

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 88, NUMBER 19

OCTOBER 5, 1966

Physical and Inorganic Chemistry

Reactions of Diatomic Molecules. I. A Method for Predicting Mechanisms

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Received October 28, 1966*

Abstract: If a system contains only diatomic molecules and their dissociation products, any appreciable net chemical reaction will almost certainly proceed either by a bimolecular mechanism or by an atomic chain. Factors influencing the relative rates by these two mechanisms have been analyzed. Entropy terms can be estimated with modest confidence. If bond energies are known, activation energies for chain-propagating steps can be estimated with uncertainties that probably do not exceed 3 kcal/mole. A method has been developed to estimate the activation energy for the four-center bimolecular mechanism if bond distances, bond energies, and bond force constants are known for the reactant and product molecules. One disposable parameter is used to get agreement with the known value for hydrogen iodide synthesis. For transition states containing four atoms of the same element, the ratio of predicted activation energy to bond dissociation energy is four times as great for hydrogen (known to exchange by the atomic chain mechanism) as for iodine (predicted to exchange by the bimolecular mechanism). The results of these empirical calculations agree with the qualitative prediction that increased polarizability of electron clouds should favor bimolecular mechanisms.

Presumably the ultimate objective of chemical kinetics is to deduce all aspects of molecular behavior from a few basic postulates such as those of quantum mechanics. This objective is clearly unattainable in the foreseeable future.

A more limited objective is to predict mechanisms and rate constants for all conceivable chemical reactions with the use of properties of the reactant and product molecules and a few empirical relationships.

The reactions of diatomic molecules probably represent the first type of system for which this limited objective will be attained. If no stable or metastable species contains more than two atoms, permissible mechanisms will usually be restricted to the direct bimolecular mechanism illustrated by hydrogen iodide synthesis and the atomic chain mechanism illustrated by hydrogen bromide synthesis.

The present paper develops a method for predicting rate constants and mechanisms of such reactions if bond energies, bond distances, and bond force constants are

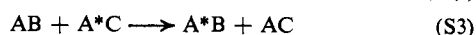
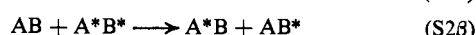
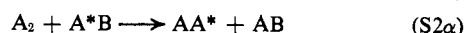
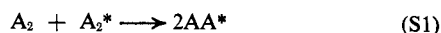
known for all reactant and product species. In the following paper of this series,¹ the method is applied to several reactions, and the results are compared with available experimental evidence.

Classification of Reactions

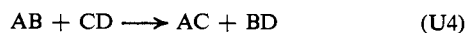
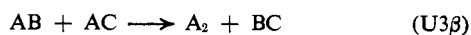
The possible reactions of diatomic molecules can conveniently be classified as symmetrical (S) if they involve no net reaction except exchange of atoms of the same element or unsymmetrical (U) if they lead to net chemical change. They can also be classified with regard to the number of elements whose atoms are involved in the reaction.

Four different types of symmetrical processes are possible. Asterisks are used to designate specific atoms so that changes in bonding can be shown. Because of the symmetry along the reaction coordinate, these reactions are particularly valuable for testing theories of chemical kinetics.

(1) R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4318 (1966).



Five different types of unsymmetrical processes are possible. The letters A, B, C, and D designate atoms



of different elements. The α reactions (which have homonuclear molecules as reactants) are somewhat more apt to be exothermic than are the β reactions (which have them as products).

Most unsymmetrical reactions that have been studied belong to the U2 classes because only one net process is possible in a system containing two elements. Systems containing three elements are complicated by additional possible reactions involving B₂ and C₂. Although the reaction $KF + HCl \rightarrow KCl + HF$ undoubtedly goes to completion cleanly without side reactions, most systems containing four elements will be too complicated for easy study.

Kinetics of Possible Mechanisms

Kinetics of Molecular (m) Mechanism. The simplest possible mechanism is that in which the equation of net reaction describes an elementary process involving two molecules. For a U2 α reaction, the rate of over-all reaction, v_m , is given by

$$v_m = k_m[A_2][B_2] \quad (1)$$

The rate constant can be written²

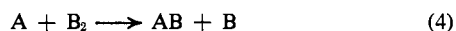
$$k_m = \frac{kT}{h} \exp [2 + (S_m^\ddagger - S_{A_2}^\circ - S_{B_2}^\circ)/R - E_m/RT] \quad (2)$$

In this equation, $S_{A_2}^\circ$ is the standard-state entropy at the temperature of interest, S_m^\ddagger is the standard-state entropy of the transition state neglecting contributions from motion along the reaction coordinate, and E_m is the conventional activation energy if k_m is expressed in concentration units.

Kinetics of Atomic Chain (c) Mechanism. For an exothermic U2 α reaction in which $D_0^\circ(A_2) < D_0^\circ(B_2)$, the rate of initial³ reaction is

$$v_c = K_{A_2}^{1/2} k_c [A_2]^{1/2} [B_2] \quad (3)$$

where K_{A_2} is the equilibrium constant for the dissociation of A₂ and k_c is the rate constant for the step



More general kinetics for chain mechanisms are discussed in Appendix I.

(2) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, p 199.

(3) This equation neglects potential reversibility of the first step of the chain. In a mixture of hydrogen and bromine, the rate of HBr synthesis will be reduced from that predicted by this simple equation long before thermodynamic equilibrium is approached. However, the equation is valid until the concentration of product HBr begins to be significant compared to that of reactant Br₂.

