pendence of intrinsic viscosity on chain length is correctly described. Finally, the results described in this paper further confirm the observation that the transition from small ion to polyion behavior requires a rather large number of charges and a long chain.

[Contribution from the Department of Chemistry, University of California, Berkeley 4, Calif.]

Activation Energies from Bond Energies. I. Hydrogen Transfer Reactions

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A new procedure is proposed that uses bond energies and other properties of reactant molecules and no adjustable parameters from kinetic data to calculate activation energies and rate constants of elementary bimolecular hydrogen-transfer reactions. The new method is compared with theoretical treatments of this problem and with the semi-empirical approach of London, Eyring, Polanyi, and Sato. For all reactants of fairly well known bond energies, the method calculates activation energies within about 2 kcal. and rate constants within about an order of magnitude. The concepts used in this treatment are from ultra-simple valence-bond theory and ultra-simple activated-complex theory. The success of the method is regarded not to reflect validity on the assumptions used.

Introduction

The "activation energy" of a chemical reaction is the measure of how the specific rate k of the reaction changes with temperature

$$E = -R\, \partial \ln k / \partial\, (1/T) \qquad (1)$$

where R is the gas constant. Over a finite range of temperature the activation energy is usually regarded as if constant, and the specific rate expressed in the Arrhenius form

$$k = A e^{-E/RT} \qquad (2)$$

For many years chemists have been interested in calculating activation energies. These efforts can be classified as one of the following: I, theoretical; II, semi-empirical; III, 100% empirical, but the empiricism 100% *outside* the field of chemical kinetics.

The only chemical reaction for which serious attempts have been made to carry out a theoretical evaluation of activation energy is the hydrogen molecule–hydrogen atom exchange reaction, observable as para–ortho conversion of H_2, ortho–para conversion of D_2, or isotopic exchange between hydrogen and deuterium. These reactions are represented as

$$H + H\text{--}H \longrightarrow H\cdots H\cdots H \longrightarrow H\text{--}H + H \quad (3)$$
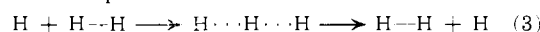
These calculations start with London,[1] in 1928, were pursued over the years by Eyring and co-workers,[2] and brought to the highest stage of development yet reported by Boys and Shavitt in Hirshfelder's group.[3,4] References to other workers in this area are given in the articles cited.[2-4] The calculations by Boys and Shavitt were much more refined and complete than previous ones, and only these calculations will be reviewed here. The potential energy surface for three hydrogen atoms was constructed by[4] "a linear variational calculation of the superposition of configuration type...6 1s-orbitals...66 configurations..." This major computation gave remarkably good agreement so far as absolute energy is concerned: the calculated binding energy of H_2 was 80.2 kcal./mole and the experimental value is about 102. The calculated binding energy for H_2 (using the same level of approximation) was 95.6 kcal./mole, and the experimental value is 109.32. The calculated potential energy of activation

was 15.4 kcal./mole, and the observed value is about 6 to 8. For the hydrogen molecule the H–H bond distance was calculated accurate to 1.4% and the force constant to 5.2%. The most stable form of the complex was found to be linear, in agreement with all earlier theoretical work on this case. The potential energy surface when plotted against the two bond lengths of the H_3 complex gave a smooth, single, symmetrical saddle point. From the location of the saddle point and from curvatures evaluated at the saddle point, Shavitt[4] used activated complex theory to calculate the specific rate or rate constant k for reaction 3. This 100% theoretical calculation of the rate constant is shown as the dashed line in Fig. 1, along with the experimental data[5-7] on the para–ortho H_2 conversion. The theoretical line lies below the experimental points by about a factor of 10^2 at $1000°K$. and 10^4 at $300°K$. A chemical kineticist is not satisfied with the accuracy of this theoretical calculation, yet one certainly agrees with Shavitt[4] that "it is not expected that this situation will be much improved except by a calculation that is some orders of magnitude greater than that of Boys and Shavitt." The qualitative aspects of these theoretical studies (linear, symmetrical complex, and the general nature of the potential energy surface) are of great value to the kineticist, who is forced to seek a chemist's solution to a chemical problem in going beyond the H_3 reaction.

The "semi-empirical" approach to evaluating potential energy surfaces was developed by Polanyi and Eyring[8,9] from the theoretical work of London.[1] The simplest quantum mechanical theory of the hydrogen molecule is that of Heitler and London,[10] and the theoretical expressions for stable singlet and unstable triplet hydrogen molecule are

$$W_S = (A + \alpha)/(1 + \Delta), \quad W_T = (A - \alpha)/(1 - \Delta) \quad (4)$$

where A, α, and Δ are definite integrals defined in the Heitler–London theory (sometimes named, respectively, the Coulomb, exchange, and overlap integrals). The Heitler–London theory gives the dissociation

(1) F. London, "Probleme der modernen Physik, Sommerfeld Festschrift." S. Hirzel, Leipzig, 1928, p. 104; Z. Elektrochem., **35**, 552 (1929).

(2) R. S. Barker, R. L. Snow, and H. Eyring, J. Chem. Phys., **23**, 1686 (1955).

(3) S. F. Boys and I. Shavitt, University of Wisconsin Naval Research Laboratory Technical Report WIS-AF-13 (1959).

(4) I. Shavitt, J. Chem. Phys., **31**, 1359 (1959).

(5) A. Farkas, Z. physik. Chem., **B10**, 419 (1930); Table 2 (factor of 4 error in this table was corrected).

(6) M. van Meerssche, Bull. soc. chim. Belges, **60**, 99 (1951); Table III.

(7) K. H. Geib and P. Harteck, Z. physik. Chem. Bodenstein-Festband, 849 (1931), experiments 9-13.

(8) H. Eyring, Naturwissenschaften, **18**, 914 (1930); H. Eyring and M. Polanyi, Z. physik. Chem., **12B**, 279 (1931); H. Eyring, J. Am. Chem. Soc., **53**, 2537 (1931).

