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Theoretical Studies on the S_N2 Processes at Primary and Secondary Carbon Centers[†]

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Ab initio MO calculations with the 6-31+G* basis sets are carried out on the identity exchanges $X^- + RX \rightleftharpoons XR + X^-$ with X = F and Cl, and geometries and the HF ($\Delta E_{HF}^{\ddagger}$) and MP2 activation barriers ($\Delta E_{MP}^{\ddagger}$) are reported. Relatively constant transition-state tightness, $d^{\ddagger}(X\cdot\cdot X)$, is found for R with primary (R = CH_2Y) and secondary (R = CHY^1Y^2) carbon centers, respectively. The difference in $d^{\ddagger}(X\cdot\cdot X)$ between primary and secondary carbon centers is ca. 0.10 Å. For highly electronegative X and/or Y, the correlated energy barrier, $\Delta E_{MP}^{\ddagger}$, is invariably lower than the Hartree−Fock energy barrier, $\Delta E_{HF}^{\ddagger}$. A satisfactory correlation with $r = 0.90$ for 11 R groups is found between the theoretical $\Delta E_{MP}^{\ddagger}$ values for the identity exchanges and the experimental log k_2 values for the reactions of $ROSO_2C_6H_5$ with aniline in acetonitrile at 65.0 °C.

In the course of our works on developing the cross-interaction constants, ϱ_{ij} in eq 1,where i, j = X, Y, or Z

$$\log(k_{ij}/k_{HH}) = \varrho_i\sigma_i + \varrho_j\sigma_j + \varrho_{ij}\sigma_i\sigma_j \qquad (1)$$

represent three fragments, the nucleophile, substrate, and leaving group, respectively, in a typical S_N2 transition state (TS) in Scheme 1, as a mechanistic tool for organic reactions in solution, it has been found that the magnitude of ϱ_{XZ} (Scheme 1 where C_i's denote reaction centers) provides a measure of the TS tightness: The greater the $|\varrho_{XZ}|$, the tighter the TS is.[1] Moreover we found a quite interesting, somewhat unexpected, result about the TS tightness for S_N2 processes at primary and secondary carbon centers: The magnitude of ϱ_{XZ} is a relatively large *constant* value (≅ 0.29−0.40 in MeCN or MeOH at 45.0−65.0 °C) at a primary carbon, whereas it is smaller *constant* value (≅ 0.10−0.11 in MeCN at 65.0 °C) at a secondary carbon center, irrespective of the size of the group attached to the reaction center carbon (Table 1). These constant ϱ_{XZ} values suggest that the TS is tight or loose ($d_{XZ}^{\ddagger}$ in Scheme 1 is short or long), depending on whether the reaction center (C_Y) carbon is primary or secondary, but the TS tightness varies very little with regard to the group attached to C_Y.

Scheme 1

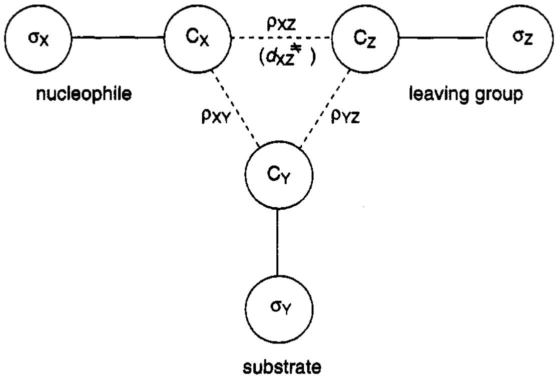

Table 1. ϱ_{XZ} Values for Reactions of $ROSO_2C_6H_4Z$ with $XC_6H_4NH_2$

R	solvent	T (°C)	ϱ_{XZ}	ref
	Primary Compounds			
CH_3	MeCN	65.0	0.32	2
	MeOH	65.0	0.30	2
C_2H_5	MeCN	65.0	0.34	2
	MeOH	65.0	0.33	2
$CH_2{=}CHCH_2$	MeCN	45.0	0.37	3
$CH_2{=}C(CH_3)CH_2$	MeCN	45.0	0.40	4
$CH{\equiv}CCH_2$	MeCN	45.0	0.29	5
$(CH_3)_3CCH_2$	MeOH	55.0	0.31	6
$(CH_3)_3SiCH_2$	MeCN	65.0	0.33	7
	MeOH	65.0	0.31	7
	Secondary Compounds			
$(CH_3)_2CH$	MeCN	65.0	0.10	8
cyclobutyl	MeCN	65.0	0.11	9
cyclopentyl	MeCN	65.0	0.11	9
cyclohexyl	MeCN	65.0	0.11	9