By reasoning similar to that behind eq 2

$$K_{A_2}^{1/2} k_c = \frac{kT}{h} \exp [2 + (S_c^\ddagger - 1/2 S_{A_2}^\circ - S_{B_2}^\circ)/R - (1/2 \Delta E_{A_2}^\circ + E_c)/RT] \quad (5)$$

In this equation, S_c^\ddagger is the standard-state entropy of the transition state for reaction 4, E_c is the activation energy for that reaction, and $\Delta E_{A_2}^\circ$ is the energy change of the equilibrium dissociation of A₂ at the temperature of interest.

Relative Importance of Mechanisms. Equations 1 and 3 are valid regardless of which mechanism makes the major contribution to the observed rate. Other mechanisms are possible in principle and are discussed in Appendix II, but they will seldom be significant compared to the two types considered above.

The ratio of rates by the two independent mechanisms is

$$Q = v_c/v_m \quad (6)$$

Then for a U2 α reaction

$$Q[A_2]^{1/2} = \exp [(1/2 S_{A_2}^\circ + S_c^\ddagger - S_m^\ddagger)/R - (1/2 \Delta E_{A_2}^\circ + E_c - E_m)/RT] \quad (7)$$

Similar expressions can be written for the chain kinetics of other reaction classifications. Certain qualitative mechanistic conclusions are obvious from this equation.

(1) *Changing concentrations of reactants have rather little influence upon which mechanism is observed.*

(2) *Entropy effects favor the atomic chain mechanism.* Since translation makes the major contribution to entropy, the quantities S_c^\ddagger and S_m^\ddagger will approximately cancel each other and leave $1/2 S_{A_2}^\circ$ uncompensated.

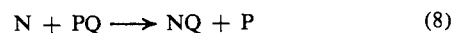
(3) *At sufficiently high temperatures, the atomic chain mechanism will prevail.* This conclusion follows from (2) because energy differences become less important at high temperatures. If E_m is greater than $1/2 \Delta E_{A_2}^\circ + E_c$, the relative importance of the bimolecular mechanism will increase with temperature, but the absolute contribution of this mechanism will then be negligible at all temperatures.

(4) *The atomic chain mechanism is favored by a weak bond in A₂ and by AB bond energy little if any less than that of B₂.* The detailed reasoning will be made apparent by the discussion of procedures for estimating E_c .

More quantitative mechanistic conclusions require estimates of the various quantities in eq 7. Entropies and dissociation energies are well known for most stable molecules of interest. Entropies of transition states can be calculated by established equations⁴ if the geometries and vibration frequencies can be estimated reasonably well. Procedures for estimating the energies of activation, E_c and E_m , are developed in the following sections.

Estimation of E_c

An atom-molecule reaction can be represented by



(4) Reference 2, pp 193-194.

The energy profile for this reaction is illustrated⁵ in Figure 1.

For generalization of this figure, it is convenient to define the function $H'(x)$ where

$$H'(x) = 0 \quad x \leq 0 \\ = x \quad x \geq 0 \quad (9)$$

It can also be defined by

$$H'(x) = xH(x) \quad (10)$$

where $H(x)$ is the Heaviside or step function that has the value zero for negative x and unity for positive x .

It is apparent from Figure 1 that

$$E_c = \Delta_c + H'[D_0^\circ(\text{PQ}) - D_0^\circ(\text{NQ})] \quad (11)$$

Since bond dissociation energies of these simple molecules are well established, values of E_c for different reactions can be calculated almost as reliably as Δ_c values can be estimated.

Table I presents values of Δ_c measured for a number of reactions of atoms with diatomic molecules. Only a

Table I. Some Experimental Values of Δ_c

Reaction	Δ_c , kcal/mole	Reference
$\text{I} + \text{H}_2 \rightarrow \text{HI} + \text{H}$	1.3	<i>a</i>
$\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$	2.9	<i>b, c</i>
$\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$	2.9 ^l	<i>d</i>
$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	4.5	<i>c</i>
$\text{H} + \text{p-H}_2 \rightarrow \text{o-H}_2 + \text{H}$	5.5	<i>e</i>
$\text{Na} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl}$	0 ^m	<i>f</i>
$\text{Cl} + \text{Na}_2 \rightarrow \text{NaCl} + \text{Na}$	0 ^m	<i>f</i>
$\text{Na} + \text{I}_2 \rightarrow \text{NaI} + \text{I}$	0 ^m	<i>g</i>
$\text{I}^* + \text{I}_2 \rightarrow \text{II}^* + \text{I}$	4.7 ^m	<i>h</i>
$\text{Br}^* + \text{Br}_2 \rightarrow \text{BrBr}^* + \text{Br}$	1.9 ^m	<i>i</i>
$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$\leq 3.6^m$	<i>j</i>
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	6.2	<i>j</i>
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	1.2	<i>k</i>
$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	7.0	<i>k</i>

