state should have a much deeper potential energy curve and a smaller equilibrium separation under high pressure than atmospheric pressure, and hence this phenomenon is more predominant as the number of methyl groups on the benzene ring increases in Figure 6. This model can account for the sensitivity of the charge transfer band maximum to pressure changes and for the absence of broadening. This is in agreement with the observed results.

References

(1) J. R. Kim and O. C. Kwun, *Bull. Korean Chem. Soc.,* **6,** 74 (1985).

(2) O. C. Kwun and J. R. Kim, *J. Korean Chem. Soc.,* **27,** 102 (1983).

(3) O. C. Kwun and H. Lentz, *Zeit. Phisik. Chem. N. F.,* **96,** 177 (1975).

(4) O. C. Kwun, *J. Korean Chem. Soc.,* **22,** 245 (1978).

(5) O. C. Kwun, J. G. Jee and J. R. Kim, *J. Korean Chem. Soc.,*

(6) O. C. Kwun and J. R. Kim, *J. Korean Chem. Soc.,* **27,** 9 (1983).

(7) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.,* **71,** 2703 (1949).

(8) E. Kuss and M. Taslimi, *Chemie Ing. Techn.,* **42,** 1073 (1970).

(9) G. Briegleb, "Electronen Donator Acceptor Komplexe," Springer, Berlin, 1961.

(10) J. R. Gott and W. G. Maisch, *J. Chem. Phys.,* **39,** 2229 (1963).

(11) A. H. Ewald, *Trans. Faraday Soc.,* **64,** 733 (1968).

(12) A. H. Ewald and J. A. Scudder, *J. Phys. Chem.,* **76,** 249 (1972).

(13) S. C. Wallwork, *J. Chem. Soc.,* 496 (1961).

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell, 1960.

(15) H. Tsubomura and R. P. Lang, *J. Amer. Chem. Soc.,* **83,** 2085 (1961).

(16) J. Prochorow and A. Tramer, *J. Chem. Phys.,* **44,** 4545 (1966).

24, 405 (1980).

MNDO Studies on the Gas–Phase S_N2 Reaction*

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The MNDO was found to be the most reliable semi-empirical SCF–MO method for the studies of S_N2 reactions involving anion and neutral molecule. The results of our MNDO calculations on the S_N2 reactions of $CH_3X + Y^- \rightarrow CH_3Y + X^-$ where X = H, F, Cl, CN, CH_3 and Y = F, CH_3 showed that the order of the leaving group ability is the reverse of the order of proton affinities. It was also found that there is no symbiosis involved in the S_N2 transition state and the departure of the leaving group is relatively late in contrast to the early bond formation of the nucleophile. The Marcus equation was found to apply to the MNDO barriers and energy changes.

For many years bimolecular nucleophilic substitution (S_N2) reaction has been one of the most extensively investigated types of reactions in chemistry. These studies have played an important role of developing ideas such as structure-reactivity relationships[1], linear free energy relationships[1], kinetics as a probe of mechanism[2] and solvent effects[3]. Since the pioneering works of Hughes and Ingold[4] numerous studies on the S_N2 reaction conducted mainly in solution have been reported[5]. It has since been established that the reaction is first order in both nucleophile and substrate, and proceeds in one step involving concerted formation of the new bond by backside attack at carbon center and cleavage of the leaving group with inversion of configuration at the site of attack.

Recently however much interest has been focussed upon pure structure–reactivity relationships without any interfering solvent effect[6]. This type of studies has become possible since 1971 through the novel experimental works of gas–phase S_N2 reac-

tions using ion cyclotron resonance (ICR) spectrometry[7]. On the theoretical side, a number of *ab initio*[8] and CNDO/2[9] MO calculations have been carried out on the S_N2 reactions. These calculations were usually for the reactions proceeding in vacuo, *i.e.,* in the absence of solvent, so that direct comparisons with the experimental results of gas–phase studies are possible. However the CNDO/2 results[10] were in complete disagreement with the *ab initio* results[11], whereas the excessive cost of computation limited the use of *ab initio* calculations; theoretical works on the S_N2 reaction were mostly on simple model reactions with *ab initio* method. In practice however chemists are interested in somewhat larger molecular systems undergoing bimolecular nucleophilic substitution, and hence it is desirable to deal with the problem with an appropriate semiempirical MO method which is sufficiently reliable in reproducing essential features of the experimental results.