In order to examine these trends theoretically, we carried out *ab initio* MO calculations on the identity exchange reactions (eq 2), using seven primary and four secondary compounds, RX, with X = F and Cl.

$$X^- + RX \rightleftharpoons XR + X^- \qquad (2)$$

Calculations

The 6-31G extended basis sets with diffuse and polarization functions (6-31+G*)[10] were used in the determi-

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[†] Determination of Reactivity by MO Theory. Part 88. Part 87: Lee, I.; Chung, D. S.; Jung, H. J. *Tetrahedron*, in press.

[®] Abstract published in *Advance ACS Abstracts*, July 1, 1994.

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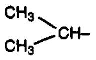
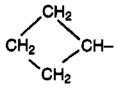
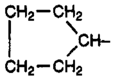
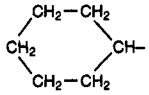
Table 2. The HF(HF/6-31+G*//HF/6-31+G*) and MP2(MP2/6-31+G*//MP2/6-31+G*) Geometries and Activation Barriers for the Reactions of $X^- + RX \rightleftharpoons XR + X^-$ with X = F

R		d^0(C−F) (Å)	$d^‡$(C−F) (Å)	$\Delta d^‡$ (Å)	$d^‡$(F···F) (Å)	θ (deg)	%CX‡	$\Delta E^‡$
CH_3-	HF	1.3713	1.8461	0.4748	3.6923	0.0	34.6	5.69
	MP2	1.4073	1.8369	0.4296	3.6737	0.0	30.4	−1.05
CH_3CH_2-	HF	1.3795	1.8878	0.5083	3.7602	10.3	36.9	9.29
	MP2	1.4167	1.8659	0.4492	3.7178	9.9	30.4	2.31
$CH_2{=}CHCH_2-$	HF	1.3790	1.8575	0.4785	3.7047	8.5	34.7	9.69
	MP2	1.4194	1.8510	0.4316	3.6954	6.8	30.4	−0.00
$CH{\equiv}CCH_2-$	HF	1.3685	1.8221	0.4536	3.6366	7.4	33.2	7.21
	MP2	1.4107	1.8302	0.4195	3.6543	6.6	29.7	−3.47
$PhCH_2-$	HF	1.3813	1.8480	0.4667	3.6877	7.7	33.8	6.90
	MP2	1.4054	1.8356	0.4302	3.6680	4.8	30.6	−3.84
$(CH_3)_3CCH_2-$	HF	1.3800	1.9018	0.5218	3.7444	20.2	37.8	15.55
	MP2	1.4159	1.8729	0.4570	3.6937	19.1	32.3	7.26
$(CH_3)_3SiCH_2-$	HF	1.3944	1.8730	0.4786	3.7435	4.2	34.3	0.67
	MP2	1.4328	1.8561	0.4233	3.7107	3.3	29.5	−6.95
	HF	1.3880	1.9370	0.5490	3.8431	14.5	39.6	12.29
	MP2	1.4265	1.8990	0.4725	3.7703	13.8	33.1	5.29
	HF (eq)	1.3812	1.9310	0.5498	3.8442	11.0	39.8	11.84
	(ax)	1.3813	1.9310	0.5497			39.8	11.84
	MP2 (eq)	1.4193	1.8955	0.4762	3.7116	23.5	33.6	4.85
	(ax)	1.4193	1.8850	0.4657		20.2	32.8	4.85
	HF (eq)	1.3784	1.9453	0.5669	3.8700	11.8	41.1	10.84
	(ax)	1.3895	1.9489	0.5594		13.7	40.3	12.11
	MP2 (eq)	1.4155	1.9124	0.4969	3.7839	16.8	35.1	2.84
	(ax)	1.4268	1.8929	0.4661		3.6	32.7	4.77
	HF (eq)	1.3851	1.9324	0.5473		0.0	39.5	13.66
	(ax)	1.3912	1.9717	0.5805	3.8656	22.8	41.7	13.56
	MP2 (eq)	1.4242	1.8992	0.4750		0.0	33.4	5.62
	(ax)	1.4294	1.9137	0.4843	3.7991	13.9	33.9	5.71

nation of TS structures and activation barriers, $\Delta E^‡$ ($=E_{TS} - E_{reactants}$). To account for the electron correlation, second-order Möller−Plesset perturbation theory[11] (MP2) was adopted. Two types of results are reported: HF (HF/6-31+G*//HF/6-31+G*) and MP2 (MP2/6-31+G*//MP2/6-31+G*).

