, in atomic mass units and α in units of 10^{-24} cm³. B_e is based on $g_e(\mathrm{Cl})=4$, $g_e(\mathrm{radicals})=2$, $g_e(\mathrm{molecules})=1$. Temperature 400°K.

[c] It is to be remembered that an activation energy of 1.8 kcal/mole at 400°K would reduce the observed K by a factor of 10. However, there is no reason to presume that experimental error accounts for discrepancies between calculated and observed constants.

when α is given in units of 10^{-24} cm³. κ is the probability that reactants with favorable spin orientation (already counted in B_{e1}) will react once they have crossed the sphere of critical diameter R_c. For reactions with activation energy, κ is the probability that a complex, having crossed the potential-energy saddle, will proceed to form products; in that case the reactants are intimately associated and oriented as if products. For the present case activated-complex theory calculates a barrier-crossing rate at which point the reactants are rotating and vibrating as if the other was not near. It might be anticipated that κ in this case is more important than for reactions with high activation energy. In any case one always assumes κ to be unity to carry through the computation. (The intimate relation of activated-complex theory and collision theory for this class of reactions was emphasized recently by Mahan.[16])

Table I of reference 2 has 23 bimolecular reactions involving free radicals or chlorine atoms with about zero activation energy. These include 9 cases of radical recombination or disproportionation, 10 cases of combination of a free radical with a chlorine atom, and four cases of chlorine addition to a double bond. For each reaction the polarizabilities were found from reference 15, the effective number of electrons from reference 15, and the rate constants were calculated for all cases. These data are listed in Table III, along with a comparison of the logarithms of observed and calculated rate constants. Of the observed rate constants the average of the logarithm is 13.5 and the average deviation from the mean is 0.75 logarithm units. The observed rate constants vary from log$k$ = 11.7 to 14.4 in units of cc/mole-sec. The calculated rate constants vary from log$k$ = 13.6 to 14.3. The average deviation of observed and calculated rate constants is 0.85 logarithm units, or more than the deviation of the observed constants from the mean. Where the observed constants show a trend, the calculated constants do not detect the trend.

DISCUSSION

In this article a large family of reactions are treated uniformly and simultaneously by activated complex

---

[16] B. H. Mahan, J. Chem. Phys. **32**, 362 (1960).

theories. The reactions fall into three sets, indicated by the outline:

A. Reactions with activation energy.
   1. Hydrogen-atom transfer, Table I.
   2. Chlorine-atom transfer, Table II.

B. Reactions with zero activation energy.
   3. Radical recombination, dismutation, and atom addition to olefin, Table III.

For the 60 different reactions, only two parameters are fitted from kinetic data; all other parameters are obtained unambiguously from the structural and spectroscopic properties of the reactants and products. It is shown (Fig. 1) that the properties of the activated complex as deduced by the London–Polanyi–Eyring–Sato method (which involves extensive computations) and that derived from the bond-energy–bond-order method (which involves very simple computations) give virtually the same predictions for hydrogen atom abstraction by a chlorine atom, and thus the further discussion of reactions with activation energy is based on the BEBO method. The reactions with no activation energy are discussed by Gorin's theory[8] of radicals with a central attractive potential and unchanging internal structure; no adjustable parameters are used in this theory. The comparison of observed and calculated quantities is reviewed below.

For the series of reactions with activation energy, the computed Arrhenius A factors were in excellent agreement with experiment, Tables I and II. The calculated A factors correctly follow the observed decreasing trend from CH_4 to $CHCl_3$ in the hydrogen-atom abstraction by chlorine atoms. They correctly note that the A factor for CH_4+Cl is about ten times as big as that for CH_3+Cl_2. Again the decreasing trend for the series $R+Cl_2$ from CH_3 to CCl_3 was correctly followed.

For chlorine-atom attack on saturated hydrocarbons either method, LEPS or BEBO, correctly predicts the trend of activation energy with bond energy of the bond being broken, Fig. 2. However, the trend of activation energy with bond energy for chlorine-atom attack on hydrogen in chlorinated methanes or chlorinated ethanes is in strong disagreement with that calculated from potential-energy surfaces by either method, Fig. 2. (Extensive calculations by one of the authors, HSJ, on similar families of reactions with methyl radicals, sodium atoms, and others show in general good agreement between calculated and observed trends of activation energy with bond energy). Thus so far as these data are concerned, the activation energy trends give one "success" and one "failure" in the comparison of theory and experiment.