(9) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.
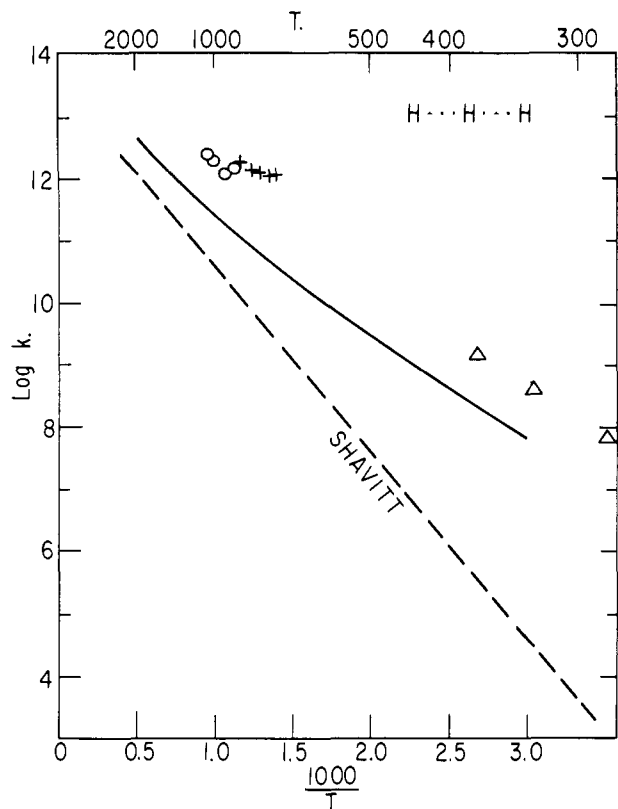
(10) Any textbook on quantum chemistry.

Fig. 1.—Rate constants for para–ortho hydrogen conversion compared with Shavitt's theoretical line, - - -, and a line calculated by this method, ———— : O, ref. 5; +, ref. 6; △, ref. 7.

Fig. 2.—Bond energy, D_e, plotted against bond length for triple, double, and single bonded NN and CC compounds.

energy D_e of hydrogen as 72 kcal./mole; the observed value is 109.3.

The values of the integrals in eq. 4 and their relative values one to another are rather strong functions of H–H distance R, except that at large distances the theory gives a more or less constant value to the ratio

$$f = A/(A + \alpha) \qquad (5)$$

Eyring's semi-empirical method of evaluating these integrals is to set Δ to zero, to assume that eq. 5 is valid for all values of R with the value it has at large R, and to use the empirical value of potential energy function $V(R)$ for the hydrogen molecules. In this way the integrals are given by

$$A = fV(R)$$
$$\alpha = (1 - f)V(R) \qquad (6)$$

Actually, Eyring used the Morse function to represent the empirical potential energy function

$$V(r) = D_e(e^{-2\beta r} - 2e^{-\beta r}) \qquad (7)$$

where $r = R - R_{eq}$ and β is an empirical scale factor.

London's theory of the H_3 complex regards it as a linear structure of three superimposed H–H diatomic molecules. For isolated molecules, the energy has the simplified form

$$W_1 = A + \alpha, \; W_2 = B + \beta, \; W_3 = C + \gamma \qquad (8)$$

and the energy of the complex is

$$W = A + B + C \pm \{^1/_2[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{1/2} \qquad (9)$$

Eyring's semi-empirical method, eq. 6 and 7, is applied to each of "three molecules," eq. 8, and the values substituted into eq. 9. In this way a complete potential energy surface is readily constructed, as shown by Fig. 27, p. 108, ref. 9. In this figure the theoretical value of 0.14 is used for f, eq. 5. The calculated potential energy of activation is 14 kcal., but the observed activation energy is about 6–8 kcal. By re-
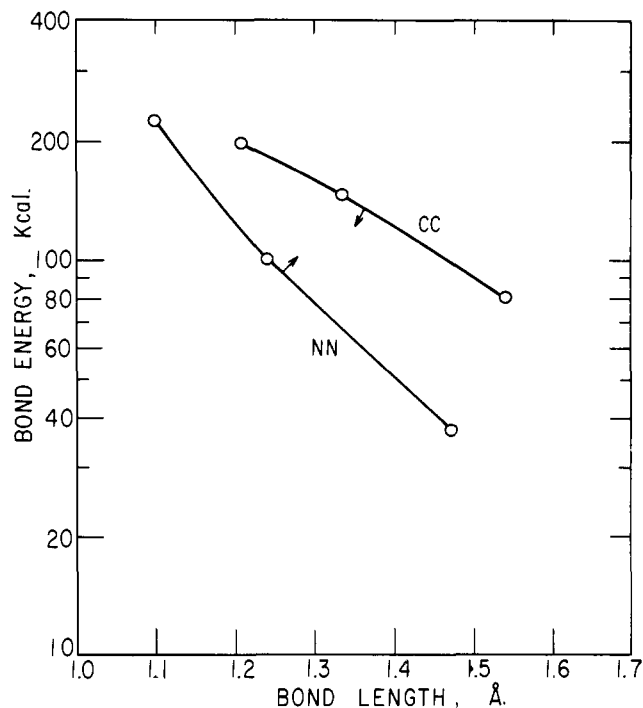
garding f as an adjustable parameter, one can fit the observed activation energy to some value of f. The potential energy surface so calculated shows a "well in the top of the pass" or a symmetrically placed basin about 2.5 kcal. deep. The two bonds at the top of a barrier are highly unsymmetrical; however, Boys and Shavitt's much more accurate quantum mechanical surface showed no such basin. It is clear that the approximations behind eq. 5, 7, and 9 are so bad that the resulting potential energy surface is qualitatively incorrect. It is felt that one should not use this method, even for qualitative purposes.

In 1955, Sato[11] introduced a modification of the London–Eyring–Polanyi semi-empirical method. He returned to eq. 4—which, however, are only marginally better than eq. 8—and Sato proposed that the attractive singlet H_2 be given by a Morse curve

$$(A + \alpha)/(1 + \Delta) = D_e(e^{-2\beta r} - 2e^{-\beta r}) \qquad (10)$$

and the repulsive triplet H_2 be given by an anti-Morse curve

$$\frac{A - \alpha}{1 - \Delta} = \frac{D_e}{2}(e^{-2\beta r} + 2e^{-\beta r}) \qquad (11)$$

In the Heitler–London theory, Δ is a function of H–H distance, but Sato takes it to be a constant, his adjustable parameter. In Sato's method the parameter Δ must absorb all the crude approximations in the Heitler–London theory of H_2, the London theory of H_3, the Morse curve, and the anti-Morse curve. It does not have the magnitude nor the properties of the term Δ in the Heitler–London theory itself.

For reactions other than H_3, the activation energy is not predicted by these semi-empirical methods, but rather the observed activation energy is used up to adjust Eyring's f or Sato's Δ. In an effort to calculate activation energies, one may turn to 100% empirical methods, where the empiricism is in the area of molecular structure and molecular spectroscopy.