^a J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292 (1959). ^b M. Bodenstein and H. Lütkemeyer, *Z. Physik. Chem.*, **114**, 208 (1925). ^c G. C. Fettes and J. H. Knox, *Progr. Reaction Kinetics*, **2**, 1 (1964). ^d L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, New York, N. Y., 1932, p 135. ^e A. Farkas and L. Farkas, *Proc. Roy. Soc. (London)*, **A152**, 124 (1935). ^f M. Polanyi and G. Schay, *Z. Physik. Chem.*, **B1**, 30 (1928). ^g H. Ootuka and G. Schay, *ibid.*, **B1**, 62 (1928). ^h R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950). ⁱ H. Steinmetz and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 4141 (1952). ^j G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **27**, 1141 (1957). ^k D. L. Ripley and W. C. Gardiner, Jr., *ibid.*, **44**, 2285 (1966). ^l Based on the observation that over a 300° temperature range there is no change in ratio of rate constants for $\text{H} + \text{Br}_2$ and $\text{H} + \text{HBr}$ reactions. ^m Based on rate constants measured at a particular temperature rather than on temperature dependence of a rate constant. The $\text{Br}^* + \text{Br}_2$ value also assumes the equilibrium constant for bromine dissociation is the same in carbon tetrachloride as in gas phase.

few of the entries are based on accurate measurements over a range of temperatures, and many values may be in error by 2 kcal/mole or even more. Since the total range of Δ_c values is only 7 kcal/mole, the most important conclusion from Table I is that this quantity is always rather small.

(5) The diagram and the equations for activation energy neglect the temperature-dependent vibrational excitation of ground and transition states. This conceptual and computational simplification is valid if $D_0^\circ(\text{A}_2)$ is substituted for $\Delta E^\circ_{\text{A}_2}$ in eq 7 and if vibrational entropy terms of the type $(\bar{E} - \bar{E}_0)/T$ are systematically neglected.

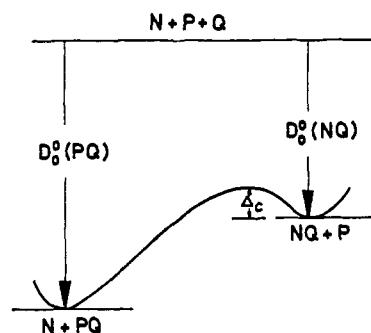


Figure 1. Energy profile for chain-propagating step (eq 8).

A few additional generalizations are possible. Δ_c tends to be greatest for isotopic substitution reactions where there is no net change of energy and to be least when the energy change in the reaction is considerable; this conclusion is in agreement with the postulate of Hammond.⁶ There also seems to be some tendency for Δ_c to be larger for reactions involving the lighter and less polarizable elements.

These generalizations form the basis for the procedures for estimating Δ_c presented in Table II and used in subsequent calculations. The justification for Table

Table II. Principles for Estimating Δ_c

Reaction type	Δ_c , kcal/mole
$\text{H} + \text{H}_2$	6
End atoms identical and no heavier than fluorine	4
End atoms identical and heavier than fluorine	3
End atoms different but not representing both halogen and alkali metals	2
One end atom halogen and other alkali metal	0

II is purely empirical, and it is much less sophisticated than various more theoretical attempts to estimate these quantities;⁷⁻⁹ however, the presently available data hardly justify any more complicated treatment. It is hoped that activation energies computed in this way will usually be reliable to within about 2 kcal/mole. Fortunately, uncertainties of this magnitude are seldom important for predicting which mechanism is dominant, and activation energies estimated for bimolecular mechanisms are much less certain.

Estimation of E_m

General Considerations. The quantity E_m can be estimated with much less confidence than any other in eq 7. This fact has been recognized for some time. Altar and Eyring¹⁰ apparently developed the first general procedure for estimating such a quantity, and Benson and Haugen¹¹ have proposed the most recent one. The empirical procedure presented here differs substantially from these previous methods.

(6) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(7) A. Wheeler, B. Topley, and H. Eyring, *J. Chem. Phys.*, **4**, 178 (1936).

(8) W. Kleinpaal, *Z. Physik. Chem. (Frankfurt)*, **26**, 313 (1960); **27**, 343 (1961); **29**, 201 (1961); **30**, 262, 279 (1961).

(9) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).

(10) W. Altar and H. Eyring, *J. Chem. Phys.*, **4**, 661 (1936).

(11) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

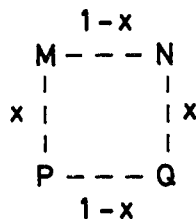
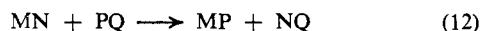


Figure 2. Distribution of atoms and bond fractions during reaction by bimolecular mechanism.

The reaction of interest is the elementary process



The atom designated by any letter may or may not be of the same element as that by any other letter.

The extent of reaction can be described in terms of a reaction parameter, x , whose value moves from zero to unity for stages representing isolated pairs of molecules. During the process, each atom loosens its bonding to one neighbor at the same time that it strengthens that to another. Especially for species like hydrogen and halogens whose valence shells are filled with electron pairs in both reactants and products, it may not be a bad assumption to say that the sum of the fractional bonds to each atom is unity at all times. Then x will also be a measure of the extent to which the product bonds have been formed, and the distribution of bond fractions shown in Figure 2 will hold for all stages of the reaction. This argument is very similar to the constancy of bond order invoked by Johnston and Parr⁹ to treat hydrogen transfer (three-center) reactions. Benson and Haugen¹¹ assume bond polarization during reaction and make no pretense of conserving bond order.

