Trans., 71, 2431 (1975).
(9) N. L. Arthur, K. F. Donchi, and J. A. McDonell, *J. Chem. Soc., Faraday Trans.*, 71, 2442 (1975).
(10) D. G. Truhlar, *J. Am. Chem. Soc.*, **94,** 7584 (1972).
(11) R. M. Jordan and F. Kuafman, *J. Chem. Phys.*, **63,** 1691 (1975).
(12) For a preliminary report see R. D. Gilliom, *J. Chem. Phys.*, **65,** 5028 (1976).
(13) H. S. Johnston, *Adv. Chem. Phys.*, **3,** 131 (1960).
(14) L. Pauling, *J. Am. Chem. Soc.*, **69,** 542 (1947).
(15) D. R. Lide, Jr., *Tetrahedron*, 17, 125 (1962).
(16) C. H. Chen, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.*, **59,** 601 (1973).
(17) A. L. J. Burgmans, J. M. Farrar, and Y. T. Lee, *J. Chem. Phys.*, **64,** 1345 (1976).
(18) A. A. Zavitsas, *J. Am. Chem. Soc.*, **94,** 2779 (1972).
(19) A. A. Zavitsas and A. A. Melikian, *J. Am. Chem. Soc.*, **97,** 2757 (1975).
(20) S. Sato, *J. Chem. Phys.*, **23,** 592 (1955).
(21) W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32,** 219 (1960).
(22) H. Endo and G. P. Glass, *J. Phys. Chem.*, **80,** 1519 (1976).
(23) C. P. Baskin, C. F. Bender, C. W. Bauschlider, and H. F. Schaefer, *J. Am. Chem. Soc.*, **96,** 2709 (1974).
(24) S. V. O'Neil, H. F. Schaefer, and C. F. Bender, *Proc. Natl. Acad. Sci. U.S.A.*, 71, 104 (1974).
(25) B. Liu, *J. Chem. Phys.*, **58,** 1925 (1973).
(26) C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, *Science*, 176, 1412 (1972).
(27) D. G. Truhlar and A. Kuppermann, *J. Am. Chem. Soc.*, **93,** 1840 (1971).

An Empirical Correlation of Activation Energy with Molecular Polarizability for Atom Abstraction Reactions

R. H. Krech and D. L. McFadden*

Contribution from the Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167. *Received July 26, 1976*

Abstract: Activation energies for a homologous series of exoergic atom transfer reactions of the type $A\cdot + BC \rightarrow AB + C\cdot$ are shown to correlate inversely with molecular polarizability of the reactant BC. A linear relationship between activation energy and reciprocal polarizability provides relatively good agreement with experiment for 13 reaction series comprised of 65 reactions. Activation energies are predicted for the reactions of $CH_3\cdot$, $C_2H_5\cdot$, and $CF_3\cdot$ with F_2 using this correlation.

Activation energy is an important property of chemical reactions. For simple exoergic atom transfer reactions differences in activation energy are primarily responsible for the wide variation observed in reaction rates. Although accurate theoretical calculations of activation barriers are not possible in most cases, several empirical and semiempirical formulas for estimating activation energies have been developed. In one approach, activation energies for a series of similar reactions are correlated with molecular properties of the separated reactants and products. If one or two activation energies in the series of reactions are known, the others can be predicted using the correlation. In this paper we discuss three correlation schemes which have been proposed and offer a fourth which yields improved agreement with experiment.

For many series of exoergic reactions of the type $A\cdot + BC \rightarrow AB + C\cdot$, activation energy is observed to decrease with increasing exoergicity. Evans and Polanyi first discussed this correlation and analyzed it in terms of intersecting Morse curves.[1,2] They proposed a linear dependence on exoergicity.