In this work, we have shown that MNDO method[12] is the most reliable semi-empirical SCF MO method for the investigation

*Determination of Reactivity by MO Theory (Part XXXVII)

of S_N2 reactions; we used the reaction (1) as a model and performed MNDO calculations, and the results are compared with *ab initio* and experimental data.

$$XCH_3 + Y^- \rightarrow YCH_3 + X^-$$
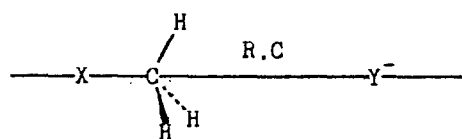$$X = H, F, Cl, CN, CH_3; \quad Y = F, CH_3 \qquad (1)$$
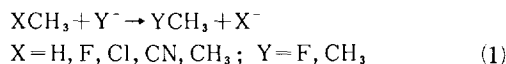
We have also discussed MNDO theoretical nucleophilicities and leaving group abilities relative to the sequence of proton affinities.

Calculations

Geometric configuration of reacting system was taken as shown in Figure 1, where the nucleophile, carbon center and leaving group form a straight line. The distance(d_N) between carbon center and nucleophile was then used as the reaction coordinate. The transition stats (TS) was searched by the reaction coordinate method.[13] Optimizing all geometrical parameters under C_{3v} symmetry condition. Both structure and energy of complexes are also obtained optimizing all geometrical parameters under C_{3v} symmetry condition. For reaction FCH_3 + CH_3^- and CH_4 + F^-, the TS determination by this method gave sudden changes of energy and structure toward the product side ion-molecule complex, so that a stationary point corresponding to the TS was found by gradient norm minimization[14], and then it was confirmed that the TS had only one negative eigenvalue in the Hessian matrix[15]. Structures of anion-molecule complexes were determined by geometry optimization starting from the distance between the carbon center and nucleophile of 4 Å in Figure 1. Ground states for neutral molecules and anions were found by geometry optimization using known symmetry conditions (*eg.* CH_4(Td), CH_3^- C_{3v})).

Results and Discussion

Preliminary Calculations. The gas-phase S_N2 reactions(1)

X - H, F, Cl, CN, CH$_3$ (leaving group)

Y = F, CH$_3$ (nucleophile)

R.C = reaction coordinate

Figure 1. Geometric configuration of reacting system.

TABLE 1: Energy Values (shown in Figure 2) in Kcal/mol and Distances Involved in Complex (I) (d_L^c) and Transition State (d_L^*) for Reaction(1) with X = Y = F[†]

Method	ΔE_a	ΔE_b	ΔE_c	d_L^c	d_N^c	d_L^*	d_N^*
CNDO/2		−87.4		1.45	1.45		
MINDO/3		−64.5		1.45	1.45		
MNDO	39.1	−5.8	44.7	1.36	3.36	1.64	1.64
Ab initio[a]	7.9	−12.5	20.4	1.47	2.65	1.80	1.80
Experiment			26.2[b]				

[†] d_L and d_N represent distances between carbon center and leaving group, and that between carbon center and nucleophile respectively. [a]A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972). [b]M. J. Pellerite and J. I. Brauman, *J. Am. Chem. Soc.*, **105**, 2672 (1983).

with $X = Y = F$ and $X = Y = Cl$ have been extensively studied both experimentally and theoretically.[11] The reliabilities of semi-empirical SCF MO methods, CNDO/2, MINDO/3[16], and MNDO, were tested using these reactions by comparing the results with the available *ab initio* and experimental data. Geometric parameters for stationary points and energy values on potential energy profile shown in Figure 2 were obtained by three semi-empirical MO methods and the results are summarized in Tables 1 and 2 together with the available *ab initio* and experimental values.

The sum of two separate energy values for the two reactants, neutral molecule and anion, was used for reactant energies except for the CNDO/2 method for which energy corresponding to a supper-molecule of the two reactants separated by 10 Å was used; CNDO/2 method gave unreasonably large value of ΔE_b when the sum of two reactants energies was used. The CNDO/2 and MINDO/3 results exhibited an energy profile with a single well without central barrier (ΔE_c), whereas the MNDO method gave an expected normal double well energy profile that was found with the *ab initio* and experimental results. Inspection of Tables 1 and 2 reveals that the MNDO method consistently gives (i) a double well energy profile, (ii) greater reactivity for the system $X = Y = Cl$ compared with the system $X = Y = F$, and (iii) reasonable geometric as well as energy values wherever comparisons with the *ab initio* and experimental values are possible. We therefore conclude that the MNDO method is the only reliable semi-empirical SCF MO method we have studied, *i.e.*, CNDO/2, MINDO/3 and MNDO, for studies of S_N2 reactions involving a neutral molecule and an anion. All the rest of our calculations were performed accordingly with the MNDO method.