One naturally seeks the explanation of the "failure" in terms of nonbonding interactions between the attacking chlorine atom and the chlorine atom or atoms in the other reactant. To evaluate the magnitude of this effect one may construct a Lennard-Jones 6–12 interaction function

$$V(R)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^{6}] \tag{27}$$

from the "van der Waals radius"[15] of chlorine and the polarizability[15] of the chlorine atom. The long-range attraction of one symmetrical group for another is simply

$$V(R)=-a/R^6=-4\epsilon\sigma^6/R^6, \tag{28}$$

where a is obtained from (26). In this way one finds a Lennard-Jones function for intermolecular interactions of chlorine atoms

$$V(R)=1000[(3.60/R)^{12}-(3.60/R)^{6}]\ \text{cal/mole} \tag{29}$$

where R is internuclear separation in ångström units. For the dimensions of the activated complexes, $Cl_3C\cdots H\cdots Cl$, CH_3—$CHCl\cdots H\cdots Cl$, or CH_2Cl—$CH_2\cdots H\cdots Cl$, the $Cl\cdots Cl$ interactions are on the *attractive*, not repulsive part of the Lennard-Jones potential. Thus the anomalous activation energies in Fig. 2 are not to be ascribed to van der Waals repulsions between bound and free chlorine atoms. A reasonable explanation is in terms of dynamic effects, not equilibrium effects nor static properties of the potential-energy function: As a chlorine atom approaches a $CClH_3$ molecule, for example, the $Cl\cdots Cl$ dispersion forces are greater than the $Cl\cdots H$ dispersion forces (polarizability[15] of Cl is 2.28×10^{-24} and that of H is 0.42×10^{-24} cm^3) or the $Cl\cdots H$ bonding forces. The preferential attraction of the chlorine atom by the bound chlorine results in collision complexes of the form H_3C—$Cl\cdots Cl$ predominating over those of the form H_2ClC—$H\cdots Cl$. Thus unless the approaching atom has a relatively high kinetic energy, the "activated complex" or hydrogen-atom-transfer complex never forms. (This explanation predicts that the kinetic isotope effect for chlorine-atom attack on $CHCl_3/CDCl_3$ would be small, similar to that for chlorine-atom attack on C_2H_6/C_2D_6, and much less than that for chlorine-atom attack on CH_4/CD_4 (this has been confirmed experimentally and the results shall be published in the near future).

For the series of reactions with no activation energy, the simple activated-complex theory gives 13.8 for $\log k$ for 23 cases, and the observed average is 13.5. The range of calculated values is 13.7 to 14.3, and the range of observed values is 11.7 to 14.4. For the series as a whole the calculated average value is within a factor of 2 of the observed average value. For any individual case the worst discrepancy between theory and experiment is a factor of 100. The average discrepancy between calculated and observed values is × or ÷ a factor of 7. The experimental data show several strong trends that the calculations do not detect. One may evaluate these comparisons in either of two ways: the theory correctly predicts the order of magnitude of the class of reactions as a whole, but it does not detect several interesting, large-scale trends for the various cases.

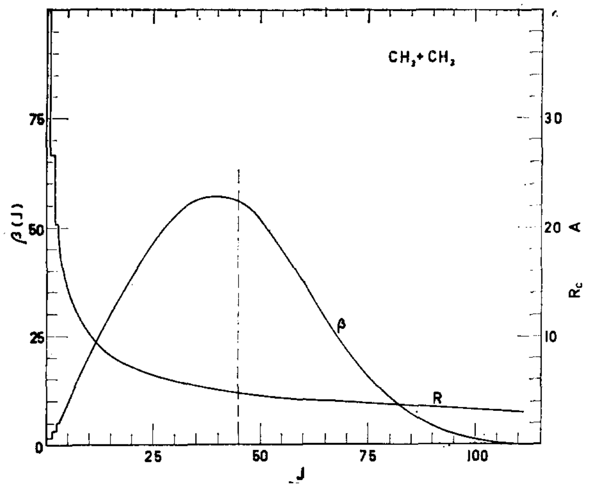


FIG. 4. Recombination of methyl radicals according to activated complex theory. The abscissa is the rotational quantum number of the activated complex. The left-hand ordinate is the relative rate of reaction per quantum state, (22). The right-hand ordinate is the diameter of balance R_c, (20). The dotted line gives the distance at which the hydrogen atoms on the methyl radical come within their van der Waals diameter. The theory is derived on the assumption that essentially all area under the curve β lies to the left of the dotted line.