Geometries of reactants and TSs were optimized and all positive eigenvalues and only one negative eigenvalue, respectively, in the Hessian matrix were identified to confirm the equilibrium and transition states[12] in all the HF level calculations. All *ab initio* calculations were carried out using the Gaussian 92 programs.[13]

For cycloalkyl compounds, the leaving group at an equatorial position was found to be preferred to that at an axial position in all cases. However, the activation processes (and barriers) from both reactants with the equatorial and axial leaving groups were considered, albeit the TS structure was common to the two processes.

Results and Discussion

Bond length of the C−X bond in the reactant, d^o(C−X) and TS, $d^‡$(C−X), the angles of deflection, θ, from the ideal trigonal bipyramid five-coordinate (TBP-5C) structure and activation barriers, $\Delta E^‡$, are summarized in Tables 2 and 3 (also see Scheme 2). The distance $d^‡$(X··X) provides a measure of the TS tightness, which is not equal to 2 × $d^‡$(CX). The percentage of C−X stretching, %CX‡ [$=100 \times (d^‡ - d^o)/d^o$] is also shown in the tables. The C−X stretching deformation has been shown to be a dominant factor determining the intrinsic barrier,[14] $\Delta E_o^‡$, which is normally defined as the energy difference between the TS ($E^‡$) and the reactant complex, R··X$^-$, (E_{RC}). In this work, we only considered the activation barriers, $\Delta E^‡$, from the reactant.

Scheme 2

(a) primary carbon center (R = CH_2Y)

(b) secondary carbon center (R = CHY^1Y^2)

Geometries

Electron correlation leads to an increase of more than 0.03 Å in calculated bond lengths (d^o) of the C−F bonds for all RF systems, whereas it leads to a decrease of less than 0.01 Å in d^o of the C−Cl bonds. Thus the structures of second-row systems are influenced less significantly by electron correlation effects than those of the analogous first-row compounds.[15] In contrast, bond lengths ($d^‡$) of the C−X bonds for both X = F and Cl in the TS are invariably contracted by incorporation of electron correlation. There is one exception to this, however: For a system with highly electronegative groups, X = F (group electronegativities,[16] χ, are 3.95 and 3.03 for F and Cl, respectively) and Y = CH≡C (χ = 3.30), $d^‡$(C−F) is lengthened by including electron correlation. According

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(15) Reference 10; p 146−164.

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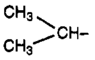
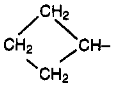
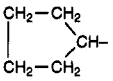
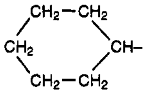
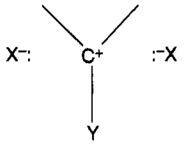
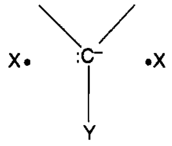
Table 3. The HF(HF/6-31+G*//HF/6-31+G*) and MP2(MP2/6-31+G*//MP2/6-31+G*) Geometries and Activation Barriers for the Reactions of $X^- + RX \rightarrow XR + X^-$ with X = Cl