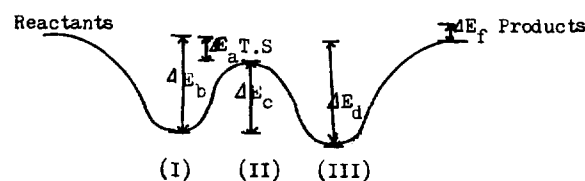*Reaction Type $XCH_3 + F^-$.* The rate of an S_N2 reaction

Figure 2. Energy values of potential energy profile for the reaction $CH_3X + Y^- \rightarrow CH_3Y + X^-$. Stationary points, (I), (II) and (III) represent reactants anion-molecule complex, transition state and products anion-molecule complex, respectively. $\Delta E_a = \Delta H_f(T.S) - \Delta H_f(Reactant)$. $\Delta E_b = \Delta H_f(I) - \Delta H_f(Reactant)$. $\Delta E_c = \Delta H_f(T.S) - \Delta H_f(I)$. $\Delta E_d = \Delta H_f(III) - \Delta H_f$ (Product), $\Delta H_f = \Delta H_f$ (Product) $- \Delta H_f$ (Reactant)

TABLE 2: Energy Values (shown in Figure 2) in Kcal/mol and Distances Involved in Complex (I) (d_X^c) and Transition State (d_X^*) for Reaction(1) with X = Y = Cl

Method	ΔE_a	ΔE_b	ΔE_c	d_L^c	d_N^c	d_L^*	d_N^*
CNDO/2		−67.3		1.81	1.81		
MINDO/3		−21.9		1.96	1.96		
MNDO	3.2	−7.3	10.5	1.83	3.37	2.15	2.15
Ab initio	2.2[a]		5.5[b]			2.39	2.29[a]
Experiment	1.6[c]	−8.6[d]	10.2[e]				

[a]reference 11b; [b]reference 11c; [c]$\Delta E_a = \Delta E_b + \Delta E_c$; [d]R. C. Dougherty, J. Dalton and J. D. Robert, *Org. Mass. Spectra.*, **8**, 77 (1974); [e]M. J. Pellerite and J. I. Brauman, *J. Am. Chem. Soc.*, **105**, 2672 (1983).

TABLE 3: Energy Values (shown in Figure 2) in kcal/mol for Reaction $XCH_3 + F^- \rightarrow CH_3F + X^-$

X	ΔE_a	ΔE_b	ΔE_c	ΔE_d	ΔE_f
F	39.1	−5.8	44.7	−5.8	0.0
	4.21(SCF)[a]	−12.5[b]	11.7[c]		
	8.85(CEPA)[a]		26.2[e]		
	7.0[d] 7.9[b]				
H	40.6	−0.3	41.0	−8.1	42.0
	72.0[b]				
Cl	−3.4	−8.5	5.1	−5.1	−76.0
	−15.1[a]				
CN	27.3	−7.1	34.4	−5.1	−7.7
	17.0[d]				
CH₃	50.8	−0.5	51.2	−5.6	32.8

[a]reference 11b; [b]reference 11a; [c]reference 11c; [d]A. J. Duke and R. F. W. Bade, *Chem. Phys. Lett.*, 10, 631 (1971); [e]Calculated from experimental values using Marcus eqn. M. J. Pellerite and J. I. Brauman, *J. Am. Chem. Soc.*, 105, 2672 (1983).

is affected by the nucleophilicity of the nucleophile, the leaving group ability (LGA) and the structure of the substrate.[17] Here we investigated the LGA for a nucleophile of hard base[18] type, F^-, using the MNDO calculations. Various energy values on the potential energy surface (Figure 2) are summarized in Table 3, and geometries and charge distributions for the stationary points (I), (II) and (III) corresponding to reactants ion-molecule complex, TS and products ion-molecule complex, respectively, are shown in Figure 3.

Reference to Table 3 reveals that in all cases the reactions have double well potential energy profile and for the leaving group Cl(X = Cl) the TS has an energy lower than that for the reactants (a negative energy barrier ΔE_a) in qualitative agreement with the *ab initio* results.[11] The complex (I) formed from a neutral molecule with permanent dipole moment has greater anion-dipole interaction energy compared with a molecule with no permanent dipole. In complex (III), interaction between a common neutral molecule CH_3F and an anion is strongly stabilizing in all cases; for the contracted anions H^- and F^- closer approach to the neutral molecule is possible and anion-dipole interaction energies are more stabilizing compared with those for the other anions, CH_3^-, CN^-, and Cl^-.