Bond Energy–Bond Order Method.—In previous publications[12,13] a semi-empirical method, an alterna-

(11) S. Sato, J. Chem. Phys., 23, 592, 2465 (1955).
(12) H. S. Johnston, Advan. Chem. Phys., 3, 131 (1960).
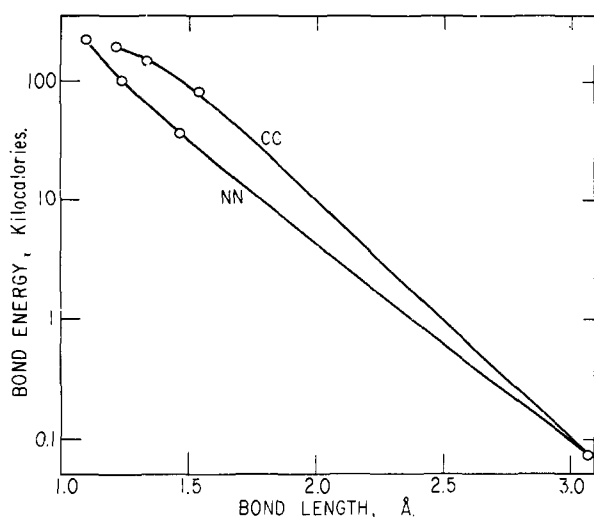(13) H. S. Johnston and P. Goldfinger, J. Chem. Phys., 37, 700 (1962).

Fig. 3.—Extension of Fig. 2 to very long distance "bond" based on Lennard-Jones Ne–Ne.

tive to the London–Eyring–Polanyi–Sato (LEPS) method, of obtaining potential energy parameters for activated complexes was proposed. In this article the approach is extended, and now it seems to be 100% empirical.[14]

There are two different senses in which bond energy may be related to bond length. On the one hand, one has the potential energy function, V, for a given diatomic molecule as a function of internuclear separation, R. Such a function can be obtained from a detailed spectroscopic study or approximated by functions, such as the Morse function. On the other hand, one can consider a series of similar compounds, for example, acetylene, ethylene, and ethane. Each of these molecules has equilibrium internuclear carbon–carbon distance R_e and dissociation energy D_e. An empirical correlation of log D_e vs. R_e for a family of nitrogen–nitrogen and a family of carbon–carbon bonds is given by Fig. 2. These data give a line that is almost straight, but there is still some positive curvature for the N–N bonds and some negative curvature for the C–C bonds. For purposes of later kinetic computations, one needs to extrapolate these functions out to about 2 Å. How does one extrapolate a not-quite-linear empirical function? There is no satisfactory way to do so. What is needed is another point to the right of the last point in Fig. 2, so that interpolation as opposed to extrapolation can be done. The following argument leads to a postulate that permits just such an extension of the curves in Fig. 2. Table I gives a list of homonuclear molecules from elements in the first row of the periodic table corresponding to more-or-less integral bond orders. (To a chemist the concept of bond order is an intuitive one, with a fairly wide breadth of meaning. In molecular orbital theory of molecular structure, the term "bond order" has a specific, technical meaning, and in valence bond theory of molecular structure there is another, somewhat different, specific technical meaning to the term. In Table I the chemists' loose meaning is attached to the term: in a later paragraph an arbitrary but specific definition will be adopted.) The Lennard-Jones "moiecule" between two neon atoms[15] represents the approximately zero-order bond and is the limiting case in Table I. A postulate made here is that the Ne–Ne cluster or molecule provides a reasonable last term to all rows of Table I and an extension to either of the curves in Fig. 2.

(14) Or is it really 100% empirical? See the section on Evaluation.

(15) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.
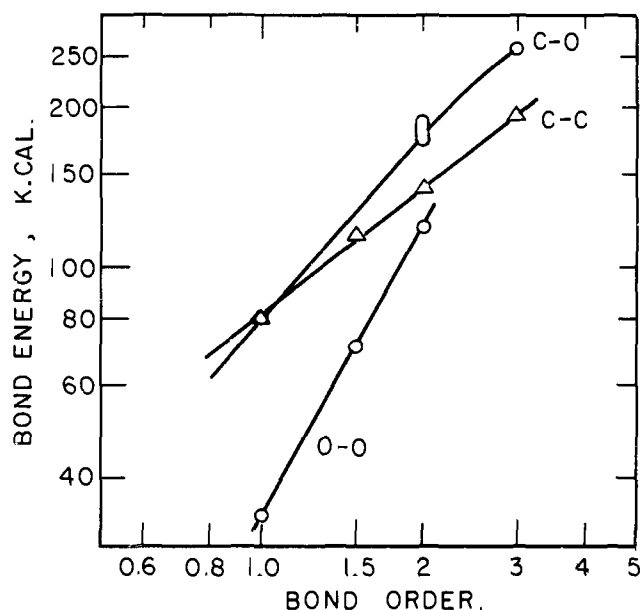

Fig. 4.—Log–log plot of bond energy against chemists' conventional "bond order."

A test of this postulate is given by Fig. 3, for the Ne–Ne molecule with R given by $2^{1/6} \sigma$ and with D_e given by ϵ from ref. 15, p. 1110, for the cases based on a quantum mechanical treatment of the second virial coefficient. It is proposed that if one had a perturbed N–N bond such that the equilibrium bond length came out to be 2 Å., for example, then one could make an estimate of its dissociation energy by using Fig. 3 as an empirical

TABLE I

MOLECULES IN THE FIRST ROW OF PERIODIC TABLE ILLUSTRATING APPROXIMATELY INTEGRAL BOND ORDERS

─────────Approximate bond order─────────			
III	II	I	0
			NeNe
		FF	
	OO	HOOH	
NN	MeNNMe	H_2NNH_2	
HCCH	H_2CCH_2	H_3CCH_3	

interpolation function. This postulate is extended to bonds such as C–H by assuming that there is continuity between the C–H single bond in methane and the "molecule" Ne–He, and that a linear plot of log D_e vs. R_e between these two points gives a suitable interpolation graph. The Lennard-Jones parameters for mixed noble gas "molecules" XY are obtained from the parameters for the pure species XX and YY by the usual relations[15]

$$\sigma_{xy} = (\sigma_{xx} + \sigma_{yy})/2 \qquad (12)$$

$$\epsilon_{xy} = (\epsilon_{xx}\epsilon_{yy})^{1/2}$$

As noted previously[12] an empirical log–log plot of dissociation energies against the chemists' "bond order" is approximately linear; for example, Fig. 4. Thus one has two approximate linear relations among bond energy D, bond length R, and bond order n.

$$\ln D/D_s = C(R_s - R) \qquad (13)$$

$$D = D_s n^p \qquad (14)$$

where subscript s stands for "single bond order," and C and p are empirical constants.

For a bond of any order n Pauling[16] proposed a simple relation between bond length and bond order

$$R = R_s - 0.6 \log n = R_s - 0.26 \ln n \qquad (15)$$

(16) L. Pauling, J. Am. Chem. Soc., 69, 542 (1947).