The forces that oppose the relative motions of nuclei during reaction will be much the same as those that oppose relative motions during vibration of an isolated molecule. Therefore bond energies and force constants, even though they are measured for somewhat different electronic distributions from those in the transition state, will be taken as the best types of molecular properties to use for estimating activation energies.

Bond Parameters for Diatomic Molecules. The potential energy, V , of a molecule as a function of internuclear distance, r , is assumed to obey the formula

$$V = Ae^{-r/B} - C/r^3 \quad (13)$$

where A , B , and C are empirical parameters to be evaluated from experimental measurement. This form of function was chosen so that attractive and repulsive terms would be cleanly separable. The exponent 3 in the attractive term is the minimum that can describe interactions of species having no net charge. Although larger exponents certainly describe better the interaction of nonreacting atoms separated by greater distances, results presented below indicate that use of a larger exponent here would increase the magnitude of the empirical correction that must ultimately be applied. Calculations with this formula were well advanced before it was realized that Linnett¹² had proposed an identical function.

Let X be the repulsive term and Y the attractive term at the equilibrium internuclear separation r_e . Also,

(12) J. W. Linnett, *Trans. Faraday Soc.*, **36**, 1123 (1940).

let D_e and k_e be the dissociation energy and bond force constant corresponding to this separation and disregarding zero-point vibrational energy. Then eq 13 and its first and second derivatives can be combined to give

$$-D_e = Ae^{-r_e/B} - C/r_e^3 = X - Y \quad (14)$$

$$0 = -X/B + 3Y/r_e \quad (15)$$

$$k_e = X/B^2 - 12Y/r_e^2 \quad (16)$$

Since r_e , D_e , and k_e are known for most diatomic molecules of interest, these equations permit evaluation of the parameters X , Y , and B .

Applications to 34 stable or metastable molecules are illustrated in Table III. Values of r_e , D_e , and k_e were taken from standard sources.¹³⁻¹⁵ Use of a uniform computational procedure throughout resulted in some entries containing figures that are not significant.

The calculations show big differences in molecular properties. Thus the ratio of repulsion to attraction, X/Y , varies from 0.673 for H_2 to 0.170 for I_2 . In general, compounds containing only halogen atoms have low values of X/Y , compounds containing either hydrogen or alkali atoms have high values, and the compounds of carbon, nitrogen, and oxygen are intermediate. B values fall into two very sharply separated groups depending upon whether or not alkali atoms are present and show definite trends within these groups.

Extension to Fractional Bonds. If two atoms are not bonded fully to each other because of interaction with another pair of atoms, it is proposed as a working hypothesis that the repulsive forces remain the same function of distance but that the attractive forces be proportional to the bond fraction, b . Then

$$V_b = Ae^{-r/B} - bC/r^3 \quad (17)$$

If r_b is the interatomic distance at which V_b is a minimum, and if D_b is the dissociation energy from this minimum, then

$$-D_b^u = Xe^{-(r_b - r_e)/B} - bYr_e^3/r_b^3 \quad (18)$$

$$0 = -\frac{X}{B}e^{-(r_b - r_e)/B} + 3bYr_e^3/r_b^4 \quad (19)$$

The superscript u on D_b^u indicates that the quantity defined by these equations is uncorrected.

Equations 18 and 19 permit calculation of r_b and D_b^u for any value of b for any molecule on which data are available. When such calculations are performed for the molecules of Table III, H_2 and I_2 exhibit the extremes of behavior. Values of D_b^u/D_e for these molecules are plotted as functions of b in Figure 3.

For molecules like iodine, energy gained in bond formation will be almost as great as that lost in bond breaking during all stages of the formation of a four-center transition state. For such big and easily polarizable molecules, activation energy will be a small fraction of bond dissociation energy.

(13) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(14) T. L. Cottrell, "The Strengths of Chemical Bonds", 2nd ed, Academy Press Inc., New York, N. Y., 1958.

(15) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., New York, N. Y., 1950.