$$E_{\text{act}} = E_0 - \gamma q \tag{1}$$

Here E_0 and γ are empirical parameters and q, the heat of reaction, is positive for exoergic reactions. This relationship was substantiated with a large body of data by Semenov.[3] The correlation with exoergicity has also been expressed in another formula which was derived as part of the bond energy–bond order (BEBO) method for obtaining potential energy parameters of activated complexes.[4-7] This relationship is given by

$$E_{\text{act}} = (D^0{}_{AB} - q)\left\{1 - \left[1 + \left(1 - \frac{q}{D^0{}_{AB}}\right)^{1/p-1}\right]^{1-p}\right\} \tag{2}$$

where p is an empirical parameter and $D^0{}_{AB}$ is the bond energy of the product molecule. Activation energies and exoergicities for numerous reactions are listed in Table I. Although the exoergicity rule is obeyed in many series of reactions, exceptions are also found in the table. In series A the $O + F_2$ reaction is the most exoergic but has the highest activation energy. In series B the predicted trend is completely reversed, and in series H the $Na + CHCl_3$ reaction is out of line with the predicted variation. Two other series not listed in the table, $CF_3\cdot + CH_3X \rightarrow CF_3X + CH_3$[33] and $H\cdot + CH_3X \rightarrow HX + CH_3$[25] ($X =$ halogen atom), also show the reverse trend. These exceptions involve halogen atom abstraction reactions, and they were anticipated in the original analysis of the exoergicity rule.[1,2,39]

Another empirical scheme due to Spirin[8] establishes a relationship between activation energy and both the reaction exoergicity and the polarizabilities of the reacting species. Spirin proposed the expression which is given by

$$E_{\text{act}} = d(0.75D_{AC} - q)\left(\frac{1}{p_A} + \frac{1}{p_C}\right) \tag{3}$$

where D_{AC} is the bond energy of molecule AC, q is the exoergicity, and d is an empirical parameter. p_A and p_C are the polarizabilities of the reactant and product atoms (or radicals), respectively. The dependence on bond strengths is derived from the London formula for the energy of three atoms, and the formula includes a contribution from bonding between the two end atoms in the intermediate complex. The inverse dependence on the polarizability is based on the following reasoning. Attractive dispersion forces lower the interaction energy as reactants approach to distances characteristic of the onset of reaction. These forces are proportional to polarizability among other factors; thus the greater the polarizabilities of the reactants, the less repulsive the approach.[11] In many cases Spirin's