TABLE II

EVALUATION OF THE INDEX p FROM BOND ENERGIES AND BOND LENGTHS

| Bond	D_0^0, kcal.	ω, cm.$^{-1}$	D_{es}, kcal.	R_s, Å.	Bond	ϵ_x, cal.	R_x, Å.	p
H–H	103.2	4395	109.4	0.74	He–He	20.4	2.89	1.041
H$_3$C–H	101.3	2914	105.5	1.09	Ne–He	38.0	2.99	1.087
H$_2$N–H	92.2	3336	97.0	1.01	Ne–He	38.0	2.99	1.032
HO–H	109.4	3735	114.7	0.96	Ne–He	38.0	2.99	1.028
F–H	134.6	4138	140.5	0.92	Ne–He	38.0	2.99	1.036
Cl–H	102.1	2989	106.4	1.27	Ar–He	69.6	3.36	0.914
Br–H	86.7	2649	90.5	1.42	Kr–He	83.2	3.46	.892
I–H	70.6	2309	73.9	1.61	Xe–He	94.6	3.75	.811

where R is in Ångstrom units. If one takes the chemists' intuitive view of bond orders, Table I, the constant in eq. 15 is more nearly 0.7 than 0.6. Thus if one uses eq. 15, it becomes the *definition* of "bond order" in a particular technical sense. By combining eq. 13, 14, and 15, one readily finds that the constant C in eq. 15 can be expressed in terms of Pauling's constant 0.26 in eq. 15, and the index p of eq. 14, $C = p/0.26$. Thus if R_x is the equilibrium internuclear distance in a noble gas diatomic cluster or "molecule" and if ϵ_x is the depth of its Lennard-Jones potential, one can calculate the index p for any pair of atoms for which the single-bond parameters R_s and D_s are known

$$p = \frac{0.26 \ln (D_s/\epsilon_x)}{R_x - R_s} \qquad (16)$$

Thus the parameter p, fitted in ref. 12 to kinetic data, can be readily evaluated from nonkinetic data. A few values of p obtained in this way are given in Table II. These values of p are lower than those found from kinetics[12,13]: H–H, 1.041 vs. 1.086; C–H, 1.087 vs. 1.195; Cl–H, 0.914 vs. 1.05. However, the previous treatment[12,13] did not explicitly account for the interaction between end atoms, which the present treatment shows to be very important.

For transfer of a hydrogen atom

$$R\text{—H} + X \longrightarrow R\cdots H\cdots X \longrightarrow R + H\text{—X} \qquad (17)$$
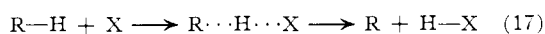
the R–H or H–X bond energy is typically about 100 kcal., and the activation energy is the order of magnitude 0 to 10 kcal. Thus the mechanism is certainly not the breaking of one bond followed later by the formation of the final bond. At all stages of the reaction, the formation of the second bond must be "paying for" the breaking of the first bond; there must be very strong correlation between changes in one bond and the other during reaction. As before,[12] this strong correlation is approximated for *hydrogen-atom transfer* by the assumption that the path of lowest energy from reactants to products is given where the sum of the bond orders is unity

$$n_1 + n_2 = 1 \qquad (18)$$

The discussion so far has neglected the interaction of R and X of eq. 17. Consider the H–H–H reaction where there are only three electrons, each having electron spin function α or β. A valence-bond discussion of the situation gives an indication of the magnitude of the R$\cdots$X interaction. Suppose the electron on the end atom has spin function α and it forms a fractional bond with the central electron, which then must have spin β. The central electron also forms a fractional bond with the electron on the other end atom, which then must have spin function α. Thus the relative spin functions of the electrons must be either

$$\alpha\cdots\beta\cdots\alpha \text{ or } \beta\cdots\alpha\cdots\beta \qquad (19)$$
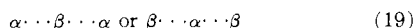
In any case. the electrons on end atoms have opposite spins and repel each other with a triplet interaction. The complex may be regarded as in eq. 20.

$$\begin{array}{c} R_1 \quad R_2 \\ R\cdots H\cdots X \qquad (20) \\ R_3 \\ |\longleftrightarrow| \end{array}$$

The fractional bonds R_1 and R_2 are "bonding" and the bond R_3 "antibonding." If the ends, R or X, are radicals instead of atoms, there may also be nonbonding interactions or "steric hindrance." The energy in the bonding terms has already been given by eq. 14 and 16. The antibonding energy may be estimated by use of one of Sato's proposals.[11] Sato proposed that the triplet repulsion between two atoms be given by a modified anti-Morse function, eq. 11. The triplet repulsion between two hydrogen atoms has not been measured (presumably it could be deduced from appropriate scattering experiments), but it has been calculated by means of quantum mechanics. A discussion of the various calculations is given by ref. 15, pp. 1062–1064. An exact quantum mechanical calculation[17] was made for three points, and more extensive, less
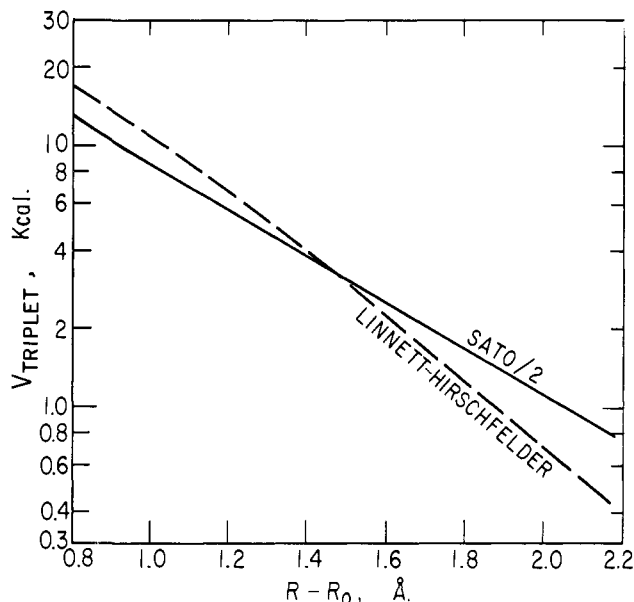

Fig. 5.—Comparison of Sato's anti-Morse function with theoretical curve by Hirschfelder and Linnett for H $\cdots$ H triplet interaction.

exact calculations were made by Hirschfelder and Linnett.[18] Where these calculations overlap, the latter calculation is somewhat (10 or 33%) too high. A comparison is made of Sato's proposed function (in terms of the variable $r_3 = R_3 - R_{3s}$) against the Hirschfelder–Linnett function over the range of distances of most interest for kinetic considerations, Fig. 5. The two functions do not have the same slope. Sato's triplet function, eq. 11, must again be divided by two to cross

(17) H. M. James, A. S. Coolidge, and R. D. Present. *J. Chem. Phys.*, **4**, 187, 193 (1936).