R		d°(C−Cl) (Å)	$d^{\ddagger}$(C−Cl) (Å)	$\Delta d^{\ddagger}$(C−Cl) (Å)	$d^{\ddagger}$(Cl··Cl) (Å)	θ (deg)	%CX‡	$\Delta E^{\ddagger}$
CH_3-	HF	1.7857	2.3955	0.6078	4.7869	4.7	34.0	6.59
	MP2	1.7801	2.3171	0.5370	4.6341	0.0	30.2	7.66
CH_3CH_2-	HF	1.8002	2.4906	0.6904	4.9224	17.6	38.4	9.24
	MP2	1.7917	2.3698	0.5781	4.6967	15.4	32.3	11.15
$CH_2{=}CHCH_2-$	HF	1.8045	2.4981	0.6936	4.9320	18.4	38.4	9.26
	MP2	1.7987	2.3705	0.5718	4.7093	13.2	31.8	8.21
$CH{\equiv}CCH_2-$	HF	1.7932	2.4370	0.6438	4.8218	16.8	35.9	10.87
	MP2	1.7939	2.3489	0.5550	4.6686	12.8	30.9	6.87
$PhCH_2-$	HF	1.8087	2.4985	0.6898	4.9236	19.7	38.1	8.18
	MP2	1.8015	2.3557	0.5542	4.6867	11.7	30.8	5.70
$(CH_3)_3CCH_2-$	HF	1.8032	2.5802	0.7770	4.8901	37.3	43.1	17.86
	MP2	1.7941	2.4258	0.6317	4.6534	32.9	35.2	17.96
$(CH_3)_3SiCH_2-$	HF	1.8070	2.4574	0.6504	4.8514	18.0	36.0	9.27
	MP2	1.7995	2.3502	0.5507	4.6627	14.5	30.6	6.94
	HF	1.8161	2.6246	0.8085	5.1327	24.2	44.5	10.06
	MP2	1.8040	2.4385	0.6345	4.7856	22.2	35.2	14.00
	HF (eq)	1.8109	2.6389	0.8280	5.1818	21.9	45.7	11.27
	(ax)	1.8110	2.6459	0.8349		24.4	46.1	11.27
	MP2 (eq)	1.8033	2.4441	0.6408	4.8102	18.8	35.5	15.21
	(ax)	1.8034	2.4377	0.6343		20.5	35.2	15.21
	HF (eq)	1.7998	2.5929	0.7931	5.2473	0.0	44.1	10.51
	(ax)	1.8176	2.7653	0.9477		36.8	52.1	10.56
	MP2 (eq)	1.7900	2.4432	0.6532	4.8212	18.7	36.5	13.63
	(ax)	1.8045	2.4680	0.6635		24.8	36.8	14.23
	HF (eq)	1.8122	2.5739	0.7617	5.1859	0.0	42.0	13.11
	(ax)	1.8223	2.8130	0.9907		45.6	54.37	11.99
	MP2 (eq)	1.8019	2.4509	0.6490	4.8199	20.9	36.0	15.91
	(ax)	1.8089	2.5116	0.7027		32.7	38.9	14.95

to the valence bond configuration mixing model,[17] the TS structure can be represented by a mixing of VB structures for the reactant, product and excited state configurations like, I and II. The excited-state configuration I is known



I



II

to contribute in large extent when both X and Y are highly electronegative.[18] The contribution of structure I (i = 3) relative to that of the reactant structure (i = 1 = 2), C_3/C_1, in equation $\Psi_{TS} = \Sigma c_i \Phi_i$, where i = 1−3 and i = 1 = 2, is indeed greater when X = F and Y = CH≡C with C_3/C_1 = 1.23 than when X = Cl and Y = H (χ = 2.28) with C_3/C_1 = 1.18 calculated by the method of Shaik et al.[19] Since the bond length of C··X in I is greater than that in the reactant,[19] a greater contribution of I will lead to a longer C··X bond length.

The $\Delta d^{\ddagger}(=d^{\ddagger} - d^{\circ})$ and %CX‡ values in all systems decrease by inclusion of electron correlation. The deflection angle, θ, in Tables 2 and 3 is seen to depend on the size of the group Y (or Y^1 and Y^2) in R. The ideal TBP-5C structure is exhibited for R = CH_3 and also for some equatorial 5- and 6-member cycloalkyl systems. In general, θ is larger for X = Cl than for X = F, and as expected θ decreases by inclusion of electron correlation. The largest MP2 θ value (32.9°) is encountered for X = Cl with Y = $(CH_3)_3C$. In this respect, the MP2 θ value of 14.5° for X = Cl with Y = $(CH_3)_3Si$ is notably small, reflecting a longer bond length of the Si−CH_2 bond.