Table I. Summary of Reaction Data for Figure 1

Refers to Fig. 1		REACTION	q(a)	E_{act} (b)	α(c) ×10^{25}	$α^{-1}$ ×10^{-23}	Reference for E_{act}
Panel	Point						
A	a	$O + I_2 \rightarrow OI + I$	10.5	0	124	0.805	9
	b	$O + Br_2 \rightarrow OBr + Br$	9.9	0.9	69.9	1.43	9
	c	$O + Cl_2 \rightarrow OCl + Cl$	6.5	3.3	46.1	2.17	9
	d	$O + F_2 \rightarrow OF + F$	13	10.4	12.1	8.24	9
B	a	$H + I_2 \rightarrow HI + I$	35	0	124	0.805	15
	b	$H + Br_2 \rightarrow HBr + Br$	41	1.2	69.9	1.43	22-23
	c	$H + Cl_2 \rightarrow HCl + Cl$	47	1.4	46.1	2.17	23-24
	d	$H + F_2 \rightarrow HF + F$	98	2.4	12.1	8.24	23,25
C	a	$H + HI \rightarrow H_2 + I$	33	0.7	54.5	1.83	25
	b	$H + HBr \rightarrow H_2 + Br$	17	2.2	36.1	2.77	26
	c	$H + HCl \rightarrow H_2 + Cl$	1.1	3.5	26.3	3.80	27
	d	$H + HF \rightarrow H_2 + F$	-31.7	35	24.6	4.07	15
	e	$H + H_2 \rightarrow H_2 + H$	0	7.7	7.9	12.7	25
D	a	$H + CH_4 \rightarrow H_2 + CH_3$	0.2	11.9	26.0	3.85	25
	b	$H + C_2H_6 \rightarrow H_2 + C_2H_5$	6	9.4	44.7	2.24	25
	c	$H + C_3H_8 \rightarrow H_3 + C_3H_7$	7.5	8	62.9	1.59	25
	d	$H + n\text{-}C_4H_{10} \rightarrow H_2 + C_4H_9$	9	7.6	81.2	1.23	25
	e	$H + i\text{-}C_4H_{10} \rightarrow H_2 + C_4H_9$	9	6.4	81.2	1.23	25
E(d)	a	$N + CH_4 \rightarrow$ Products		10.1	26.0	3.85	15
	b	$N + C_2H_6 \rightarrow$ Products		7	44.7	2.24	15
	c	$N + C_3H_8 \rightarrow$ Products		5.5	62.9	1.59	15
	d	$N + n\text{-}C_4H_{10} \rightarrow$ Products		3.6	81.2	1.23	15
	e	$N + i\text{-}C_4H_{10} \rightarrow$ Products		3.1	81.2	1.23	15
F	a	$O + CH_4 \rightarrow OH + CH_3$	-1.7	9.1	26.0	3.85	28-29
	b	$O + C_2H_6 \rightarrow OH + C_2H_5$	4	6.4	44.7	2.24	28-29
	c	$O + C_3H_8 \rightarrow OH + C_3H_7$	5	5.0	62.9	1.59	15
	d	$O + n\text{-}C_4H_{10} \rightarrow OH + C_4H_9$	7	4.8	81.2	1.23	15,29
	e	$O + C_7H_{16} \rightarrow OH + C_7H_{15}$		3.3	136	0.735	15
	f	$O + n\text{-}C_8H_{18} \rightarrow$ Products		4.2	154	0.648	15
	g	$O + i\text{-}C_8H_{18} \rightarrow OH + C_8H_{17}$		2.9	154	0.648	15
G	a	$Cl + CH_4 \rightarrow HCl + CH_3$	-1	2.9	26	3.85	28,30
	b	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5	0.4	44.7	2.24	31-32
	c	$Cl + C_3H_8 \rightarrow HCl + n\text{-}C_3H_7$	6.5	0.8	62.9	1.59	32
	d	$Cl + C_3H_8 \rightarrow HCl + i\text{-}C_3H_7$	6.5	0.4	62.9	1.59	32
	e	$Cl + n\text{-}C_4H_{10} \rightarrow HCl + n\text{-}C_4H_9$	6	0.8	81.2	1.23	15
	f	$Cl + n\text{-}C_4H_{10} \rightarrow HCl + i\text{-}C_4H_9$	8	0.3	81.2	1.23	15
	g	$Cl + i\text{-}C_4H_{10} \rightarrow HCl + i\text{-}C_4H_9$	8	0.6	81.2	1.23	32
	h	$Cl + i\text{-}C_4H_{10} \rightarrow HCl + t\text{-}Bu$	11	0.3	81.2	1.23	32
H	a	$Na + CH_3Cl \rightarrow NaCl + CH_3$	17	10	45.6	2.19	15
	b	$Na + CH_2Cl_2 \rightarrow NaCl + CH_2Cl$	23.6	7.4	64.8	1.54	15
	c	$Na + CHCl_3 \rightarrow NaCl + CCl_2H$	31	5.0	82.3	1.22	15
	d	$Na + CCl_4 \rightarrow NaCl + CCl_3$	24	3.5	105	0.952	15
I	a	$H + CH_4 \rightarrow H_2 + CH_3$	0.2	11.9	26.0	3.85	25
	b	$H + CH_3Cl \rightarrow$ Products		$\geqslant$ 7.2	45.6	2.19	15,29
	c	$H + CH_2Cl_2 \rightarrow$ Products		$\leqslant$ 5.8	64.8	1.54	15,29
	d	$H + CHCl_3 \rightarrow$ Products		$\leqslant$ 4.3	82.3	1.22	15,29
	e	$H + CCl_4 \rightarrow HCl + CCl_3$	30	$\leqslant$ 3.3	105	0.952	15,29
J	a	$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	0	14.75	26.0	3.85	15
	b	$CH_3 + CH_3Cl \rightarrow CH_4 + CH_2Cl$	3	9.4	45.6	2.19	15
	c	$CH_3 + CH_2Cl_2 \rightarrow CH_4 + CHCl_2$	5	7.2	64.8	1.54	15
	d	$CH_3 + CHCl_3 \rightarrow CH_4 + CCl_3$	8	5.8	82.3	1.22	15
K	a	$CF_3 + CH_4 \rightarrow CF_3H + CH_3$	2	10.2	26.0	3.85	15,[illegible]
	b	$CF_3 + C_2H_6 \rightarrow CF_3H + C_2H_5$	8	7	44.7	2.24	15,[illegible]
	c	$CF_3 + C_3H_8 \rightarrow CF_3H + i\text{-}C_3H_7$	9.5	6.4	62.9	1.59	15
	d	$CF_3 + n\text{-}C_4H_{10} \rightarrow CF_3H + i\text{-}C_4H_9$	11	5.6	81.2	1.23	15
	e	$CF_3 + i\text{-}C_4H_{10} \rightarrow CF_3H + C(CH_3)_3$	14	4.7	81.2	1.23	15
L(e)	a	$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	0	14.75	26.0	3.85	15
	b	$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	6	11	44.7	2.24	16,17,34
	c	$CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7$	7	11.3	62.9	1.59	15
	d	$CH_3 + n\text{-}C_4H_{10} \rightarrow CH_4 + C_4H_9$	9	9.0	81.2	1.23	15
	e	$CH_3 + i\text{-}C_4H_{10} \rightarrow CH_4 + C_4H_9$	9	7.8	81.2	1.23	15
	f	$CH_3 + C_5H_{12} \rightarrow CH_4 + C_5H_{11}$		8.1	99.5	1.01	15
	g	$CH_3 + C_6H_{14} \rightarrow CH_4 + C_6H_{13}$		8.1	118	0.849	15
	h	$OH + CH_4 \rightarrow H_2O + CH_3$	15	3.6	26.0	3.85	28,36,37
	i	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	21	2.4	44.7	2.24	37
	j	$OH + C_3H_8 \rightarrow H_2O + C_3H_7$	22.5	1.3	62.9	1.59	37
	k	$OH + C_4H_{10} \rightarrow H_2O + C_4H_9$	24	1	81.2	1.23	37,38