(18) J. O. Hirschfelder and J. W. Linnett. *ibid.*, **18**, 130 (1950).

the Linnett–Hirschfelder function at a distance of interest. Thus in this article the triplet interaction between end atoms of a three-atom complex is given by the anti-Morse function

$$V_{TR} = D_e[(1/2)e^{-\beta r_3}][1 + (1/2)e^{-\beta r_3}] \quad (21)$$

This expression can be put in terms of bond order, since

$$r_3 = R_3 - R_{3s} = R_1 + R_2 - R_{3s} =$$
$$R_{1s} + R_{2s} - R_{3s} - 0.26 \ln n_1 n_2$$
$$V_{TR} = D_e[(1/2)e^{-\beta \Delta R_s}(n_1 n_2)^{0.26\beta}][1 + (1/2)e^{-\beta \Delta R_s}(n_1 n_2)^{0.26\beta}] \quad (22)$$

where $\Delta R_s = R_{1s} + R_{2s} - R_{3s}$.

With these assumptions the locus of the line of minimum energy between reactants and products on the R_1–R_2 plane is given by the one progress variable n and spectroscopic parameters where q is the index for bond

$$V = D_1 - D_1 n^p - D_2(1 - n)^q +$$
$$D_3 B[n(1 - n)^{0.26\beta}\{1 + B[n(1 - n)^{0.26\beta}\} \quad (23)$$

2 and B is $(1/2)e^{-\beta \Delta R_s}$. The origin of energy is the minimum potential energy of the reactant molecule. The function V may be evaluated point by point for values of n from 0 to 1, and the maximum value of V is directly the potential energy of activation of the chemical reaction. Alternatively, eq. 23 may be differentiated with respect to n to find the maximum value of V between reactants and products, where dV/dn is zero. Since dV/dn is zero at the maximum V^*, the second derivative gives the negative curvature at the maximum

$$-F_\rho^* = -\frac{\partial^2 V}{\partial n^2}\left(\frac{\partial n}{\partial R}\right)^2 \cong \quad (24)$$

$$\frac{10.22}{\frac{1}{n^2} + \frac{1}{m^2}}\left[\frac{D_{1s}p(p-1)}{n^{2-p}} + \frac{D_{2s}q(q-1)}{m^{2-q}} + \frac{D_{3s}\gamma(\gamma-1)}{2(nm)^{2-\gamma}}\left\{\frac{2nm}{\gamma-1} - (1 - 2n)^2\right\}e^{-\beta \Delta R_s}\right]$$

where n is n_1, m is n_2, γ is 0.26β, $F\rho$ is in dynes/cm., and D_s are in cal./mole. The bending force constant is readily obtained from eq. 21

$$F_\phi = -\frac{R_1 R_2}{R_3}\left(\frac{\partial V}{\partial R_3}\right)_{R_1, R_2} = \frac{R_1 R_2}{R_3}\frac{F_{3s}(nm)^\gamma e^{-\beta \Delta R_s}}{4\beta} \quad (25)$$

The distance along the line of constant order is the progress variable ρ; small displacements perpendicular to this line is a progress variable σ. A modified Badger's rule, as discussed in ref. 13, gives the force constant along this perpendicular line

$$F_\sigma = \frac{F_{s1}n^3 + F_{s2}m^3 + F_{s3}(1/4)(nm)^\gamma e^{-\beta \Delta R_s}}{n^2 + m^2} \quad (26)$$

The expressions for force constants neglect the second term in the square bracket in eq. 22, since it greatly complicates the algebra and contributes only a few per cent to the triplet term; the additional correction can be made if desired. Finally it may be noted that the force constants for Wilson's F-matrix in the internal coordinates R_1 and R_2 are given in terms of $F\rho$ and $F\sigma$ by

$$F_{11} = \frac{F_\rho m^2 + F_\sigma n^2}{n^2 + m^2} \quad (27)$$

$$F_{22} = \frac{F_\rho n^2 + F_\sigma m^2}{n^2 + m^2} \quad F_{12} = \frac{(-F_\rho + F_\sigma)nm}{n^2 + m^2}$$

The structural and spectroscopic data used to evaluate the Morse parameters and the triplet energies are summarized in Table III. Three examples of energy of the "three-atom" complex for various orders of reaction are given in Table IV. These examples show that the bonding terms and the antibonding terms are about equally important in determining the value of the activation energies. For all cases the antibonding, triplet energy goes through a maximum at order 0.50.

The magnitude of this term at 0.5 order varies from 2 to 8 kcal./mole. For some cases the bonding contribution also goes through a maximum, but the order of the bond being formed at the maximum is less than 0.50 for exothermic reactions. The bonding contribution shows a maximum if both p and q are greater than one. For thermoneutral reactions, the bonding terms shows a minimum if p and q are less than one. For exothermic reactions with p or q less than one, the bonding contribution is always negative, and the activation energy is due to the triplet repulsion. The maximum values of the potential energy along the path of constant order are printed in italic type in Table IV. From tables such as these the potential energy of activation can be readily found by inspection.

TABLE III

SPECTROSCOPIC DATA USED TO EVALUATE MORSE PARAMETERS AND TRIPLET ENERGIES BETWEEN END ATOMS

Bond R · · X	D_e, kcal.	R_s, Å.	$\beta \times 10^{-8}$, Å.$^{-1}$
H–H	109.4	0.74	1.94
C–H	105.5	1.09	1.78
O–H	114.7	0.96	2.22
F–H	140.5	0.92	2.23
Cl–H	106.4	1.27	1.87
Br–H	90.5	1.42	1.81
I–H	73.9	1.61	1.75
C–C	84.4	1.54	1.94
C–F	107	1.38	2.00
C–Cl	80	1.76	1.81
C–Br	67	(1.91)	(1.81)
C–I	58	(2.10)	1.81
C–O	85.4	1.43	2.05
F–F	38	1.44	2.85
F–Cl	60	1.63	2.34
F–Br	51	1.76	2.39
Cl–Cl	58	1.99	2.02
Cl–Br	52	2.10	2.52
Br–Br	46	2.28	1.98
I–I	36	2.67	1.87
O–O	35	1.47	2.69
O–F	(46)	1.42	(2.77)
O–Cl	50	1.69	2.65
O–Br	(45)	(1.77)	(2.35)

This method gives the potential energy of activation, V^*. The observed activation energy, eq. 1 or 2, differs not only by the difference in zero point energy between reactants and complex, but also in thermal excitation of the reactant and complex. The zero point energy of R–H varies from about 4 to 6 kcal. The zero point energy of a complex R···H···X probably lies between 1 and 6 kcal., depending on the mass of R and X. Thus in general potential energies of activation should be slightly larger than observed energies of activation; for deuterium transfer reactions, the difference between V^* and E should be less than for hydrogen transfer.