We can see from Figure 3 that the neutral molecules, methane and ethane, which have no permanent dipole moment also show non-symmetric charge distribution for complex (I); owing to the induced polarization, charges are localized to the opposite side of the complex from the approaching anion. In all cases no charge transfer is seen to occur from anion to substrate in complexes (I) and (III), whereas substantial charge transfer takes place from nucleophile to leaving group in the TS and large positive charge develops at the TS.

Comparison of the reactivity scale ΔE_a gives an order of LGA Cl>CN>F>H>CH₃, which is in accord with the order found with the *ab initio* calculations[19], Cl>F>H.

As a measure of the gas-phase basicity, we carried out MNDO calculations of the proton affinity and the results are shown in Table 4 together with the experimental values[19]; it is seen that the agreements between the MNDO and experimental values are gratifying except one reversal of order for H and CH₃. It is noteworthy that the order of proton affinity (experimental)
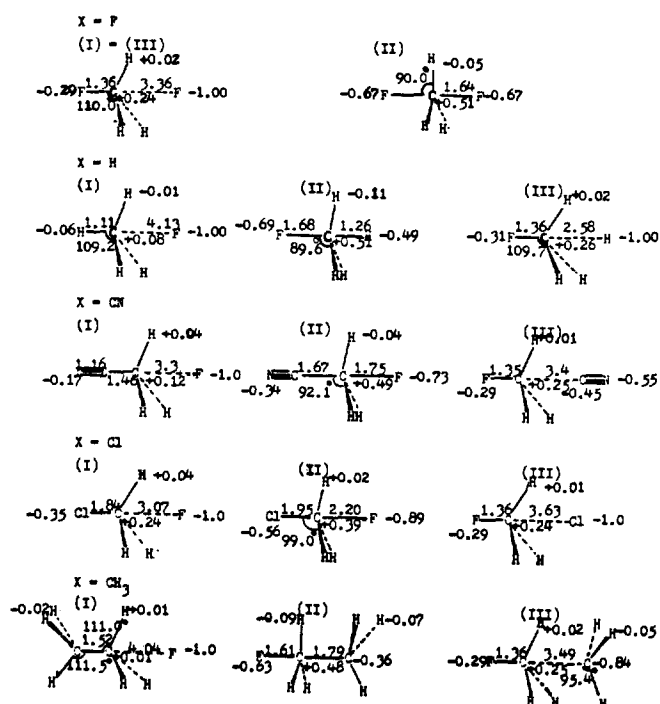
Figure 3. Geometric parameters and charge distributions for the stationary points (I), (II) and (III) of reactions $CH_3X + F^- \rightarrow CH_3F + X^-$. (angle, in degree; distance, in Å; charge, in au)

TABLE 4: Proton Affinities (PA) in kcal/mol determined by MNDO Method

$$PA = \Delta H_f(X^-) + \Delta H_f(H^+) - \Delta H_f(XH)$$

X	PA (MNDO)	PA (Exp.)
H	399.8	400.0
CH₃	395.5	417.0
F	369.3	370.0
CN	346.7	340.0
Cl	287.3	335.0

is exactly the reverse of the order of LGA; this is in good accord with the well-known rule in organic chemistry that the LGA is inversely correlated with the basicity of the leaving group.[19]

Interaction energies ΔE between an acidic and a basic species are normally approximated as[20],

$$\Delta E = \frac{q_a q_b}{R_{ab}\varepsilon} + 2\sum_m \sum_n \frac{(C_a^m C_b^n \beta_{ab})^2}{E_m - E_n} \tag{2}$$

where the first term represents an electrostatic interaction energy between the two species while the second term represents an energy arising from orbital interactions between occupied and unoccupied orbitals of the basic and acidic species respectively. Approximations however can be made for the second term using only the frontier orbitals (FMO)[21], *i.e.*, the highest occupied MO(HOMO) of the anion and the lowest unoccupied MO(LUMO) of the carbon center-leaving group (C−X) bond which is always a sigma antibonding nature. The orbital interaction energy will therefore be inversely proportional to the energy difference between the HOMO and the LUMO, and will be proportional to the square of the resonance integral (and hence of the overlap integral S^{22}) between the two FMO's. Since in the present case the HOMO of the anion, F^-, is fixed, we need on-

ly the σ antibonding energy (Table 5) to consider in the estimation of the effect of the second term on ΔE in eq.(2).