A deeper analysis of the theory than blind use of (25) and (27) can be carried out by examining: the relative rate $\beta(J)$, (23), for each rotational state of the complex; the critical diameter $R_c(J)$ of each state; and by comparison of this diameter with the range of central forces of the reactants and, more important, with the length at which repulsions set in between the noncentral atoms on the reactants. Theory and experiment are, famously, in almost perfect agreement for recombination of methyl radicals, and this was chosen as one test case. One of the worst disagreements between theory and experiment in Table III is the recombination of trichloromethyl radicals CCl_3, and thus this was chosen for the second test case for a detailed examination.

For these two reactions, the relative rate per rotational state $\beta(J)$ and the critical diameter of the complex $R_c(J)$ are plotted in Figs. 4 and 5 against rotational quantum number of the complex as a whole. The theory (24), is based on central-force attraction, with no repulsions. The central-force model will be very seriously perturbed when the C—H···H—C or C—Cl···Cl—C distances come within the van der Waals diameter of the central nonbonding pair. Also, the assumption of free rotation of the radicals (see Fig. 3) breaks down before this point. The carbon-carbon distance C—H···H—C is 4.6 Å when H···H is at its van der Waals diameter 2.4 Å. This distance is shown as the dotted line in Fig. 4. The carbon-carbon distance C—Cl···Cl—C is 7 Å when Cl···Cl is at its van der Waals diameter 3.6 Å. This distance is shown as a dotted line in Fig. 5. The assumptions behind (24) have broken down completely for all area in Figs. 4 and 5 to the right of the dotted line and some area to the left of the dotted line is seriously perturbed by noncentral-force effects. Thus the range of intermolecular forces and bond lengths are such that Gorin's simple theory is not expected to be very good for recombination of either methyl radicals or trichloromethyl radicals. The case with good agreement between theory and experiment is almost as bad internally as the case showing a deviation of a factor of 100. Further physical consideration does point up a real difference between the two cases. At large distances the van der Waals attraction of CH_3 radicals for each other largely arises from the carbon atoms,[15] and the methyl radical case can be corrected by an appropriate solid angle factor in the rotational partition functions of the radicals themselves. For the CCl_3 radicals, the attractions are largely chlorine–chlorine, and collision complexes of the form $Cl_2C—Cl\cdots Cl—CCl_2$ predominate over collision complexes such as $Cl_3C\cdots CCl_3$.

The experimental results in Table III show some interesting trends that may provide further clues to the problem. The addition of a chlorine atom to a radical, chlorinated or not, all proceed with large rate constant. The addition of a chlorine atom to an olefin occurs at about one-tenth the rate of addition to a free radical, and it will be recalled that the BEBO method predicts a small activation energy for these reactions. The recombination of free radicals shows a strongly decreasing trend as hydrogens in the radical are substituted by chlorine atoms, and this trend may be explained qualitatively by the unfavorable orienting effect of permanent dipoles in one complex on the other.

Evaluation

Sato's modification of the London–Polanyi–Eyring method of obtaining potential-energy surfaces or the bond energy-order method gives new life to activated-complex theory as a predictive tool in chemistry. Predictions are limited, but they are not zero.

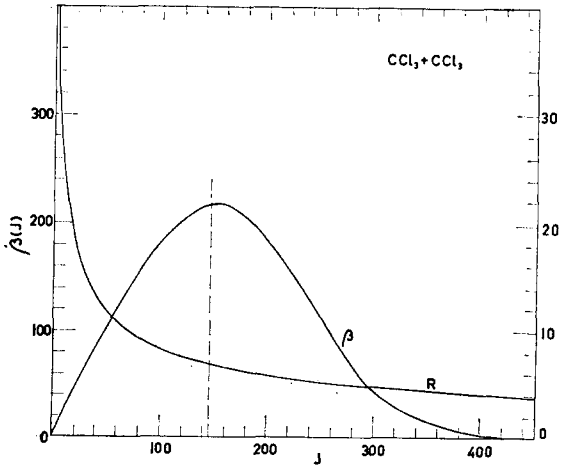


FIG. 5. Recombination of trichloromethyl radicals. Similar to Fig. 4.