Table III. Bond Parameters for Diatomic Molecules

Molecule	r_e , Å	D_e , kcal/mole	k_e , kcal/ Å ² mole	X , kcal/mole	Y , kcal/mole	B , Å	$D_{0.5}/D_e$
H ₂	0.742	109.53	825.3	226.6	336.1	0.1668	0.306
F ₂	1.435	37.28	640.6	11.08	48.36	0.1096	0.435
Cl ₂	1.988	57.88	473.0	19.16	77.04	0.1648	0.429
Br ₂	2.284	45.92	353.8	11.75	57.67	0.1551	0.443
I ₂	2.666	35.86	247.7	7.33	43.19	0.1508	0.453
HF	0.917	139.92	1389.8	193.62	333.54	0.1774	0.325
HCl	1.274	106.48	742.4	112.81	219.29	0.2184	0.343
HBr	1.414	90.29	592.5	82.43	172.72	0.2249	0.354
HI	1.604	73.80	452.1	55.31	129.11	0.2290	0.370
ClF	1.628	61.63	656.4	23.72	85.35	0.1508	0.420
BrF	1.756	55.96	585.9	18.47	74.43	0.1453	0.429
IF	1.985	46.29	524.0	10.60	56.89	0.1233	0.448
BrCl	2.138	52.71	384.3	16.77	69.48	0.1720	0.431
ICl	2.321	50.18	343.0	14.26	64.44	0.1712	0.437
IBr	2.470	42.28	297.1	10.12	52.40	0.1590	0.446
Li ₂	2.672	25.50	36.7	29.58	55.08	0.4783	0.336
Na ₂	3.078	17.53	24.8	15.65	33.18	0.4839	0.356
K ₂	3.923	11.93	14.1	7.61	19.54	0.5093	0.383
NaK	3.500	14.50	18.7	10.84	25.34	0.4991	0.370
LiH	1.595	60.01	147.7	101.36	161.37	0.3340	0.314
NaH	1.887	48.68	112.4	68.19	116.87	0.3670	0.324
KH	2.244	44.41	80.8	57.00	101.41	0.4204	0.330
LiI	2.392	81.64	112.3	118.22	199.86	0.4716	0.322
NaCl	2.361	98.54	171.3	120.53	219.07	0.4330	0.334
NaBr	2.502	88.45	149.7	99.78	188.23	0.4421	0.338
NaI	2.712	71.41	135.3	61.18	132.59	0.4171	0.360
KF	2.55	118.56	178.5	143.71	262.27	0.4658	0.333
KCl	2.667	101.40	123.8	136.03	237.43	0.5093	0.327
KBr	2.821	91.33	119.5	104.69	196.02	0.5022	0.338
N ₂	1.094	228.37	3305.1	154.0	382.4	0.1469	0.379
O ₂	1.207	120.22	1693.6	66.8	187.0	0.1437	0.393
NO	1.151	152.72	2294.6	87.93	240.65	0.1402	0.391
CO	1.128	258.90	2737.9	230.1	489.0	0.1770	0.357
OH	0.971	106.84	1121.5	128.2	235.1	0.1766	0.334

For molecules like hydrogen, bonds being formed contribute little stabilization until considerable breaking of the original bonds has taken place. For these small and difficultly polarizable molecules, the activation energy will be much greater.

For a symmetrical reaction of type S1, the energy of two isolated molecules relative to atomization is $-2D_e$. The apparent activation energy of the atomic chain mechanism will be somewhat in excess of $0.5D_e$. The activation energy of the bimolecular mechanism will be less than this if the energy of atomization of the transition state is more than $1.5D_e$, which requires that $D_{0.5}$ be greater than $0.375D_e$. Observed values of $D_{0.5}^u$ range from $0.233D_e$ for H₂ to $0.436D_e$ for I₂. Apparently either mechanism may be favored depending upon the properties of the specific molecules.

Application to Activation Energies. If Figure 2 can be used to describe all stages of reaction 12, the energy relative to atomization for any value of x is

$$-D_x^c(\text{MP}) - D_x^c(\text{NQ}) - D_{1-x}^c(\text{MN}) - D_{1-x}^c(\text{PQ}) \quad (20)$$

In this equation, D_x^c is the corrected dissociation energy for a particular fractional bond; it will presumably be similar to D_x^u but will not be identical unless the potential energy function was very well chosen.

The quantity in eq 20 can be calculated as a function of x and its maximum value determined. The difference between this maximum and the initial value of $-D_e(\text{MN}) - D_e(\text{PQ})$ is then the activation energy for reac-

tion. When D_x^u values are used to apply this procedure to the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, the maximum energy occurs at $x = 0.451$ and corresponds to an activation

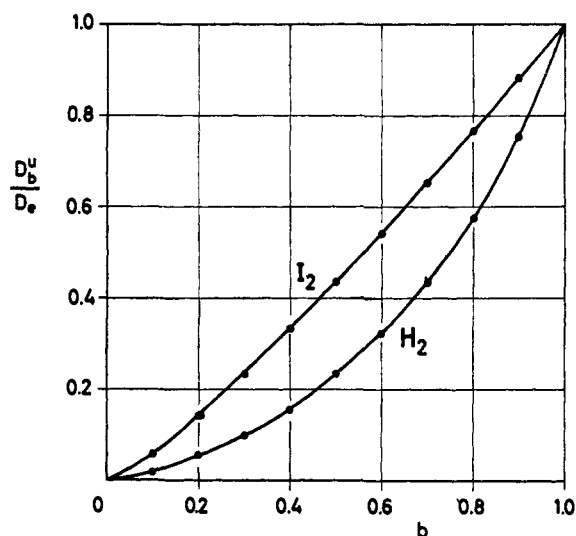


Figure 3. D_b^u/D_e as a function of b for H₂ and I₂.

energy of 57.27 kcal/mole. The observed value¹⁶ is 41.42 kcal/mole.

Values of D_b^u can be corrected by shifting each one closer to bD_e by an amount proportional to the dif-

(16) See Table I, footnote *a*.