Since the HOMO level of anion is fixed and lower than the σ antibonding levels of the C–X bond, the lower the LUMO of the C–X bond, the narrower will be the energy gap and hence the greater will be the orbital interaction energy resulting in the greater LGA.

For the reactants with permanent dipole moments the MNDO results are in agreement with the expected order of LCA from the energy gap consideration only, *i.e.*, Cl>CN>F. However the energy gap consideration predicts X = H or, CH₃ to be a better leaving group than X = F, which is disagreement with the MNDO order of LGA. This indicates that the total interaction energy ΔE is not controlled by the orbital interaction energy term alone; the first term becomes predominant when large ion-dipole interaction is involved as in the case of X=F.

Reaction Type $XCH_3 + CH_3^-$. We have carried out similar calculation on reaction (1) with a nucleophile of soft base type, CH_3^-. Various energy values on the potential energy profile (Figure 2) for reaction are summarized in Table 6, and geometric parameters and charge distributions for the three stationary points (I)-(III) are shown in Figure 4.

The results show that the stability of complex (I) is greater for $F^-\cdot CH_3X$ than that for $CH_3^-\cdot CH_3X$, since the former has more contracted charge and hence has greater anion-dipole interaction. For the reaction of X = Cl(CH₃Cl), a single well corresponding to a stable intermediate with no central barrier is formed. For the overall change of (I) → (II) → (III) (complex(I) → TS → complex (III)), we have estimated the degree of structural changes according to eq. (3) in order to treat the structural changes from (I) to (II) quantitatively.

$$X\overset{d_L^c}{-}CH_3\overset{d_N^c}{\cdots}Y\to[X\overset{d_L^*}{\cdots}CH_3\overset{d_N^*}{\cdots}Y]^*\to X\overset{d_L}{-}CH_3\overset{d_N}{-}Y$$

$$\delta d_L=\frac{d_L^*-d_L^c}{d_L-d_L^{c'}}\quad \delta d_N=\frac{d_N^c-d_N^*}{d_N^c-d_N}\tag{3}$$

The results are summarized in Table 7. Reference to this table indicates that in unsymmetric S_N2 reactions, *i.e.*, for X≠Y, with double potential energy surfaces, d_L scarcely changes until d_N changes substantially ; departure of the leaving anion is relatively late along the reaction coordinate as has been found with the

TABLE 5: Sigma Antibonding Orbital Energies for C—X bond

X	Antibonding orbital E(eV)
H	4.38
CH₃	4.38
F	5.14
CN	3.66
Cl	1.00

TABLE 6: Energy Values (shown in Figure 2) in kcal/mol for Reaction $XCH_3+F^- \to CH_3CH_3+X^-$

X	ΔE_a	ΔE_b	ΔE_c	ΔE_d	ΔE_f
F	18.0	−5.6	23.6	−0.5	−32.8
H	18.6	−0.3	18.8	−0.8	−9.2
Cl		−109.1		−0.4	−108.7
CN	6.6	−6.8	13.5	−0.3	−40.4
CH₃	26.5	−0.4	26.9	−0.4	0.0

ab initio calculations.[11a]

The order of LGA for the soft nucleophile [18]CH₃ is seen to be the same as it was found for the hard nucleophile F⁻, *i.e.*, Cl>CN>F>H>CH₃. These results are also in accord with the conclusions derived from *ab initio* studies that there is no symbiosis[23] involved in the S_N2 transition state. Comparison of data in Tables 3 and 6 reveals that the relative nucleophilicity is greater for CH₃ than for F⁻, which corresponds to the sequence of proton affinities (Table 4).

Application of Marcus Equation: The Marcus equation[24](4) is known to apply to an elementary process[24b] such as (I) → (II) → (III) in Figure 2.

$$\Delta E_{X,Y}^*$$
$$=\frac{1}{2}(\Delta E_{X,X}^*+\Delta E_{Y,Y}^*)+\frac{1}{2}\Delta E+((\Delta E)^2/8(\Delta E_{X,X}^*+\Delta E_{Y,Y}^*))\tag{4}$$

This equation relates the barrier height for the cross-reaction (X≠Y) of Y displacing X, ΔE_{XY}^*, to the energy change ΔE (thermodynamic term) and to the intrinsic barriers ΔE_{XX}^* and ΔE_{YY}^* (Kinetic term). The intrinsic barriers are the barrier heights for the identity reaction, *i.e.*, reaction (1) with X = Y, and the MNDO values obtained in this work are given in Table 8.