(a) q, the reaction exoergicity, is given in kcal·mol^{-1}. Bond energies are taken from refs. 18 and 19.

(b) All activation energies are in kcal·mol^{-1}.

(c) α is the mean polarizability of the stable molecular reactant expressed in units of cm^3. Values are taken from reference 10.

(d) These reactions of nitrogen with a series of alkanes are not simple atom abstraction reactants.

(e) Arrhenius plots show curvature for CH_3 reactions. Low temperature values of E_a were used.

Table II. Activation Energies Calculated from Equation 3 in Text

A· + BC	D_{AC}, kcal mol^{-1}	q, kcal mol^{-1}	P_A, Å^3	P_C, Å^3	Calcd.[a] kcal mol^{-1}	Obsd, kcal mol^{-1}
$O + I_2$	47	10.5	0.77	4.5	2.0	0
$O + Br_2$	56.2	9.9	0.77	3.6	2.6	0.9
$O + Cl_2$*	64.3	6.3	0.77	2.61	3.3	3.3
$O + F_2$	50.7	13.2	0.77	0.567	4.4	10.4
$H + I_2$	71.4	35	0.667	4.5	0.8	0
$H + Br_2$	87.4	41	0.667	3.6	1.0	1.2
$H + Cl_2$*	103.1	47	0.667	2.61	1.4	1.4
$H + F_2$	136	98	0.667	0.567	0.3	2.4
$H + HI$	71.4	33	0.667	4.5	0.9	0.7
$H + HBr$	87.4	17	0.667	3.6	2.1	2.2
$H + HCl$*	103.1	1.1	0.667	2.61	3.5	3.5
$H + HF$[b]						
$H + H_2$	104.2	0	0.667	0.667	5.7	7.7

[a] In each series, d is obtained by fitting eq 3 to the data for the reaction denoted by an asterisk. [b] Endoergic reaction.

