[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING]

Theoretical Pre-exponential Factors for Hydrogen Atom Abstraction Reactions[1]

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RECEIVED AUGUST 29, 1956

For a series of bimolecular reactions involving hydrogen atom abstraction, pre-exponential factors in the Arrhenius equation $k = A \exp(-E/RT)$ have been calculated by means of activated complex theory. The structure and mechanical properties of the activated complex are unambiguously assigned from a set of empirical rules from the fields of molecular structure and molecular spectroscopy. Bond distances around the transferred hydrogen atom are evaluated by Pauling's rule for fractional bonds, stretching force constants are assigned by means of Badger's rule, reduced moments of inertia for internal rotation are evaluated by means of Pitzer's simple approximate method, bending force constants are assigned by analogy with hydrogen-bonded molecules, and the reaction coördinate is explicitly introduced as the (highly perturbed) antisymmetric vibrational mode of the atom transferred. With these assignments of structure and force constants, a vibrational analysis was carried out by Wilson's FG matrix method; for the larger activated complexes this detailed vibrational analysis was made only for degrees of freedom close to the transferred hydrogen atom. For 8 cases out of 9 the agreement between calculated and observed pre-exponential factors is quite satisfactory. For the reaction of bromine with isobutane calculated and observed pre-exponential factors disagree by a factor of 10^5. It is argued that this method of assigning properties to the activated complex is realistic enough to constitute strong theoretical grounds for suspecting that the experimental results were interpreted by means of an incorrect mechanism.

Introduction.—The general theory of bimolecular gas phase reactions is presented in several well known books [3] To use the theory one needs to know the structure and mechanical properties of the activated complex. Semi-empirical rules have been formulated for constructing potential energy surfaces from which to estimate the structure, mechanical properties and electronic energies for especially simple activated complexes.[3] For complexes of many atoms, 4 or more in cases of low symmetry, this procedure becomes forbiddingly complicated. For quite complicated complexes one surrenders the hope of calculating activation energies and concentrates on the pre-exponential factor A in $k = A \exp(-E/RT)$. Rules have been proposed[3] whereby one makes a realistic guess of the moments of inertia of the activated complex, and the vibrational frequencies are assumed to be so high that the vibrational partition functions are unity. Computations based on this level of approximation give pre-exponential factors lower than observed ones by a factor of 10^2 to 10^6 for activated complexes containing 4, 5, or 6 atoms.[4] This discrepancy is removed if one makes a realistic estimate of vibration frequencies and makes an adequate allowance for the effect of internal rotations.[4] In an effort to refine and extend the method proposed in ref. 4 for computation of pre-exponential factors, we are following a suggestion made by Professor Pauling for the calculation of bond distances in activated complexes. For calibration of the method we have treated the well-known reactions $H + H_2$ and $Br + H_2$, and the calculations are extended to cover typical cases of hydrogen atom abstractions from organic molecules by methyl free radicals and by bromine atoms.

Method of Computation.—In order to calculate pre-exponential factors A for bimolecular reactions, one needs to know, both for reactants and the activated complex, the molecular weight, moments of inertia for over-all rotation, moments of inertia for internal rotation, barriers to internal rotation, all vibration frequencies and electronic degeneracy. (One also needs the transmission coefficient.) These data can be obtained for the reactants from spectroscopy. The problem is thus reduced to one of determining the structure and mechanics of the activated complex. It is assumed[3] that the excitation energy of the reactants has gone into the potential energy of a single separable reaction coördinate, so that the rest of the activated complex is like a normal molecule. Thus, except for the reaction coördinate, one may make heavy use of analogy with ordinary molecules. This analogy means, in particular, that normal bond distances and normal force constants are to be expected.

For purposes of kinetics any of the rules or the tables of normal covalent radii are adequate, and for single, double or triple bonds we use the convenient tables in Pauling's "Nature of the Chemical Bond."[5] However, for the H_3 complex or for a methyl radical abstracting a hydrogen from an organic compound, the bonds are more nearly "half-bonds" than any integral order, and in this treatment these bonds will be formally regarded as "half-order." There are various rules for the length of a bond of any order; the most convenient of these is Pauling's rule[6]

$$R_1 - R = 0.30 \log_{10} n \qquad (1)$$

where R is the bond radius in Å., R_1 is the radius of the corresponding single bond, and n is the order of the bond. Long standing arguments[6a] justify a linear complex for H_3, and this structure was assigned to the C–H–C links in methyl radical reactions and C–H–Br links in the bromine reactions. By these arguments and rules the detailed geometric structure of the activated complex was determined.