For the reaction of X = Cl and Y = CH₃, eq.(4) can not be applied since the reaction has no central barrier. The results of application of eq. (4) to our MNDO energy values are summarized in Table 9, which clearly shows that the Marcus equa-
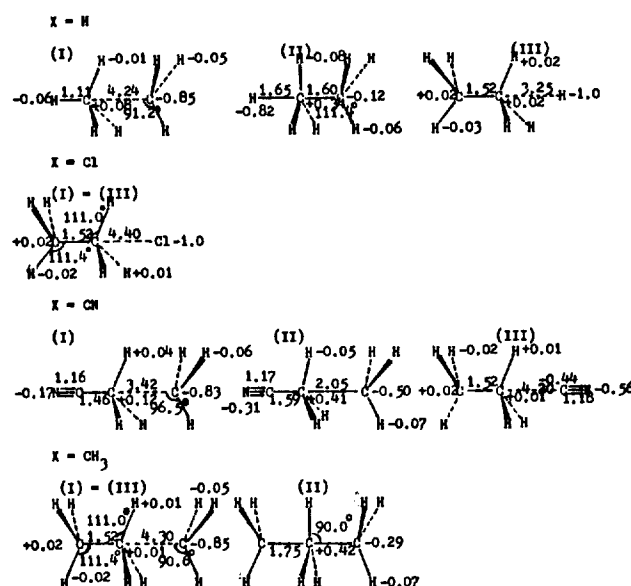

Figure 4. Geometric parameters and charge distributions for the stationary points (I),(II) and (III) of reactions $CH_3X + CH_3^- \to CH_3CH_3 + X^-$. (angle, in degree; distance, in Å; charge, in au).

TABLE 7: Degree of Distance Changes (δd_x) Accompanied in Changes from Complex (I) to Transition State (II)

L.G	Nucleophile			
	F		CH₃	
	δd_L	δd_L	δd_L	δd_N
F	0.50	0.50	0.09	0.86
H	0.10	0.88	0.09	0.86
Cl	0.06	0.51		
CN	0.11	0.79	0.05	0.72
CH₃	0.14	0.91	0.50	0.50

TABLE 8: Intrinsic Barriers,ΔE_{XX}^*, in kcal/mol for Reactions $CH_3X + X^-$ → $CH_3X + X^-$

X	ΔE_{XX}^*
F	44.7
Cl	10.5
CH_3	26.9
CN	26.9

TABLE 9: Energy Changes ΔE^a and Activation Barriers(ΔE_c in Figure 2) by MNDO Method, ΔE^* and by Marcus Equation, ΔE^* (marcus), Respectively for Reactions $CH_3X + Y^-$ → $CH_3Y + X^-$. Energy Values are in kcal/mol

X	Y	ΔE	ΔE^* (Marcus)	ΔE^*
Cl	F	−72.6	3.2	5.1
F	Cl	72.6	75.8	77.6
F	CH_3	−27.7	23.3	23.6
CH_3	F	27.7	51.0	51.2
CN	F	−5.7	33.0	34.4
F	CN	5.7	38.8	40.0
CN	CH_3	−33.9	12.6	13.5
CH_3	CN	33.9	46.6	47.4

$^a \Delta E = (\Delta E_d + \Delta E_f) - \Delta E_b$.

tion applies equally well to the MNDO barries ΔE^* and energy changes ΔE of the gas-phase S_N2 process as it was found to apply to electron[25]- and proton-transfer[26] reactions in solution, gas-phase and solution-phase[24] S_N2 reactions, various gas-phase atom transfers[28] and *ab initio* gas-phase S_N2 energies.[11c]

We conclude that: (i) the MNDO method is the most reliable semi-empirical SCF MO method for the theoretical studies of gas-phase S_N2 reactions, (ii) the LGA follows the reverse order of the proton affinities, (iii) there is no symbiosis in the S_N2 transition state, (iv) the nucleophilicity order is the same as that of the proton affinities, (v) departure of the leaving group is relatively late in contrast to the early bond formation of the nucleophile, (vi) the electrostatic interaction contributes more to the TS stabilization than the orbital interaction, (vii) the Marcus equation applies to the MNDO barriers and energy changes.