Table V gives 130 cases of calculated potential energy of activation. (The time required to make these calculations with a desk calculator was about 3 man-days; thus this method is very simple to carry through.) The computed activation potential energies vary from zero to 50 kcal., but the activation potential energies for thermoneutral or exothermic reactions vary only from zero to 12 kcal. A simple universal Polanyi relationship[19] is not obeyed down the entire series; the halogen atoms provide an exception. That the halogen atoms upset the universal Polanyi relationship is a well known experimental fact. These calculations definitely detect

(19) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. I, Princeton University Press, Princeton, N. J., 1958, pp. 29–33.

TABLE IV

EXAMPLES OF CONTRIBUTIONS OF BONDING AND ANTIBONDING TERMS AT VARIOUS STAGES OF REACTION.   ALL ENERGIES IN KCAL·MOLE^{-1}

n_2	CF$_3$ + H-CH$_3$			-Cl + H-CMe$_3$			F + HF		
	V_{bonds}	V_{TR}	V	V_{bonds}	V_{TR}	V	V_{bonds}	V_{TR}	V
0	0	0	0	0	0	0			
0.02	0.76	1.69	2.45	−0.96	2.14	1.18	0.48	0.33	0.81
.03	1.06	2.07	3.13	−1.31	2.58	1.27	.64	.45	1.09
.04	1.34	2.38	3.72	−1.60	2.94	1.34	.79	.54	1.33
.05	1.57	2.70	4.27	−1.87	3.28	1.41	.96	.67	1.63
.10	2.59	3.80	6.39	−2.93	4.53	1.60	1.57	1.06	2.63
.15	3.39	4.47	7.86	−3.77	5.28	1.51	2.11	1.37	3.48
.20	4.01	5.05	9.06	−4.45	5.94	1.49	2.51	1.60	4.11
.25	4.48	5.48	9.96	−5.02	6.40	1.38	2.77	1.82	4.59
.30	4.94	5.84	10.78	−5.51	6.80	1.29	3.02	1.99	5.01
.35	5.12	6.21	11.33	−6.03	7.21	1.18	3.23	2.18	5.41
.40	5.24	6.31	11.55	−6.41	7.35	0.94	3.38	2.25	5.63
.45	5.34	6.47	11.81	−6.80	7.48	.68	3.41	2.29	5.70
.50	5.26	6.47	11.73	−7.25	7.48	.23	3.42	2.29	5.71

TABLE V

CALCULATED POTENTIAL ENERGIES OF ACTIVATION IN KCAL. FOR HYDROGEN TRANSFER REACTIONS

D_e, kcal.	RH	F	HO	H	CF$_3$	Cl	CH$_3$	C$_2$H$_5$	Me$_2$CH	Me$_3$C	Br
140	F-H	6	26	33	36	34	38	43	45	49	50
115	HO-H	0.3	4	11	14	9	16	19	20	24	24
109	H-H	2	6	10	14	8	15	18	19	22	21
107	CF$_3$-H	3	7	12	13	9	14	15	18	21	20
106	Cl-H	0.3	0.3	5	8	0	8	10	11	15	16
105	CH$_3$-H	3	6	11	12	7	13	15	16	20	18
100	Et-H	2	4	8	9	4	10	12	13	16	14
98	Me$_2$CH-H	2	4	8	9	3	9	11	12	15	12
93	Me$_3$C-H	2	3	6	7	2	7	9	10	12	8
90	Br-H	0	0.1	2	3	0	3	4	4	5	0
90	≥C-H	2	2	5	6	1	6	8	9	10	6
85	≥C-H	2	2	4	5	1	5	6	7	8	2
74	I-H	0	0.7	1	1	0	1	2	2	2	0

this fact. In general the potential energies of activation in Table V agree with established activation energies within 2 or 3 kcal. in all cases, so far as the authors are aware.
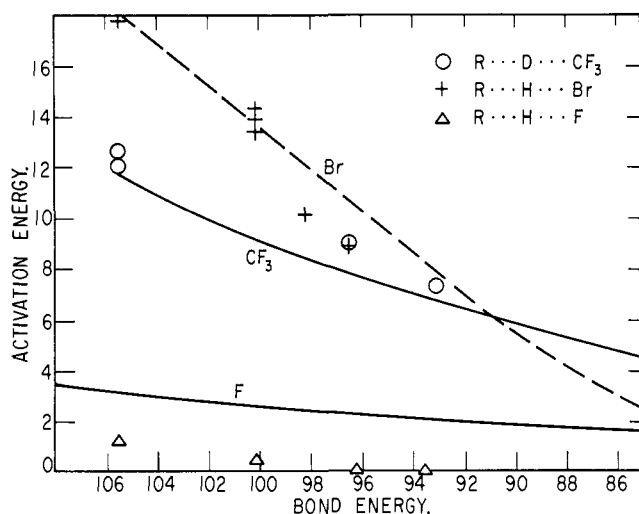
endothermic reactions approaches the endothermic heat of reaction. This behavior is more reasonable than Polanyi's linear relationship, but over the range of observations these differences are not important. The
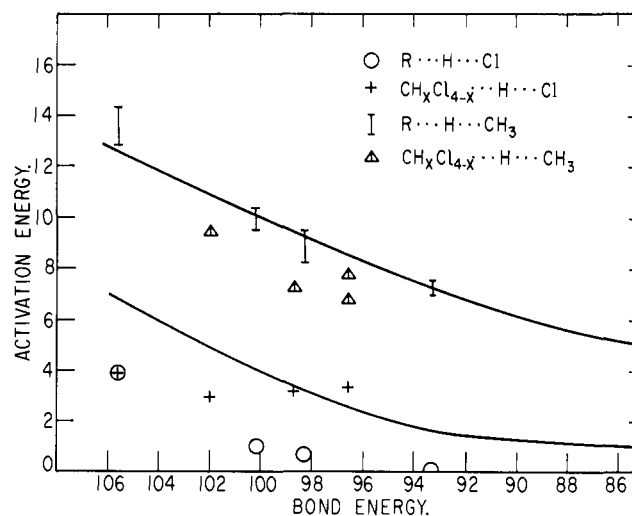

Fig. 6.—Calculated potential energy of activation and observed Arrhenius activation energy plotted against dissociation energy for carbon–hydrogen bonds: O, R···D···CF₃, ref. 21 and unpublished work by Halbert Carmichael; +, R···H···Br; Δ, R···H···F, G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *Can. J. Chem.*, **38**, 1643 (1960).

Fig. 7.—Similar to Fig. 6: O, R···H···Cl; +, CH$_x$Cl$_{4-x}$···H···Cl, ref. 13 and J. H. Knox and R. H. Nelson; I, R···H···CH₃, showing range of reported values; Δ, CH$_x$Cl$_{4-x}$···H···CH₃, A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955.