The TS tightness, $d^{\ddagger}$(X··X), and the percentage bond stretching deformation, %CX‡, are both remarkably within narrow ranges: The averages of $d^{\ddagger}$(X··X) and %CX‡ for the primary carbon centers are 3.69 ± 0.02 Å and 30.5 ± 0.8% with X = F, and 4.67 ± 0.02 Å and 31.7 ± 1.6% with X = Cl, while for the secondary carbon centers they are 3.77 ± 0.03 Å and 33.5 ± 0.5% with X = F and 4.81 ± 0.03 Å and 36.5 ± 1.5% with X = Cl. Thus differences in $d^{\ddagger}$(X··X) and %CX‡ values i.e., $\Delta d^{\ddagger}$(X··X) and Δ(%CX‡) between primary and secondary carbon centers are 0.08 ± 0.03 Å and 3.0% with X = F and 0.14 ± 0.03 Å and 4.8% with X = Cl, respectively. These results show that the differences, $\Delta d^{\ddagger}$(X··X) and Δ(%CX‡), between primary and secondary carbon centers become greater as the size of the nucleophile and/or leaving group are larger. Therefore for the aniline nucleophiles and the benzenesulfonate leaving groups (Table 1), these differences between the two types of carbon centers are expected to be even greater. We can conclude that the relatively constant values of the cross-interaction constants, ρ_{XZ}, for the reactions of $ROSO_2C_6H_4Z$ and $XC_6H_4NH_2$ for the primary and secondary carbon centers in R (Table 1) correctly reflect the relatively constant TS tightness i.e., $\Delta d^{\ddagger}$(X··X), and the difference in the two ρ_{XZ} values of ca. 0.22 (the difference in the average ρ_{XZ} values, ≅ 0.33−0.11) represents the $\Delta d^{\ddagger}$(X··X) value of ca. 0.10 Å. It is also pertinent to point out that a tighter TS with a greater experimental ρ_{XZ} value (for the primary carbon centers) has a smaller theoretical $d^{\ddagger}$(X··X) value.[1a] Moreover, the TS tightness is relatively constant, i.e., $|\rho_{XZ}|$ ≅ constant and $d^{\ddagger}$(X··X) ≅ constant, for the reactions at a particular type of carbon center i.e., primary or secondary, irrespective of the size and kind of the group or groups attached to the reaction center carbon.

The TS structure for a cycloalkyl compound is common to the two (initial) reactants with equatorial and axial leaving groups. The TS structure for the cyclopentyl and cyclohexyl chlorides are shown in Figures 1 and 2.

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[17] (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187. (b) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (c) McLennan, D. J.; Pross, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 981.

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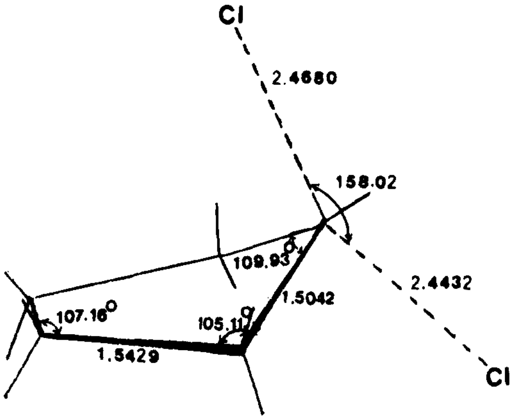

Figure 1. Transition state (TS) structure for cyclopentyl chloride.

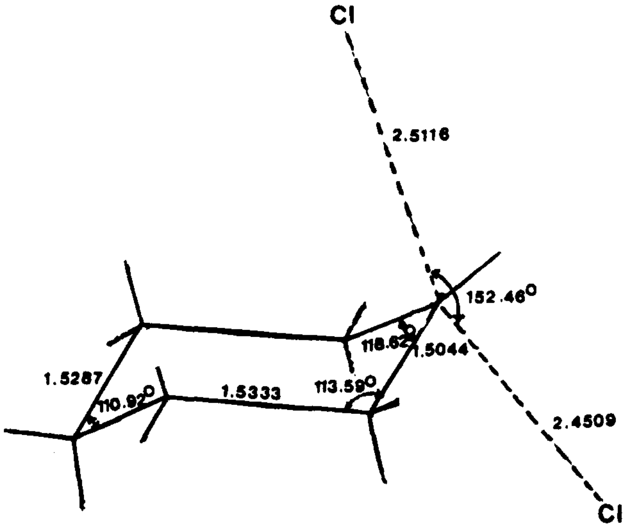

Figure 2. Transition state (TS) structure for cyclohexyl chloride.