Reference

(1) (a) F. A. Carey and R. J. Sundberg, "Advanced Organic Chemistry," Plenum press, 1977, p. 139; (b) A. Press and S. S. Shaik, *J. Am. Chem. Soc.*, **103**, 6049 (1981).

(2) (a) J. W. Moore and R. C. Pearson, "Kinetic and Mechanism," John Wiley and Sons press, 1981; (b) T.H. Lowry and K. S. Richardson, p. 174. "Mechanism and Theory in Organic Chemistry," Happer and Row press, 1981.

(3) (a) E. S. Amis and J. F. Hinton, "Solvent effect on Chemical Phenomena," Academic press, 1973; (b) A. J. Parker, *Chem. Rew.*, **1**, 1 (1969); (c) F. P. Ballistreri, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.*, **42**, 1415 (1977).

(4) (a) E. D. Hughes, C. K. Ingold, and C. S. Patel, *J. Chem. Soc.*,

526 (1933); (b) J. L. Gleave, E. D. Hughes, and C. K. Ingold., *J. Chem. Soc.*, 236 (1935).

(5) (a) I. Lee and I. S. Koo, Tetrahedron., **39**, 1803 (1983); (b) I. Lee, N. L. Kim and S. C, Sohn, *Tetrahedron Lett.*, 4723 (1983).

(6) (a) E. C. F. Ko and A. J. Parker, *J. Am. Chem. Soo.*, **90**, 6447 (1968); (b) I. Lee, N. L. Kim and S. C. Sohn, *Tetrahedron Lett.*, 4723 (1983).

(7) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass. Spectrum Ion Phys.*, **7**, 471 (1971)

(8) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University.

(9) D. P. Santry and G. A. Segal, *J. Chem, Soc.*, **43**, S129 (1965).

(10) (a) P. Cremaschi, A. Gamba and M. Simonetta, *Theoret. Chem. Acta*, **25**, 237 (1972); (b) P. D. Gillespie and I. Ugi, *Angew, Chem. Int. Ed.*, **10**, 503 (1971).

(11) (a) a. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972); (b) F. Keil and R. Ablrichs, *J. Am. Chem. Soc.*, **98**, 4787 (1976); (c) S. Wolfe, D. J. Mitchell, and H. B. Schlegel, *J. Am. Chem. Soc.*, **103**, 7692 (1981).

(12) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907, 5231 (1977).

(13) (a) M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa, and L. E. Wade, *J. Am. Chem. Soc.*, **93**, 4290 (1971); (b) L. Salem, "Electrons in Chemical Reactions: p. 28. First Principles," John Wiley and Sons, 1982.

(14) (a) A. Komornicki, K. Ishida, and K, Morokuma, *Chem. Phys. Letters.*, **45**, 595 (1977); (b) J. W. McIver, Jr., and Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).

(15) I. G. Csizmadia, "Theory and Practice of MO. Calculations on Organic Molecules, "Elsevier Scientific Publishing Company, 1976.

(16) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

(17) T. H. Lowry and K. S. Richardson, p. 342. "Mechanism and Theory in Organic Chemistry," 1981.

(18) (a) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963); (b) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).

(19) A. Dedieu and A. Veillard, "Quantum Theory of Chemical Reactions," D. Reidel Publishing Company, p. 69, 1980.

(20) (a) H. Kollmar and H. O. Smith, *Angew, Chem. Int. ED.*, **9**, 462 (1970); (b) J. E. Williams, V. Buss and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 6870 (1971).

(21) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley and Sons, 1976.

(22) I. Lee, Y. G. Cheun, and K. Yang, *J. Comp, Chem.*, **3**, 565 (1982).

(23) R. G. Pearson and J. Songstad, *J. Org. Chem.*, **32**, 2899 (1967).

(24) (a) I. Lee and H. K. Kang, *Prog. Chem. and Chem. Inds*, **24**, 457 (1984); (b) S. Wolfe and D. J. Mitchell, *J. Am. Chem. Soc.*, **103**, 7692, 7694 (1981); (c) J. R. Murdoch, *J. Am. Chem. Soc.*, **105**, 2660 (1983).

(25) R. E. Weston and H. A. Schwartz, "Chemical Kinetics," Section 7.7 (1972).

(26) (a) A. D. Cohen and R. A. Marcus, *J. Phys. Chem.*, 72, 4249

(1968); (b) R. A. Marcus, *J. Am. Chem. Soc.*, **91**, 7224 (1969).

(27) (a) W. J. Albery, *Pure Appl. Chem.*, **51**, 949 (1979); (b) E.