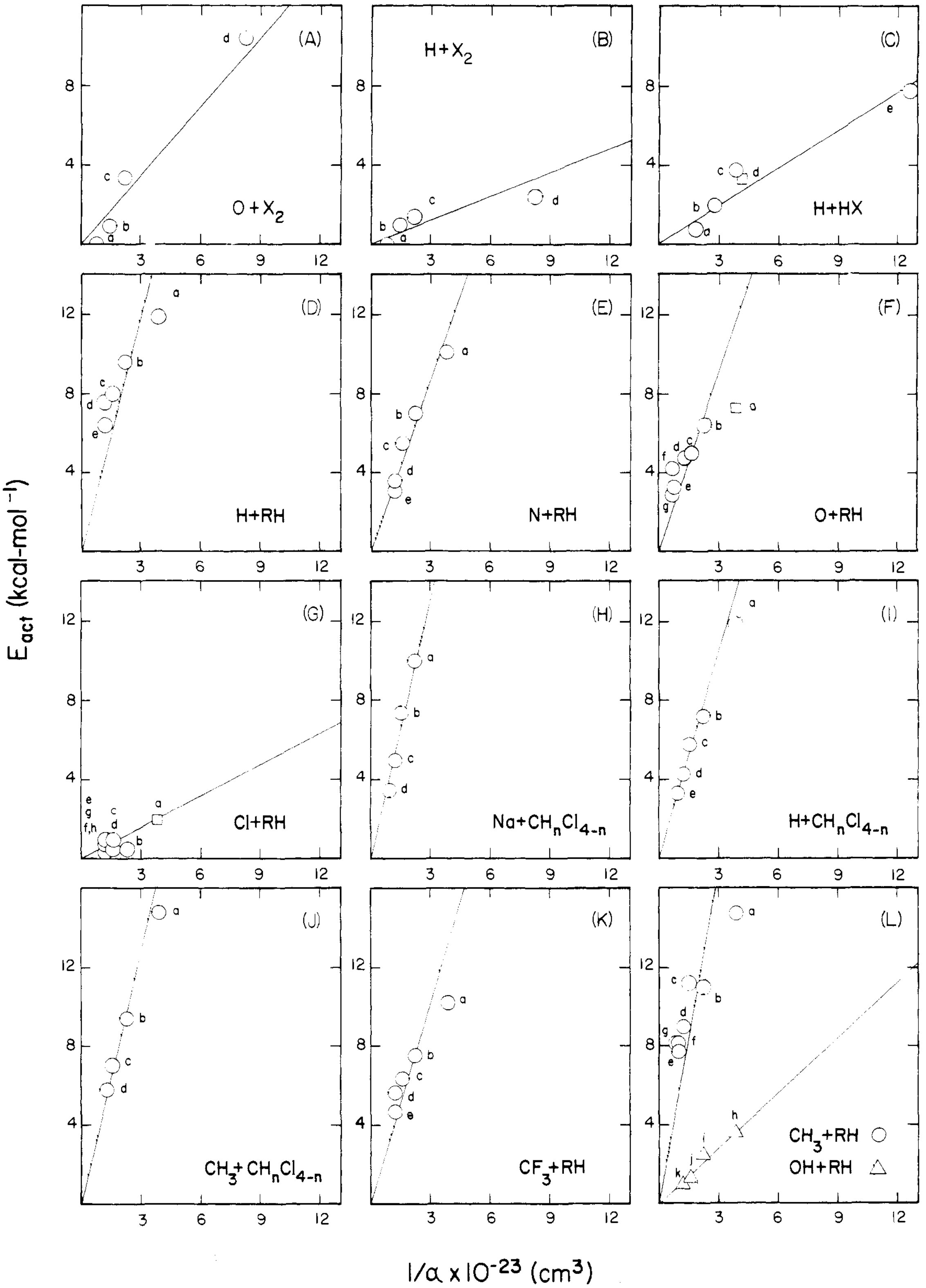

Figure 1. Plots of experimental activation energy vs. the reciprocal mean polarizability of the stable molecular reactant for the reactions listed in Table I. Endoergic reactions are denoted by square symbols. For these cases the activation energy which is plotted is the barrier in the exoergic direction.