From Badger's rule[7] stretching force constants

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[1] In support of this work one of us (DJW) is indebted to the National Science Foundation for a Fellowship. Also this work was supported in part by the Office of Naval Research, Project NR-051-246, Contract N6 onr 25131.

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[3] S. Glasstone, K. L. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

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

[5] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[6] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

[6a] F. London, "Probleme der modernen Physik," Sommerfeld Festschrift, 1928.

[7] R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1933); **3**, 710 (1934).

were assigned to all bonds in the complex. We know of no equivalent to Badger's rule for bending force constants, so we used analogy with the bending force constants in the bifluoride ion. The bending force constant was taken as the bending force constant in the bifluoride ion reduced by the ratio of bending force constants in CH_4 and CF_4. Skeletal internal rotations were regarded as essentially free; usually the methyl group internal rotations cancelled out pairwise between numerator and denominator, that is, between activated complex and the reactant. The electronic degeneracy of the complex was assumed to be the same as for the methyl radical. Transmission coefficients were taken as unity. Thus by these rules and analogies, the mechanical properties of the activated complex, aside from the reaction coördinate, were assigned.

The reaction coördinate was treated as previously.[4] The reaction coördinate for these atom-transfer reactions can be made to appear very naturally by including an interaction term in the potential energy which reduces the restoring force on the anti-symmetric vibration to zero. For the H_3 complex, the potential energy expression was taken to be

$$2V = k_s r_1^2 + k_s r_2^2 + 2k_s r_1 r_2 + k_b \alpha_1^2 + k_b \alpha_2^2 \quad (2)$$

The magnitude of the cross-product term is not an adjustable parameter; in this case it must have the value $2k_s$ in order to cause the antisymmetric stretching frequency to vanish. If the two stretching force constants differ, the interaction constant is $2(k_1k_2)^{1/2}$.

For reactions 1, 2, 3 and 9 in Table I, a detailed vibrational analysis (including a reaction coördinate such as eq. 2) was made for the entire complex by the Wilson FG matrix method,[8] and the vibration frequencies were used to calculate the pre-exponential factor.[3,4] For reaction 4, the frequencies were classified by the method of ref. 4, and most frequencies were assigned from the corresponding type in ethane and deuteroethane, but the stretching and bending frequencies including the transferring atom were calculated by the Wilson FG matrix method on the assumption that the complex was a five-atomic molecule. Thus as many frequencies as possible were cancelled out between reactants and activated complex, and all frequencies which do not match-up for cancellation were computed as carefully as possible[8]; this procedure is spoken of here as an "approximate vibrational analysis." For reactions 5, 6, 7, 8 and 10, this approximate vibrational analysis was carried out. For these cases further approximations were made: all moments of inertia for both the hydrocarbons and the complex were computed as if the hydrogens were located at the nuclei of the carbon atoms to which they are attached. The same approximation was made for skeletal internal rotations[4]; methyl group internal rotations were cancelled out between reactants and complex.

TABLE I

THEORETICAL AND EXPERIMENTAL PRE-EXPONENTIAL FACTORS FOR BIMOLECULAR REACTIONS WITH ABSTRACTION OF HYDROGEN ATOMS

Reaction	T, °K.	$\log_{10} A$ Calcd.	$\log_{10} A$ Obsd.	Ref.
(1) $H + H_2 \rightarrow H_2 + H$	1000	13.7	13.7	*a*
(2) $CH_3 + H_2 \rightarrow CH_4 + H$	455	12.0	11.5–12.5	*b*
(3) $H + CH_4 \rightarrow H_2 + CH_3$	455	13.6		
(4) $CD_3 + CH_4 \rightarrow CD_3H + CH_3$	455	11.3	11.5	*c*
(5) $CD_3 + C_2H_6 \rightarrow CD_3H + C_2H_5$	455	11.3	11.3	*d*
(6) $CH_3 + n\text{-}C_4H_{10} \rightarrow CH_4 + C_4H_9$	455	11.8	11.0–11.5	*e*
(7) $CH_3 + n\text{-}C_5H_{12} \rightarrow CH_4 + C_5H_{11}$	455	11.7	11.0	*d*
(8) $CH_3 + n\text{-}C_6H_{14} \rightarrow CH_4 + C_6H_{13}$	455	11.7	11.1	*d*
(9) $Br + H_2 \rightarrow HBr + H$	523	14.1	13.6–14.2	*f*
(10) $Br + (CH_3)_3CH \rightarrow HBr + (CH_3)_3C$	393	12.4	17.6	*g*