Table IV. Values of D_b^c (in kcal/mole) for Selected Diatomic Molecules

Molecule	$b =$									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
H ₂	4.45	10.42	16.84	24.55	33.47	43.73	55.70	69.85	86.78	109.53
F ₂	2.51	5.53	8.89	12.46	16.22	20.14	24.23	28.46	32.81	37.28
Cl ₂	3.80	8.37	13.50	19.00	24.82	30.94	37.32	43.94	50.79	57.88
Br ₂	3.25	7.03	11.26	15.70	20.35	25.15	30.14	35.28	40.54	45.92
I ₂	2.50	5.79	9.12	12.61	16.26	19.99	23.83	27.76	31.77	35.86
HF	6.05	13.78	22.88	33.40	45.46	59.26	75.07	93.27	114.57	139.92
HCl	4.86	11.12	18.48	26.94	36.54	47.38	59.57	73.31	88.83	106.48
HBr	4.29	9.78	16.26	23.66	32.00	41.34	51.72	63.27	76.03	90.29
HI	3.71	8.44	14.02	20.31	27.32	35.05	43.53	52.76	62.86	73.80
ClF	3.83	8.59	13.91	19.69	25.86	32.40	38.81	46.40	53.88	61.63
BrF	3.65	8.11	13.07	18.38	24.01	29.92	36.08	42.48	49.12	55.96
IF	3.36	7.30	11.57	16.07	20.75	25.59	30.58	35.71	40.94	46.29
BrCl	3.48	7.72	12.40	17.42	22.73	28.29	34.09	40.10	46.31	52.71
ICl	3.45	7.54	12.07	16.89	21.95	27.23	32.72	38.41	44.20	50.18
IBr	3.04	6.61	10.49	14.58	18.87	23.30	27.86	32.55	37.36	42.28
Na ₂	0.84	1.92	3.18	4.62	6.42	8.06	10.08	12.31	14.78	17.53
NaH	2.10	4.78	7.93	11.59	15.78	20.57	26.06	32.38	39.83	48.68
NaCl	4.36	9.94	16.52	24.12	32.90	42.67	53.91	66.64	81.35	98.54
N ₂	11.82	27.01	44.65	64.47	86.44	110.50	136.65	164.99	195.53	228.37
O ₂	6.63	15.07	24.77	35.47	47.30	60.05	73.70	88.29	103.77	120.22
NO	8.31	18.94	31.17	44.77	59.69	75.85	93.24	111.85	131.66	152.72
OH	4.75	10.81	17.99	26.27	35.70	46.42	58.52	72.36	88.28	106.48

ference between these numbers. Thus

$$D_b^c = D_b^u + (bD_e - D_b^u)ff \quad (21)$$

where ff is an empirical factor. When $ff = 0.2720$, application of D_b^c values to hydrogen iodide synthesis reproduces the experimental activation energy with an x value of 0.449.

Values of D_b^c for a number of molecules were computed at intervals of 0.100 in b with the use of this value for ff , and the results are reported in Table IV. If numbers are available for all reactant and product molecules of interest, an interpolation procedure can be used with the data in this table to estimate the activation energy for any specified reaction.

The above treatment has used the exponent 3 for r in the attractive term of equations like 13 and 17. In order to test the significance of this choice, calculations for H₂ and I₂ were repeated with the use of the exponent 4. Values of $D_{0.5}^u$ were 0.186 for H₂ and 0.383 for I₂. The big difference in values of this quantity for these two molecules obviously is not an artifact of the exponent chosen but reflects a real difference in dependence of bond energy on changing bond length. If calculations with an exponent of 4 were used, a larger value of ff would be needed to bring uncorrected activation energies into agreement with experiment, and this fact dictated the choice made here. It is interesting to note that the value of $0.500 - D_{0.5}^u/D_e$ is 4.2 times as great for H₂ as for I₂ if the exponent of 3 is used and is only 2.7 times as great if the exponent of 4 is used. The use of the larger exponent would make activation energies more directly dependent upon bond energies and less influenced by additional chemical differences. It will be necessary to have kinetic data on a larger number of reactions proceeding by the bimolecular mechanism before it will be possible to decide the type of equation that best reproduces the data.

Discussion

It has sometimes been suggested that activation energies of reactions are proportional to the energies

of the bonds involved. Although it is certainly true that molecules with strong bonds tend to require higher activation energies for reaction, the results of these calculations suggest that the ratio of these quantities may vary by a factor of the order of four.

The variation is in the direction anticipated before this work was undertaken. Large polarizable molecules like the heavier halogens will tend to react with lower activation energies relative to bond strengths than will small and difficultly polarizable molecules.

It was anticipated initially that polarizability would have to be introduced explicitly if a satisfactory theory for these reactions were to be developed. Bond force constants are related to the ability of the electron cloud to reduce instabilities produced by changes in internuclear distances; hence they involve similar phenomena. Use of force constants has led to a more direct and empirical introduction of factors that certainly influence the reactivity of molecules.

The method of computation presented here is too simple to have universal applicability, but it does offer the possibility for unified interpretation of a large number of reactions. Its significance is to be judged upon conformity with a body of experimental evidence that does not yet exist.

Acknowledgment. This problem was formulated and the initial analysis carried out at the University of Oregon and was supported in part by the U. S. Army Research Office. The methods of evaluating Δ_c and E_m were developed at the Victoria University of Wellington under a Fulbright grant. The preparation of the manuscript was carried out at the Max-Planck-Institut under a National Science Foundation Senior Postdoctoral Fellowship. The author is indebted to Professor A. G. Mackie of the Department of Applied Mathematics of the Victoria University of Wellington for pointing out the relationship of $H'(x)$ to the Heaviside function.

Appendix I. Kinetics of Atomic Chain Mechanisms

General Considerations. The equations presented below can be used to calculate rates by the atomic

chain mechanism for different reaction classifications. Equilibrium constants, K , refer to dissociation of the molecule designated by subscript. Rate constants, k , are designated by superscript as symmetrical, S, or unsymmetrical, U, and for reactant species by subscript. Rates of symmetrical reactions are total rates at which exchange takes place in a system containing identical atoms of the indicated element.