Observed activation energies and calculated potential energies of activation are plotted in Fig. 6 and 7. The calculated function shows curvature, for highly exothermic reactions approaches zero, and for highly

calculated curves lie very close to the observed activation energies. The calculated potential energy of activation for fluorine atom attack on hydrocarbons is far less than the zero point energy of the bond being broken; the observed activation energies are parallel to the
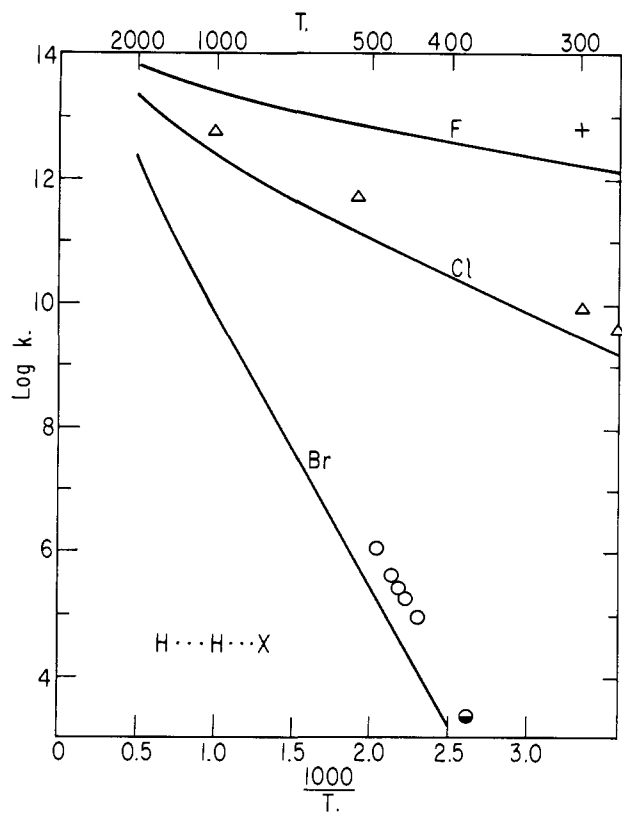
Fig. 8.—Calculated and observed rate constants for halogen atom attack on H_2: ●, Br, and +, F, Fettis, Knox, Trotman-Dickenson, Fig. 6; O, Br, M. Bodenstein and H. Lutkemeyer, *Z. physik. Chem.*, **114**, 208 (1924); Δ, Cl, H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **76**, 1201 (1954).

calculated potential energies and about 2 kcal. lower. A similar situation applies for the reactions of chlorine atoms and hydrocarbons, but the activation energies are slightly higher. For chlorine atom attack on chlorinated methanes, the observed activation energies do not follow a Polanyi-type relation. For this case, observed activation energies do not parallel the line of computed potential energies of activation. These cases presumably illustrate an effect (amounting to 2 or 3 kcal.) of nonbonding interactions.[13]

To go further and compare observed and calculated activation energies with corrections for zero point energies and thermal excitation, one must have a complete theory and detailed models. The theory used is simple, separable activated-complex theory expressed in terms of local-bond properties.[20,21] Previous calculations[21] of 3, 4, 5, and 9 atoms models confirm the simple values of the temperature-independent factors that differ from model to model, that is, the Jacobian factors J, 4π, $8\pi^2$, etc. Tunneling corrections[22] are based on the supposedly separable Eckart functions. Once the full apparatus of the theory is used, it is more interesting to compare observed rate constants with calculated values over a range of temperature, rather than to compare observed and calculated activation energies. The curve calculated for the H–H–H reaction is the solid line in Fig. 1. Calculated rate constants as a function of temperature are compared with observed values for halogen atom attack on H_2 in Fig. 8, and for CF_3 radical attack on methane, ethane, and secondary

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

(21) T. E. Sharp and H. S. Johnston, *ibid.*, **37**, 1541 (1962).

(22) H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961); H. S. Johnston and J. Heicklen, *J. Phys. Chem.*, **66**, 532 (1962).
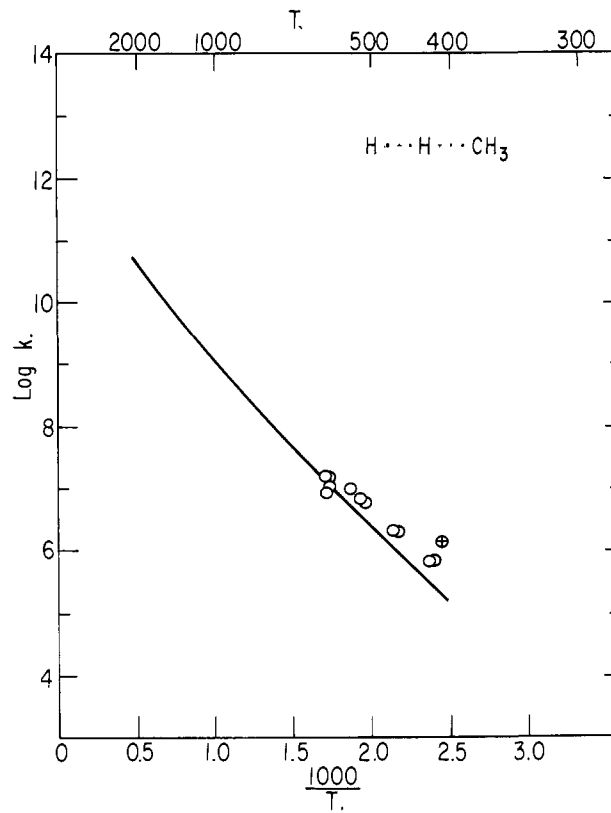
Fig. 9.—Calculated and observed rate constants for methyl radical reaction with H_2: O, T, G. Marjury and E. W. R. Steacie, *Can. J. Chem.*, **30**, 800 (1952); +, J. C. Polanyi, *J. Chem. Phys.*, **24**, 493 (1956).
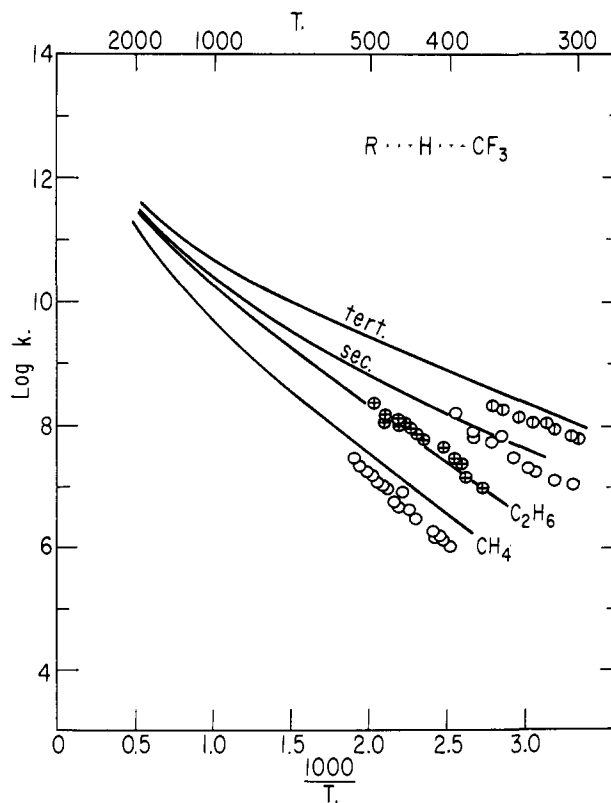
Fig. 10.—Calculated and observed rate constants for trifluoromethyl radical reaction with hydrocarbons: P. B. Ayscough, J. C. Polanyi, and E. W. R. Steacie, *Can. J. Chem.*, **33**, 743 (1955); P. B. Ayscough and E. W. R. Steacie, *ibid.*, **34**, 103 (1956).