Energetics

The 6-31+G* activation barriers, $\Delta E^{\ddagger}$, for R = CH_3, CH_3CH_2, $CH_2{=}CHCH_2$, and $CH{\equiv}CCH_2$ in Table 1 agree within ±0.20 at the HF and ±0.10 kcal/mol at the MP2 level with the corresponding values obtained using the 6-31++G** basis set.[18] Thus additional polarization and diffuse functions for hydrogen atoms have very little effect on the activation barriers. We also note that for the highly electronegative X, X = F, the HF barriers are invariably higher than the corresponding MP2 barriers in all cases. For the X of relatively lower electronegativity, X = Cl, $\Delta E_{HF}^{\ddagger}$ is lower than $\Delta E_{MP}^{\ddagger}$ when the electronegativity of Y (R = CH_2Y) is also low; $\Delta E_{HF}^{\ddagger}$ is higher than $\Delta E_{MP}^{\ddagger}$ only for the highly electronegative Y. This means that the electronegativities of X and Y have additive effects on the MP2 activation barriers, in agreement with our previous results on the allyl transfer reactions.[18]

For the secondary carbon compounds with X = Cl, $\Delta E_{MP}^{\ddagger}$ is higher than $\Delta E_{HF}^{\ddagger}$ in all cases, since both the X and Y groups have low electronegativity. The lower correlated energy barrier, $\Delta E_{MP}^{\ddagger}$, than the HF barrier $\Delta E_{HF}^{\ddagger}$, for a system with strongly electronegative X and/or Y groups is considered to arise from a greater contribution of configuration I to the TS, which leads to a larger magnitude of electron correlation energy in the TS than in the reactant;[18] a more electron-localized structure, I, has a greater electron correlation than a more delocalized structure, II. The lowering of $\Delta E_{MP}^{\ddagger}$ by an increased electron correlation energy in the TS is schematically illustrated in Figure 3.

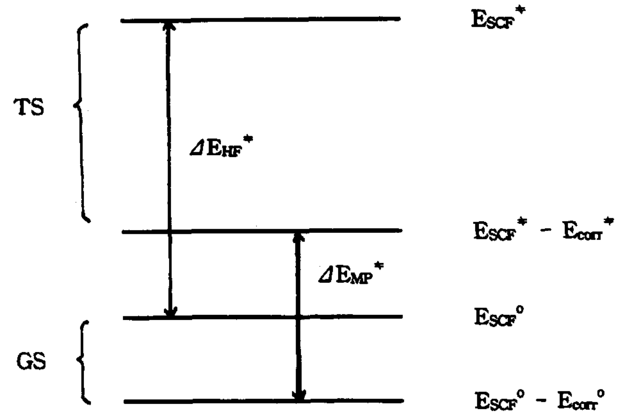

Figure 3. The SCF and correlation energy levels in the ground (GS) and transition states (TS).

A satisfactory correlation between $\Delta E_{MP}^{\ddagger}$ and $\%CX^{\ddagger}$ [$\Delta E_{MP}^{\ddagger} = a(\%CX^{\ddagger}) + b$] exists only for the reactions between primary alkyl series and X = Cl with $r = 0.96$ and $a = 2.37$. We should note here that this type of correlation is normally satisfactory between the percentage stretching deformation, $\%CX^{\ddagger}$ and the intrinsic barrier, $\Delta E_o^{\ddagger}$, which is the energy difference between the TS ($E^{\ddagger}$) and the ion–molecule (reactant) complex (E_{RC}).[14] Theoretical studies on identity methyl transfer reaction $Cl^- + CH_3Cl$ have indicated that the ion–molecule complex, $Cl^-\cdots CH_3Cl$, is important only in the gas-phase reaction and plays little role in solution.[20] In this work, we therefore disregarded such complexes (and hence $\Delta E_o^{\ddagger}$), and the $\Delta E^{\ddagger}$ values are used in the discussion. Another reason why such a correlation is poor could be relatively strong steric effect of the Y (or Y^1 and Y^2 groups) on the barrier heights, $\Delta E^{\ddagger}$. The angular deflection, θ, to ease the steric effect becomes greater as the size of the X and/or Y group is large. Thus θ is the greatest for Y = $(CH_3)_3$ with X = Cl. In general, the activation barriers are lower for the primary than for the secondary compounds due to a lesser stretching deformation, $\%CX^{\ddagger}$, required for the former.[14]