S1. The rate is given by

$$v_c = \frac{1}{2}K_{A_2}^{1/2}k_{A+A_2}^S[A_2]^{1/2} \quad (\text{I-1})$$

where the factor $1/2$ enters because two propagating steps are needed to bring about the net effect of eq S1.

S2 α . The bond energies must obey the inequality $D_0^\circ(A_2) + D_0^\circ(B_2) < 2D_0^\circ(AB)$; otherwise the system will be unstable and will not be appropriate for study. The rate is given by

$$v_c = K_{A_2}^{1/2}[A_2]^{1/2} \left\{ \frac{k_{A+A_2}^S[A_2]k_{A+AB}^S[AB]}{k_{A+A_2}^S[A_2] + k_{A+AB}^S[AB]} + k_{A+AB}^U[AB] \right\} \quad (\text{I-2})$$

If $D_0^\circ(A_2) < D_0^\circ(AB)$, the unsymmetric term makes negligible contribution; otherwise both terms between braces make comparable contributions.

S2 β . If the system is to be stable, bond energies must satisfy the same restriction as for S2 α reactions. No generality is lost by the additional restriction $D_0^\circ(A_2) < D_0^\circ(B_2)$.

The initial rate of exchange is given by

$$v_c = K_{AB}^{1/2}[AB]^{1/2} \left\{ \frac{1}{2}k_{A+AB}^S + \frac{1}{2}k_{B+AB}^S + k_{B+AB}^U \right\} \quad (\text{I-3})$$

Of course the unsymmetrical term is unimportant if $D_0^\circ(B_2) < D_0^\circ(AB)$.

Equation I-3 presupposes A and B atoms in equal concentrations. As time goes on, this restriction will become invalid and the rate will be given by

$$v_c = \frac{1}{2}k_{A+AB}^S[A][AB] \quad (\text{I-4})$$

where the value of $[A]$ is computed for an equilibrium mixture of AB with equimolar amounts of A_2 and B_2 .

S3. Systems with three elements are sufficiently complex that no attempt has been made to develop general kinetics or to consider specific examples.

U2 α . Systems will be of interest only if $D_0^\circ(A_2) + D_0^\circ(B_2) < 2D_0^\circ(AB)$. No generality is lost if $D_0^\circ(A_2) < D_0^\circ(B_2)$. Most atoms in the system are A atoms, and the rate is given by

$$v_c = K_{A_2}^{1/2}[A_2]^{1/2} \times \left\{ \frac{k_{A+B_2}^U[B_2]k_{B+A_2}^U[A_2] - k_{A+AB}^U k_{B+AB}^U[AB]^2}{k_{B+A_2}^U[A_2] + k_{B+AB}^U[AB]} \right\} \quad (\text{I-5})$$

If reaction is almost complete at equilibrium, the negative term will be unimportant during most of the reaction. If $D_0^\circ(B_2) < D_0^\circ(AB)$ or if negligible amounts of AB have been formed, eq I-5 reduces to eq 3.

U2 β . Systems will be of interest only if $2D_0^\circ(AB) < D_0^\circ(A_2) + D_0^\circ(B_2)$. If $D_0^\circ(A_2) < D_0^\circ(B_2)$, the initial rate is given by

$$v_c = K_{AB}^{1/2}k_{A+AB}^U[AB]^{1/2} \quad (\text{I-6})$$

The kinetics will subsequently become more complex,

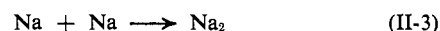
but if $D_0^\circ(A_2) < D_0^\circ(AB)$ the rate will become the negative of eq I-5 as equilibrium is approached. The kinetics will be more complex if this condition is not satisfied.

U3 and U4. If only one equation is needed to describe the net reaction in a system with more than two elements, the kinetics of the chain mechanism are easy to determine. Because side reactions are important in most such systems, a general kinetic treatment is complicated and unjustified.

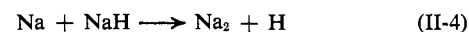
Appendix II. Alternative Mechanistic Possibilities

In certain rather unusual circumstances, diatomic molecules may react by mechanisms other than the two considered in this paper. Conceivable mechanisms and conditions under which they might be observed are considered below.

Atomic Nonchain Mechanism. Sodium hydride might conceivably decompose by the mechanism

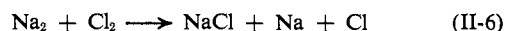
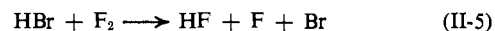


Dissociation into atoms does not initiate a chain because the activation energy of the step



is too great for significant reaction as long as the concentration of Na atoms is determined by dissociation of NaH. For this mechanism, the initial rate of over-all reaction would be just the rate of step II-1; however, as the concentration of product sodium built up, the chain of II-4 and II-2 would take over. Even initially, the nonchain process could be significant only because $D_0^\circ(\text{Na}_2) < \frac{1}{2}D_0^\circ(\text{NaH})$.

Bimolecular Chain Initiation. One product molecule may have a dissociation energy greater than the sum for the two reactants. Then reactions like



become possible. Presumably the activation energies are comparable to or higher than those for reactions producing pairs of diatomic molecules from the same reactants, but these processes might be effective for initiating chains.