Once the parameter for a potential-energy surface is fixed (Sato's Δ or p in the method of reference 6) from one activation energy, the Arrhenius A factors for an entire series of related bimolecular reactions is predicted with no further adjustment of constants allowed. Similarly any kinetic isotope effects are uniquely predicted. However, as one starts to make detailed calculations of this sort, one soon finds that the simple separable theory usually discussed (reference 3) is inadequate to enter several interesting ranges of variables. At low temperatures, especially for hydrogen-atom-transfer reactions, quantum mechanical tunneling becomes an important and unpredictable feature (references 6, 12). It becomes impossible for the microscopic rate to depend on but one degree of freedom for light atoms at low temperatures. For exothermic reactions, an equally serious obstacle to the usual form of the theory is encountered: the vibrational amplitude of the bending mode of the complex becomes so large that it is ridiculous to use small-vibration theory as the basis of the computation. The activated complex is not like a normal molecule except for one degree of freedom in these cases. It is a collision complex with the two reactant molecules undergoing a violent wide-angle "rolling" vibration relative to each other. The molecular-reaction rate can no longer depend solely on one reaction coordinate, but it must also depend in an important way on the modes of wide-amplitude vibrations.

For reactions with truly zero activation energy, activated-complex theory predicts the rate of reaction from the rate of crossing the rotational energy barrier. However, the important rotational states for reaction do not occur with the configuration shown in Fig. 3. The outer atoms of the radical are in each others repulsive range for important values of intermolecular diameters (Figs. 4 and 5). The activated complex here is the same sort as that discussed in the previous paragraph; the restricted rotations of the reactant radicals in this theory are the same unknown motions as the enormous bending vibrational amplitudes in the atom-transfer model. The two molecules are in association with each other, strongly interacting, but they are not linked as if a molecule. Also, the rate is not given by the rate of crossing the rotational barrier, but is strongly influenced by the orientation upon the turning point of the close collision.

Thus, it is judged that in its present form,[3] activated-complex theory is predictive with respect to bimolecular gas-phase reactions only if the activation energy is not too low and if the temperature is not too low. Under these circumstances trends of activation energy with bond energies, Arrhenius A factor, and kinetic isotope effects can be predicted in a useful manner by this not very general theory.

ACKNOWLEDGMENTS

We are grateful to Halbert Carmichael and the Computer Service of the University of California for carrying out computations of the Sato potential-energy surfaces. We are especially grateful to Terry Sharp for the suggestion that is developed in the Appendix.

APPENDIX

Modifications and extensions of bond-energy–bond-order method of obtaining potential-energy parameters.

In reference 6 a simple method was described for estimating potential-energy parameters from bond energies and bond orders. In that reference the force constants F_{11} and F_{22} were regarded as following Badger's rule. However, as Terry Sharp has pointed out, Badger's rule should only be applied to a cut at right angles to the "reaction path." The force constant along the reaction path is designated as F_ρ, and it is given by (12), (13), (14) in reference 6. The force constant perpendicular to the reaction path in a R_1-R_2 plane is designated F_σ, it is assumed to obey a Badger's-like rule, and it is given by

$$F_\sigma=\frac{F_{S1}n_1^3+F_{S2}n_2^3}{n_1^2+n_2^2}, \tag{30}$$

where F_{S1} is the stretching force constant of the normal single bond in position 1, F_{S2} is the stretching force constant of a normal single bond in position 2, n_1 is the order of bond 1 and n_2 is the order of bond 2. The force constants needed in the **F** matrix are evaluated from F_ρ and F_σ as follows:

$$F_{11}=\frac{F_\sigma n_1^2+F_\rho n_2^2}{n_1^2+n_2^2}, \tag{31}$$

$$F_{22}=\frac{F_\sigma n_2^2+F_\rho n_1^2}{n_1^2+n_2^2}, \tag{32}$$

$$F_{12}=\frac{(-F_\rho+F_\sigma)n_1n_2}{n_1^2+n_2^2}. \tag{33}$$

Bending force constants about bonds of any order n_1 and n_2 are assumed to be given by

$$F=F_{\phi S}n_1n_2, \tag{34}$$

where $F_{\phi S}$ is the bending force constant of the same (or a similar) set of atoms with single bonds. When hydrogen is the atom transferred $F_{\phi S}$ is taken to be 0.5×10^{-11} ergs/rad^2.