formula gives better agreement with experiment than the exoergicity rule. For example, Table II shows that eq 3 predicts the correct qualitative trend for series A, and yields improved results for series B, although the H + F_2 reaction is out of line. Since atomic polarizabilities have been calculated for most elements,[12] eq 3 is easily applied to reactions in which A· and C· are atoms. However, in cases where molecular free radicals are involved, the required polarizabilities are not available and must be estimated.[13]

We have observed a simple correlation, expressed by

$$E_{\mathrm{act}} = \frac{C}{\alpha_{\mathrm{BC}}} \tag{4}$$

between activation energy and the polarizability of the stable molecular reactant, BC. In eq 4 c is an empirical parameter and α_{BC} is the mean polarizability of BC. The results obtained by plotting the data of Table I according to eq 4 are shown in Figure 1. In all cases the required molecular polarizabilities

Table III. Activation Energies (kcal/mol) for R· + X_2 Reactions

	X_2			
R·	I_2	Br_2	Cl_2	F_2
CH_3	<1[a]	<1[a]	2.3[a]	8[b]
C_2H_5	0.2[a]		1[a]	3.5[b]
CF_3	0[a]	0.7[a]	3.6[a]	10[b]

[a] Values taken from ref 15. [b] Values predicted by polarizability relation using a least-squares fit of the experimental activation energies.

are available from refractive index measurements.[10] Qualitative agreement is good for all reactions shown, although deviations from linearity are evident in some cases. For most series of reactions quantitative agreement is also good. While all the equations presented yield similar results for many series of reactions, eq 4 also gives good results in the case of halogen atom abstraction reactions. The available data suggest that eq 4 can be used with some reliability to estimate activation energies. Therefore, in Table III we present a few predictions which future experiments will have to test. Known activation energies for the reactions of CH_3·, C_2H_5·, and CF_3· with Cl_2, Br_2, and I_2 are given in the table along with the values determined from eq 4 for the fluorine reactions, which have not been studied. We note that an estimated activation energy of 2.9 kcal mol^{-1} for the reaction $CF_3 + F_2 \rightarrow CF_4 + F$ differs substantially from the prediction based on polarizability.[14] According to eq 4 all the reactions of molecular fluorine should proceed with relatively large activation energies by virtue of the low polarizability of F_2. Both the data shown in Figure 1 (panels A and B) and the small rate reported for the reaction $Cl + F_2 \rightarrow ClF + F$, which is exoergic by 23 kcal mol^{-1}, are consistent with this prediction.[20,21]

Acknowledgment is made to the Office of Naval Research (Power Program), to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for partial support of this work. We have benefited from valuable discussions with Professor Paul Davidovits.