For the cycloalkyl series, an equatorial approach of a nucleophile displacing an equatorial leaving group is intrinsically favored compared to an axial approach replacing an axial leaving group; for X = F an equatorial approach is favored in all cases. However, when the size of X becomes greater than X = Cl, an equatorial displacement is favored for the cyclopentyl, whereas an axial displacement becomes favored for the cyclohexyl compound. This latter trend is apparently due to a greater steric hindrance in the equatorial approach for the cyclohexyl system.[9]

The MP2 activation barriers, $\Delta E_{MP}^{\ddagger}$, for the gas-phase reactions of RCl with Cl^- in Table 3 are correlated with the experimental log k_2 values in Table 4 for the S_N2 reactions of $ROSO_2C_6H_5$ with aniline in acetonitrile at 65.0 °C in Figure 4. For the 11 R groups listed in Table 4 the correlation is satisfactory with $r = 0.90$ and the slope of −3.11. There is apparently a greater uncertainty in the estimated k_2 value (for 65.0 °C from an experimental k_2 at 45.0 °C) for the allyl system.[3] This satisfactory correlation between the correlated activation barriers for the gas-phase chloride exchanges and the

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Table 4. Experimental log k_2 Values for the Reaction of $ROSO_2C_6H_5$ with Aniline in CH_3CN at 65.0 °C

R (=CH_2Y)	$\chi(Y)^d$	log k_2	$\Delta E_{MP}^{\ddagger}$ ^{e} (kcal/mol)
CH_3	2.28	0.873 (ref 2)	7.66
CH_3CH_2	2.30	−0.170 (ref 2)	11.15
CH_2=$CHCH_2$	3.00	(2.000)^a	8.21
CH=CCH_2	3.30	(1.301)^b	6.87
$C_6H_5CH_2$	3.00	(2.137)^C	5.70
$(CH_3)_3CCH_2$	2.30	−1.467 (ref 6)	17.96
$(CH_3)_3SiCH_2$		0.228 (ref 7)	6.94
$(CH_3)_2CH$		−0.386 (ref 8)	14.00
cyclobutyl		−0.772 (ref 9)	15.21
cyclopentyl		−0.130 (ref 9)	13.63
cyclohexyl		−1.51 (ref 9)	14.95

^{a} Estimated value from k_2 at 45.0 °C (ref 3). ^{b} Estimated value from k_2 at 45.0 °C (ref 5). ^{c} Extrapolated value from k_2 values at 25.0, 35.0, and 45.0 °C. Lee, J. H. Ph.D. Thesis, Hanyang University, 1992. ^{d} Group electronegativity of Y (ref 16). ^{e} For the gas-phase reactions of RCl with Cl^- calculated at the MP2/6-31+G*//MP2/6-31+G* level. Taken from Table 3.

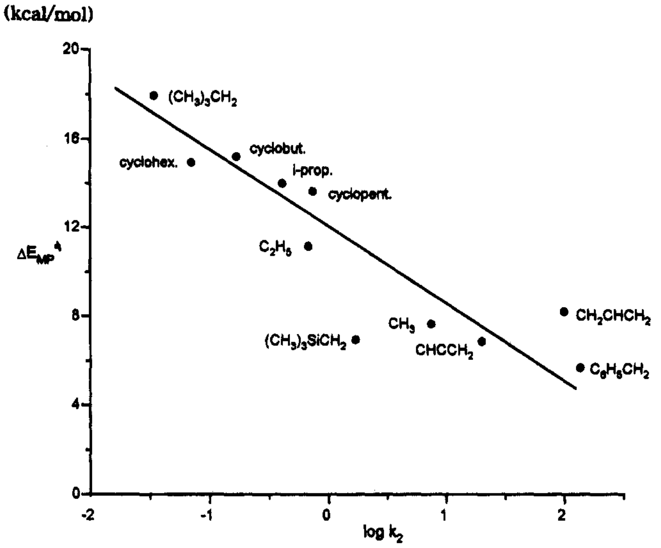

Figure 4. Correlation between log k_2 and $\Delta E_{MP}^{\ddagger}$ (Table 4).

experimental bimolecular rate constants for the benzenesulfonates with aniline in acetonitrile is indeed remarkable and gratifying. The satisfactory correlation indicates that the solvent and temperature effects are relatively small and the chloride exchanges provide a satisfactory model for the solution-phase reactions compared, despite the large steric effect expected in the solution-phase experimental results due to greater sizes of the nucleophile (Cl vs aniline) and leaving group (Cl vs benzenesulfonate).