and tertiary hydrocarbons in Fig. 10. These calculations, with no adjustable parameters, reproduce rate constants at all temperatures within about a factor of 2. An activation energy based on the experimental points in Fig. 9 would disagree with the calculated activation energy by several kilocalories, yet the observed rate constants are fairly well predicted by the computations; this point illustrates that wherever possible it is best to evaluate a theory in terms of observed rate constants, not derived quantities such as the Arrhenius parameters, A and E.

Evaluation

Although these calculations seem to have no adjustable parameters, the authors realize that the treatment is partially "adjusted" and do not take the interpretations (constancy of bond order; Pauling's bond-order relation; separability of energy between bonds 1, 2, and 3; activated-complex theory; or separable one-dimensional tunneling factors) at all literally. For fractional H···H bonds one might turn to the well-known hydrogen molecule-ion H_2^+, or one might take the He···He cluster as was done here. The first choice gives a poor value for the activation energy of hydrogen molecule reactions, and the second choice gives the good success reported here. The choice of the second model instead of the first is an adjustable concept, if not an adjustable parameter.

Weak points in the numerical aspects of this structure include: rather wide range of values of ϵ and σ in

ref. 15, uncertainty in the value and the constancy of Pauling's "constant," and uncertainty in calibrating Sato's triplet function. A strong point in his structure is that results are fairly insensitive to these numerical values; for example, an increase in Pauling's constant increases the activation energy so far as bonding terms are concerned but decreases the contribution of antibonding terms. This method does not calculate the activation energy as the difference in two large total-energy terms. Rather, it calculates directly an energy difference between reactants and the collision complex. This energy difference is further resolved into two more-or-less equal components, the bonding and antibonding terms, with recognition of further nonbonding components.

It is to be expected that further refinements of Lennard-Jones parameters, value of Pauling's constant, and magnitude of the triplet repulsion will destroy some of the remarkable success of these calculations. Thus it is well at this time to claim no more for the method than that it is a very simple technique for predicting rate constants of all hydrogen-transfer reactions based on reactant properties plus something between $1/2$ and 1 "adjustments."

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]
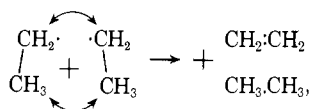
Combination and Disproportionation of Ethyl Radicals in the Gas, Liquid, and Solid Phases. Some Remarks about the Transition State of these Processes

BY P. S. DIXON, A. P. STEFANI, AND M. SZWARC

The combination and disproportionation of ethyl radicals formed by photolysis of azoethane have been investigated in the gas, liquid, and solid phases as well as in a variety of solvents (isooctane, toluene, propanol, glycol, and liquid methane). This study covered a wide temperature range, from -191 to $+85°$. It was shown unequivocally that k_{dis}/k_{com} *increases* with *decreasing* temperature both in the gas phase and in solution. This temperature dependence is attributed to terms in T^n, as it is believed that both processes proceed without any activation energy. The ratio k_{dis}/k_{com} is larger for solution reactions than for the gas reaction. The largest ratio was found in glycol, the order being glycol > propanol > toluene > isooctane > gas phase. At extremely low temperatures similar values of k_{dis}/k_{com} were obtained in all solvents. It is not clear, however, whether this observation has a deeper physical significance. It is suggested that the effect of solvent may be due to its internal pressure, and on this basis it was concluded that $v_{com}{}^{\ddagger} - v_{dis}{}^{\ddagger} \sim 2.4$ cc./mole. The desirability of studies under a few thousand atmospheres of pressure has been stressed. The effect of light of different wave length, scavengers, and concentration has also been examined and it was found that these factors do not affect the ratio k_{dis}/k_{com}. The models of various transition states for these processes have been examined and fully discussed.

The encounter of two ethyl radicals results in their combination or disproportionation. By labeling the radicals with deuterium it was demonstrated[1,2] that the latter reaction involves a transfer of a hydrogen atom from the CH_3 moiety of one radical to the CH_2 group of the other. This observation was taken as evidence for a head-to-head collision leading to combination and head-to-tail collision resulting in disproportionation.[1,2] However, such a conclusion is not unavoidable, since these experiments show only that the reaction

$$\begin{array}{c} CH_2\cdot \quad \cdot CH_2 \\ | \quad\quad\; | \quad \rightarrow \quad + \\ CH_3 \quad\; CH_3 \end{array} \quad \begin{array}{c} CH_2{:}CH_2 \\ + \\ CH_3.CH_3, \end{array}$$

does not take place. In fact, Bradley[3] and Kerr and Trotman-Dickenson[4] independently suggested that a collision may lead to a common transition state, namely

$$\begin{array}{cc} CH_2\cdot & CH_3 \\ \diagup \;\; \diagdown\;\diagup \\ H_2CH \cdots \cdot CH_2 \end{array}$$
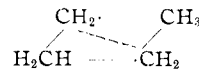
from which emerge either the products of disproportionation or combination. This idea was further elaborated in a previous paper from this Laboratory[5] where it was proposed that the combination product is formed through the intramolecular dissipation of energy, a process which competes with the intramolecular hydrogen atom transfer giving the disproportionation products.

(1) M. H. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951).

(2) J. R. McNesby, C. M. Drew, and A. S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955).

(3) J. N. Bradley, *J. Chem. Phys.*, **35**, 748 (1961).

(4) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Chemical Kinetics," Vol. 1, Pergamon Press, New York, N. Y., 1961, p. 107.

(5) M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Szwarc, *Proc. Chem. Soc.*, 304 (1962).