References and Notes

(1) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).
(2) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).
(3) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity", Vol. I, Pergamon Press, Elmsford, N.Y., 1958, p 25. See also M.A.A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, **62**, 2175 (1966).
(4) H. S. Johnston, *Adv. Chem. Phys.*, **3**, 131 (1961).
(5) H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, **37**, 700 (1962).
(6) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).
(7) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, N.Y., 1966.
(8) Yu. L. Spirin, *Russ. J. Phys. Chem.* (*Engl. Transl.*), **36**, 636 (1962).
(9) R. H. Krech, G. J. Diebold, and D. L. McFadden, *J. Am. Chem. Soc.*, **99**, 4605 (1977).
(10) Landolt-Bornstein, "Zahlenwerte und Funktionen", Vol. I, "Atom-und Molekular Physik", Part 3, p 509; Vol. II, Part 8, p 871, Springer-Verlag, West Berlin, 1951.
(11) Noyes has also noted that there "seems to be some tendency for Δ_c to be larger for reactions involving the lighter and less polarizable elements". Δ_c is the activation energy for an atom transfer reaction: R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4311 (1966).
(12) R. R. Teachout and R. T. Pack, *At. Data*, **3**, 195 (1971).
(13) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1954, p 947.
(14) A. P. Modica and S. J. Sillers, *J. Chem. Phys.*, **48**, 3283 (1968).
(15) V. N. Kondratiev, "Rate Constants of Gas Phase Reactions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. COM-72-10014 (1972).
(16) A. F. Trotman-Dickenson, J. R. Binchard, and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951): $E_a(C_2H_6) = 10.4$.
(17) M. J. Wijnen, *J. Chem. Phys.*, **23**, 1357 (1955): $E_a(C_2H_6) = 11.2$.
(18) "Handbook of Chemistry and Physics", 55th ed, CRC Press, Cleveland, Ohio, 1974, pp F-204–F-220.
(19) V. I. Vedeneyev et al., "Bond Energies, Ionization Potentials, and Electron Affinities", Arnold, London, 1966.
(20) G. Schatz and M. Kaufman, *J. Phys. Chem.*, **76**, 3586 (1972).
(21) P. S. Ganguli and M. Kaufman, *Chem. Phys. Lett.*, **25**, 221 (1974).
(22) G. B. Skinner and G. H. Ringnose, *J. Chem. Phys.*, **43**, 4129 (1965); R. A. Fass, *J. Phys. Chem.*, **74**, 984 (1970). $E_a(Br_2) = 1.4$.
(23) M. D. Pattengill, J. C. Polanyi, and J. L. Schreiber, *J. Chem. Soc., Faraday Trans. 2*, **72**, 897 (1976), and references cited therein: $E_a(Br_2) = 0.9$, $E_a(Cl_2) = 1.8$, $E_a(F_2) = 2.4$.
(24) P. P. Bemand and M. A. A. Clyne, *J. Chem. Soc., Faraday Trans. 2*, 394 (1977): $E_a(Cl_2) = 1.1$. P. F. Ambidge, J. N. Bradley, and D. A. Whytock, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1157 (1976): $E_a(Cl_2) = 1.4$. H. Gg. Wagner, U. Welzbacher, and R. Zellner, *Ber. Bunsenges. Phys. Chem.*, **80**, 902 (1976): $E_a(Cl_2) = 1.2$.
(25) W. E. Jones, S. D. MacKnight, and L. Teng, *Chem. Rev.*, **73**, 407 (1973).
(26) G. B. Skinner and G. H. Ringrose, *J. Chem. Phys.*, **43**, 4129 (1965).
(27) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **48**, 4405 (1968).
(28) R. F. Hampson and D. Garvin, Ed., *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 866** (1975).
(29) L. G. Anderson, *Rev. Geophys. Space Phys.*, **14**, 151 (1976).
(30) M. A. A. Clyne and R. F. Walker, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1547 (1973): $E_a(CH_4) = 3.6$. R. Watson, G. Machado, S. Fischer, and D. D. Davis, *J. Chem. Phys.*, **65**, 2126 (1976): $E_a(CH_4) = 2.4$. R. G. Manning and M. J. Kurylo, *J. Phys. Chem.*, **81**, 291 (1977): $E_a(CH_4) = 2.5$. D. A. Whytock, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, *J. Chem. Phys.*, **66**, 2690 (1977): $E_a(CH_4) = 3.1$.
(31) R. G. Manning and M. J. Kurylo, *J. Phys. Chem.*, **81**, 291 (1977): $E_a(C_2H_6) = 0.1$.
(32) P. Cadman, A. W. Kirk, and A. F. Trotman-Dickenson, *J. Chem. Soc., Faraday Trans. I*, **72**, 1027 (1976): $E_a(C_2H_6) = 0.8$.
(33) P. Gray, A. A. Herod, and A. Jones, *Chem. Rev.*, 71, 247 (1971).
(34) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, 77, 4719 (1955): $E_a(C_2H_6) = 11.5$.
(35) P. Camilleri, R. M. Marshall, and H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, 71, 1491 (1975).
(36) D. D. Davis, S. Fischer, and R. Schiff, *J. Chem. Phys.*, **61**, 2213 (1974): $E_a(CH_4) = 3.4$. M. A. A. Clyne and R. F. Walker, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1547 (1973): $E_a = 3.6$.
(37) N. R. Greiner, *J. Chem. Phys.*, **53**, 1070 (1970): $E_a(CH_4) = 3.8$.
(38) R. A. Perry, R. Atkinson, and J. N. Pitts, *J. Chem. Phys.*, **64**, 5314 (1976).
(39) E. Warhurst, *Q. Rev., Chem. Soc.*, **5**, 44 (1951), and references cited therein.