The satisfactory correlation found in Figure 4 also suggests that the effect of thermodynamic barrier, $\Delta E°$, on the rate (or $\Delta E^{\ddagger}$) of the reaction of $ROSO_2C_6H_5$ with aniline in acetonitrile is small, and the intrinsic barrier, $\Delta E_o^{\ddagger}$, is the dominant factor in controlling the overall activation barrier, $\Delta E^{\ddagger}$, in eq 3.[21] The thermodynamic

$$\Delta E^{\ddagger} = \Delta E_o^{\ddagger} + \frac{\Delta E°}{2} + \frac{(\Delta E°)^2}{16\Delta E_o^{\ddagger}} \qquad (3)$$

barriers calculated by the AM1 method[22] are summarized in Table 5. Reference to this table reveals that the reactions of primary and secondary compounds are all exoergic by a relatively small amounts. However, in both

Table 5. The AM1 Thermodynamic Barriers, $\Delta E°$, at 65.0 °C for Reactions of $ROSO_2C_6H_5$ with Aniline

R (=CH_2Y)	$\Delta E°$ ^{a} (kcal/mol)
CH_3	−6.0
CH_3CH_2	−6.6
CH_2=$CHCH_2$	−7.0
CH≡CCH_2	−8.7
$C_6H_5CH_2$	−7.3
$(CH_3)_3CCH_2$	−6.9
$(CH_3)_3SiCH_2$	−8.4
cyclobutyl	−8.8
cyclopentyl	−6.7
cyclohexyl	−5.5

^{a} $\Delta E° = \Delta H° - RT$ at 65.0 °C.

primary and secondary series the variations in $\Delta E°$ are very small between different R groups.

Since the gas-phase reactions studied theoretically (eq 2) are thermoneutral, the thermodynamic barriers are zero and the calculated $\Delta E^{\ddagger}$ values correspond really to the intrinsic barriers, $\Delta E_o^{\ddagger}$. Therefore it is strictly incorrect to compare the experimental k_2 values, which reflect both the intrinsic, $\Delta E_o^{\ddagger}$, and thermodynamic barriers, $\Delta E°$, with the theoretical thermoneutral $\Delta E^{\ddagger}$ values, which represent only the $\Delta E_o^{\ddagger}$ values. However, the comparison may be justified since in solution the ion–molecule complex disappears and hence $\Delta E_o^{\ddagger}$ becomes equal to $\Delta E^{\ddagger}$.

The important results of this work can be summarized as follows:

(i) The theoretical tightness of the S_N2 TS, $d^{\ddagger}(X\cdot\cdot X)$, is relatively constant depending on the type, i.e., primary or secondary, of the reaction center carbon, irrespective of the group(s) attached to it.

(ii) The difference in the tightness between the primary and secondary carbon centers, $\Delta d^{\ddagger}(X\cdot\cdot X) = d^{\ddagger}_{sec} - d^{\ddagger}_{prim}$, is ca. 0.10 Å for the reactions involving relatively large nucleophile and leaving group.

(iii) The effects of electronegativity of the groups X and Y (Scheme 2) on the correlated activation barriers, $\Delta E_{MP}^{\ddagger}$, are additive; for strongly electronegative X and/or Y, the correlated barriers, $\Delta E_{MP}^{\ddagger}$, are invariably lower than the HF barriers, $\Delta E_{HF}^{\ddagger}$.

(iv) A satisfactory correlation with $r = 0.90$ for 11 R groups is found between the theoretical $\Delta E_{MP}^{\ddagger}$ values for the gas-phase chloride exchanges, $Cl^- + RCl \rightleftharpoons ClR + Cl^-$, and the experimental log k_2 values for the reactions of benzenesulfonates with aniline in acetonitrile at 65.0 °C ($ROSO_2C_6H_5 + C_6H_5NH_2 \rightarrow$).

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Supplementary Material Available: Detailed geometries of all structures and energies studied (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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