[a] A. Farkas, *Z. physik. Chem.*, 10B, 419 (1930). A. Farkas and L. Farkas, *Proc. Roy. Soc.* (*London*), **152A**, 124 (1935). M. Van Meersche. *Bull. soc. chim. Belg.*, **60**, 99 (1951). [b] T. G. Marjury and E. W. R. Steacie, *Disc. Faraday Soc.*, 14, 45 (1953). E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953). R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **32**, 113 (1954). [c] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 4196 (1954). [d] Reference 9. [e] R. E. Rebbert and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1723 (1953). M. H. Steacie and E. W. R. Steacie, *Can. J. Chem.*, **31**, 505 (1953). [f] M. Bodenstein and S. C. Lind, *Z. physik. Chem.*, **57**, 168 (1907); M. Bodenstein and G. Jung, *ibid.*, **121**, 127 (1926). G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944). [g] Reference 10.

For the long-chain hydrocarbons calculations were made for abstraction of secondary hydrogens only, since the activation energy for abstraction of primary hydrogens is known[9] to be about 2 kcal. higher (a factor of 8 at these temperatures) than for secondary hydrogens. Calculations were made for the reaction of a methyl radical with one specific hydrogen atom, and then this result was multiplied by the total number of secondary hydrogen atoms. In this way the symmetry numbers were included in the rotational partition functions of the hydrocarbons and of the activated complexes in reactions 6, 7 and 8. For the reaction of the bromine atom with 2-methylpropane, the calculation is based on abstraction of the tertiary hydrogen atom; it is known from analysis of products[10] that this is the only reaction occurring in this system.

Results of the Calculations.—The activated complexes deduced from these rules are given in Fig. 1 together with the structure assumed for the methyl radical. In this figure small circles represent hydrogen atoms, medium circles stand for carbon atoms, large circles are bromine atoms, and the ovals represent CH_2 or CH_3 groups. From these structures the moments of inertia and symmetry numbers were evaluated, and these quantities are listed in Tables II and III. By use of Badger's rule the stretching force constants given in Table IV were found. With the data in Tables II–IV the contribution of each degree of freedom to the pre-exponential factor A_p was computed, and these

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[8] Wilson, Decius and Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[9] A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

[10] B. H. Eckstein, H. A. Scheraga and E. R. Van Artsdalen, *ibid.*, **22**, 28 (1954).

TABLE II

PROPERTIES DEDUCED FOR ACTIVATED COMPLEXES

Complex	Moments of inertia (A.M.U. Å.^{2})	I internal rotation (A.M.U. Å.^{2})	Vibration freq. (cm.$^{-1}$)
(1)	1.705	...	2930, 1190, 1190
(2), (3)	8.11, 8.11, —[a]	...	752.7, 752.7, 1441, 1441, 1643, 1643, 2984, 2984, 1322, 2665, 3145
(4)	9.53, 57.0, 57.0	2.117	711, 711, 1220, 1102, 1486, 2100, 2900, 2236, 2994, 2225, 2963, 1155, 970, 1260, 1055, 1460, 725, 753, 753
(5)	49.4, 66.0, 115.5	3.175, 6.350[b]	814, 814, 725,[c] 208, 469[d]
(6)	151, 112, 263	3.175, 13.8	1200, 1200, 725,[c] 200, 200[d]
(7)	118, 244, 362	3.175, 14.1, 14.1	Same as (6)[d]
(8)	132, 427, 559	3.175, 14.8, 17.8, 13.9	Same as (6)[d]
(9)	8.66	...	1074, 1074, 1325
(10)	240.5, 240.5, —[a]	...	158.5, 158.5, 374, 1116, 1116[d]

[a] One moment of inertia cancels with one in the reactant. [b] Only those moments of inertia for internal rotation are included which do not cancel identically with an equivalent term in the reactant. [c] This frequency is included because it is much lower than the corresponding C–H stretching frequency in the reactant. [d] These vibration frequencies include only those for which cancellation cannot be made against an equivalent frequency in the reactant.

factors are listed in Table V. From the factors in Table V one obtains the calculated preëxponential factors listed in Table I. The observed pre-exponential factors are listed there for comparison.