S. Lewis and S. J. Kukes, *J. Am. Chem. Soc.*, **101**, 417 (1979).

(28) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

A Kinetic Study of Br Atom Reactions with Trimethylsiane by the VLPR (Very Low Pressure Reactor) Technique[1]

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(Received January 30, 1985)

A Very Low Pressure Reactor (VLPR) is constructed for the kinetic study of atom-molecule bimolecular elementary reactions. The basic principles and the versatility of the method are described. By using the VLPR technique the forward (k_1) and the reverse (k_{-1}) rate constants for Br atom reaction with trimethylsilane are studied; $Br\cdot + (CH_3)_3SiH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HBr + (CH_3)_3Si$. From the kinetic data and the entropy estimation the bond dissociation energy for Si-H bond in trimethylsilane is calculated to be 90.1 kcal/mole (± 1.1 kcal/mole). The Arrhenius parameters for k_1 are found to be log A = 10.6 l/mole·sec, $E_a = 4.4$ kcal/mole respectively. For the comparison purpose analogous reaction for carbon compound ; $Br\cdot + (CH_3)_3CH \rightarrow HBr + (CH_3)_3C\cdot$ was also studied. The corresponding rate constant and equilibrium constant at 25°C are found to be 2.67×10^6 l/mole·sec and 160 respectively.

Introduction

The greater size and reduced electronegativity of the silicon atom along with the possibility of d-orbital participation cause silicon compounds to behave abnormally in comparison with their carbon analogs, although carbon and silicon both belong to the same group (group IV) in the periodic table. It has been generally accepted that silicon-silicon, silicon-carbon, and silicon-hydrogen bonds are weaker than carbon-carbon, and carbon-hydrogen bonds, respectively.

Recently the kinetic and mechanistic study of silicon compounds gained wide interests due mainly to their unusual properties in comparison with their carbon analogs. The generation and detection of silicon-centered free radicals[2], divalent silicon species[3], and double bonded (Si = R, R = O, Si, C) silicon compounds[4] has been one of the most exciting research areas in organosilicon chemistry. Because of the complexity of silicon chemistry a detailed kinetic and thermochemical parameters for reactive silicon intermediates should be known to account for complex silicon reactions properly. It would be interesting to compare the chemistry of silicon compounds with that of carbon analogs to shed light on the similarities and/or differences between those two classes of compounds.

Indirect determinations of rate constants for the elementary gas phase reactions of halogen atoms with various hydrocarbons have been carried out during the last few decades. Only recently a direct determination of the rate constants has been published. Most of the workers have used atomic absorption[5], atomic fluorescence[6], and ESR technique[7] for the detection of halogen atoms, and reaction times were usually determined by a flow or a pulse method. The drawbacks of these methods for general determination of kinetic parameters are well known; (1) the detector only detects the reactive intermediates and no

information on all the products can be obtained, (2) the species interested should have suitable spectroscopic transitions in the proper spectral range, and (3) the reactants should be inert with the flash light that is used for the generation of reactive intermediates.

We have recently constructed a Very Low Pressure Reactor (VLPR) kinetic system which is more general than the known methods for the study of elementary reaction kinetics. The system consists of the very low pressure Knudsen reactor and molecular-beam mass spectrometric detection unit by which all the reactants and products can be detected without the complication of secondlary reactions. By using the Knudsen cell reactor the absolute rate constants can be directly deduced. Successful applications of the Knudsen cell reactor system for unimolecular elementary kinetics have been reported.[8]

Br atom reaction with trimethylsilane, $Br\cdot + (CH_3)_3SiH \xrightarrow{k_1}$, is one of the elementary reactions for the bromination of silane. Since we can also measure the reverse rate constant, *i.e.* $HBr + (CH_3)_3Si\cdot \xrightarrow{k_{-1}}$, by using our VLPR system, the Si-H bond dissociation energy of $(CH_3)_3SiH$ can be estimated from the rate constants. There have been continuous controversy over the exact bond dissociation energy of Si-H bond in trimethylsilane. Reported values range from ca. 75 kcal/mole[9] to 89.8 kcal/mole.[14]

The purpose of this research is to measure the elementary reaction rate constants for the Br atom reaction with trimethylsilane and trimethylsilyl radical with HBr (k_1 and k_{-1}). From the rate data the bond dissociation energy for Si-H bond was estimated.

Although the kinetic measurements of Si-H bond energy in trimethylsilane was recently reported in our laboratory as a preliminary form[1] here we included a detailed description of