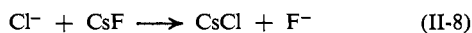
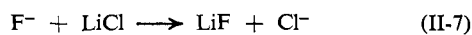
Activation Mechanism. Lifshitz, *et al.*,¹⁷ have recently reported that the exchange of deuterium with ammonia is first order in deuterium and zero order in ammonia. They interpret their observations to indicate that the rate-determining step is activation of deuterium to an excited vibrational level.

If this peculiar mechanism is substantiated, it suggests that vibrational activation of one of the molecules could be the rate-determining step for a process of the type considered here. The kinetics would be similar to those for the atomic nonchain mechanism, but the activation energy would be less than the dissociation energy of the molecule that was activated.

Although the possibility of this mechanism cannot be ruled out in principle, examples are apt to be quite rare and confined to very specific reactions.

(17) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 143 (1965).

Ionic Chain Mechanism. The compounds CsF and perhaps RbF will separate preferentially into ions rather than atoms. Moreover, if exothermic ion-molecule reactions have small activation energies, the chain

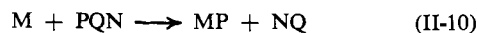


will have an apparent activation energy about 10 kcal/mole less than that for the equivalent chain involving atoms instead of ions. Hence the over-all process $\text{LiCl} + \text{CsF} \rightarrow \text{LiF} + \text{CsCl}$ might well proceed by an ionic rather than by an atomic chain mechanism.

Since preferential dissociation into ions rather than atoms appears to be a property unique to one or two compounds, and since ionic chains are not apt to be

sufficiently faster to be preferred in the reactions of other compounds, this mechanism does not warrant general consideration.

Triatomic Molecule Mechanisms. The discussion has specifically excluded consideration of mechanisms involving triatomic molecules. Such a mechanism might be



These mechanisms are probably unimportant in systems containing only hydrogen, halogens, and alkali metal atoms. However, they may be preferred paths for some reactions in systems containing carbon, nitrogen, and oxygen.

Reactions of Diatomic Molecules. II. Predictions and Comparisons with Experiment

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Received October 28, 1965

Abstract: Procedures developed in the previous paper have been used to estimate rates and mechanisms for 110 possible reactions of diatomic molecules, 47 of which involve net chemical change. For only 20 of these reactions do there appear to be experimental observations of mechanistic significance, but in all except perhaps one or two of these 20 examples kinetic and mechanistic predictions are in agreement with experiment or discrepancies can be rationalized. More experimental work is desirable, particularly for reactions by bimolecular mechanisms. The following mechanistic predictions are made. Isotopic scrambling for the elements H, Li, Na, K, and probably N and O, will proceed by atomic chain mechanisms under experimentally attainable conditions. Isotopic scrambling of the elements F, Cl, Br, and I will proceed by bimolecular mechanisms. Iodine is the only halogen that will react with hydrogen preferentially by a bimolecular mechanism, but it may be possible to detect a contribution from this mechanism in the bromine reaction. All halogen-halogen reactions will proceed by bimolecular mechanisms. The two mechanistic types are of comparable probabilities for reactions of halogens with hydrogen halides. Symmetrical (exchange) reactions of hydrogen halides with hydrogen and with other hydrogen halides will proceed by atomic chain mechanisms. Chlorine molecules will react with sodium molecules with an activation energy almost as low as that for the reaction with sodium atoms. Nitric oxide will decompose by a bimolecular mechanism, forming $\text{N}_2 + \text{O}_2$ (or perhaps $\text{N}_2\text{O} + \text{O}$), although an atomic chain mechanism will become dominant at very high temperatures. Mechanisms involving metastable triatomic molecules complicate predictions for other reactions involving carbon, nitrogen, and oxygen.

The previous paper¹ discussed the mechanisms by which diatomic molecules might react and presented general procedures for predicting activation energies. In order to test the reasonableness of these procedures, they have been applied to 110 possible reactions and the results of the calculations have been compared with available experimental data and with calculations on some of the same reactions by Benson and Haugen.²

Reactions are grouped by chemical similarity in the following tables and are designated by reactant molecules and classification from the previous paper.¹ For each reaction, generalized as $\text{MN} + \text{PQ} \rightarrow \text{MP} + \text{NQ}$, the energy as a function of extent of reaction, x , was computed in 0.100 intervals from

$$E_x = -D_x^{\circ}(\text{MP}) - D_x^{\circ}(\text{NQ}) - D_{1-x}^{\circ}(\text{MN}) - D_{1-x}^{\circ}(\text{PQ}) \quad (1)$$

with the use of Table IV of the previous paper.¹ The three values nearest the maximum were fitted to a quadratic function to calculate x^{\ddagger} (the value at that maximum) and the activation energy, E_m .

The tables also contain values of $1/2 D_0^{\circ} + E_c$, the effective activation energy for the atomic chain mechanism according to the kinetics of Appendix I of the previous paper.¹

If a reaction appeared to be of potential experimental interest, entropies of transition states were estimated by use of the assumptions in Appendix I. These were used to calculate T_r , the temperature at which the initial rate by the fastest mechanism is 10^{-6} mole/l. sec when the concentrations of both reactants³ are 0.0100

(1) R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4311 (1966).

(2) S. W. Benson and G. R. Haugen, *ibid.*, **87**, 4036 (1965).