TABLE III

PROPERTIES ASSUMED FOR THE METHYL RADICAL

I: 3.175, 1.907, 1.907; $\sigma = 3$

Vib. freq., cm.$^{-1}$ (taken from ammonia)

3336, 950, 3414 (twice), 1627 (twice)

TABLE IV

FORCE CONSTANTS FOR HALF-BONDS

Half-bond	k, dynes/cm.
C–H	2.55×10^5
H–H	2.55×10^5
H–Br	2.24×10^5
X–H–X bend, ergs/radian	0.164×10^{-11}

TABLE V

VALUES OF A_p FOR THE VARIOUS DEGREES OF FREEDOM IN THE DIFFERENT REACTIONS

Reaction	A_t	A_r	A_{fir}	A_v
1	6.79×10^{-26}	6.20	...	3.34
2	5.15×10^{-26}	0.606	...	1.954
3	1.325×10^{-25}	10.02	...	1.825
4	4.93×10^{-27}	0.0619	6.14	6.24
5	3.24×10^{-27}	.131	15.02	21.8
6	2.96×10^{-27}	.0116	9.83	34.4
7	2.80×10^{-27}	.00469	11.75	34.4
8	2.67×10^{-27}	.00424	11.30	34.4
9	3.59×10^{-26}	31.5	...	6.16
10	7.82×10^{-26}	4.5	...	58

Discussion.—In view of the uncertainties and errors in obtaining the experimental values of pre-exponential factors, perfect agreement is to be regarded as within a factor of two, and satisfactory agreement is within a factor of ten. For certain reactions the spread in experimental values from one worker to another is a factor of ten or more, and certain of the other reactions have not been investigated so intensively. By these standards there is excellent agreement between observed and calculated values of the pre-exponential factor for 8 out of the 9 comparisons in Table I. In particular it should be noted that this very quick and relatively easy computation gives values of the pre-exponential factor which agree with experiment and with calculations made by the much more tedious method of constructing energy surfaces.[8]

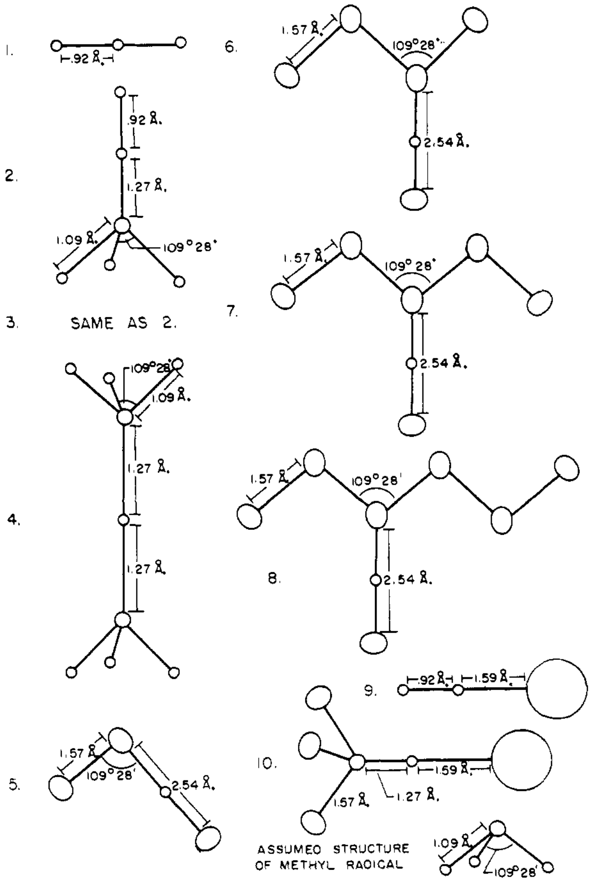

Fig. 1.—Structures of the activated complexes: small circles, H; medium circles, C; large circles, Br; ovals CH_2 or CH_3.

There may be some significance in the high values for A calcd. for the long-chain hydrocarbons, butane, pentane and hexane. If so, it is probably due to hindered skeletal internal rotations for these activated complexes.

Finally the excellent agreement between theory and experiment for reaction 9 between Br and H_2 and the 100,000 fold discrepancy between calculated and observed factors for reaction 10

$$(CH_3)_3CH + Br \longrightarrow (CH_3)_3C + HBr$$

require special comment. We make an unqualified prediction that the observed value is wrong; in particular, we believe a reinvestigation of this reaction over a wide range of reactant pressure, degree of reaction, and pressure of additives will reveal that the over-all reaction $(CH_3)_3CH + Br_2 \rightarrow (CH_3)_3CBr + HBr$ does not follow the bromination mechanism assumed for it.[10]

Evaluation.—Kinetic data are often so uncertain that order-of-magnitude estimates of pre-exponential factors are all that one can obtain from experiment. There are many empirical rules and approximation methods in the field of molecular structure and molecular spectroscopy which, though not good enough for many purposes in their own field, are more than adequate for purposes of kinetics. The rules used here for bond distances,[5,6] for stretching force constants,[6a] and for moments of inertia for internal rotation[4] appear to be cases of this type. However, we kineticists must await developments for comparable rules for barriers to internal rotation and for either a Badger's rule for bending force constants or, more likely, an adequate empirical classification of bending frequencies. With such rules, kinetic pre-exponential factors should be calculable within a factor of four or so, without undue labor, even for complicated reactant molecules. At present these calculations appear to be valid within, perhaps, a factor of about 40. It might be remarked that for practical purposes this situation is a considerable improvement over the case as stated recently by Trotman-Dickenson[11] relative to reaction 10.

(11) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 194, line 13.

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[Contribution from the Explosives Research Group, University of Utah]

Velocity–Diameter Curves, Velocity Transients and Reaction Rates in PETN, RDX, EDNA and Tetryl[1]

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Received June 11, 1956

Velocity-diameter $D(d)$ curves for cap initiated, low density PETN (Pentaerythratol Tetranitrate), RDX (Cyclotrimethylene trinitramine), EDNA (Ethylene dinitramine) and Tetryl (Trinitrophenylmethylnitramine) are presented. Analysis of these curves by the theories extant of chemical reaction rates in detonation gave total reaction times ($\tau = Mc\bar{R}_g$) expressed by average M values of 8.0×10^{-5}, 7.5×10^{-5}, 1.5×10^{-4}, and 2.5×10^{-4} sec./cm. for PETN, RDX, tetryl and EDNA, respectively; and c values of 1.0, $\sim$0.1, and $\sim$0.04 for the geometrical model, nozzle theory and curved front theory, respectively. ($\bar{R}_g$ is the average grain radius.) Low-order detonation was observed in both tetryl and EDNA in the "non-ideal" detonation region and slightly into the "ideal" region for charge lengths less than 2 to 5 cm. and diameters less than 3 to 5 cm. At the end of this low-order regime detonation changed over abruptly to normal high-order detonation in all except the smallest diameter charges of coarse tetryl where the high and low-order detonation curves could not be resolved.

Aside from their practical value, velocity–diameter or $D(d)$ curves have theoretical value in providing (by curve fitting) the parameter τ (total reaction time), or a_0 (reaction zone length), occurring in the various theoretical models of reaction rates in detonation, namely, the "nozzle" theory,[2] the "curved front"[3] theory and the "geometrical" model.[4] Moreover, comparisons of the theoretical and observed $D(d)$ curves are helpful in evaluating these theories. Previous such applications have been carried out in this Laboratory for TNT,[4a] DNT,[5] AN in the pure state and in TNT and Composition B,[6] sodium nitrate in TNT,[7] and for barium nitrate, lead nitrate, aluminum and other ingredients in TNT and in some cases, Composition B.

This paper presents velocity–diameter curves for low density PETN, RDX, tetryl, and EDNA together with the reaction rates computed by means of the three published models of reaction rates in detonation. Presented also are experimental data concerning a velocity transient observed to occur in the early stages of the detonation process in the small diameter charges of low density, cap initiated tetryl and EDNA. Another factor of importance in evaluating and applying the curved front theory aside from the $D(d)$ curves is the steady-state shape of the detonation wave. Experimental wave shape results with these and other explosives were presented by Cook, *et al.*[8]

Experimental Methods and Results

The explosives used in this study were of the highest (service) available purity and were screened using U. S. standard Tyler screens. The screen cuts used for PETN were −35 +48 mesh and −65 +100 mesh, −65 +100 mesh

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(1) This investigation was supported by Office of Naval Research, Contract No. N7-onr-45107, Project No. 357239.

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