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Theoretical Studies on the Nucleophilic Substitution Reactions of 1-Phenylethyl Chlorides

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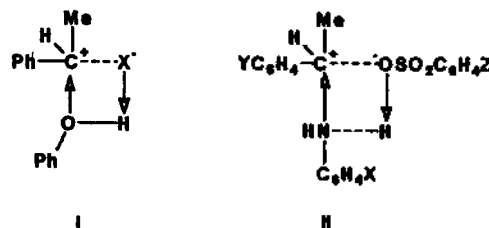
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Nucleophilic substitution reactions of 1-phenylethyl chlorides (1-PEC; $\text{YC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{Cl}$) with phenoxides ($\text{XC}_6\text{H}_4\text{O}^-$) and thiophenoxides ($\text{XC}_6\text{H}_4\text{S}^-$) are investigated theoretically using the PM3 method. The Brønsted α and β values are greater for the phenoxides indicating a more advanced reaction in the transition state (TS) than for the thiophenoxides. This is supported by a greater magnitude of ρ_X (-6.4 – -7.4) and ρ_{XY} (-0.76) for the phenoxides than for the thiophenoxides ($\rho_X = -3.6$ – -4.4 and $\rho_{\text{XY}} = -0.60$). The percentage bond order changes, $\% \Delta n^\ddagger$, suggest that the extents of bond making and breaking are similar for the phenoxides and hence the TS is symmetrical, but bond making is somewhat greater than bond cleavage for the thiophenoxides indicating an unsymmetrical TS. The reactions in the gas phase for both nucleophile series proceed by a $\text{S}_{\text{N}}2$ mechanism with a tight TS and negative charge development on the reaction center carbon, C_α . The reactions in water investigated with model systems of benzyl and 1-phenylethyl chlorides using the Cramer-Truhlar solvation model (PM3-SM3) indicate that the reactions of 1-PEC are far more complex due to enhanced stabilization of the carbocation by the methyl substitution for a benzylic hydrogen.

Introduction

Nucleophilic substitution reactions of 1-phenylethyl derivatives in solution have been studied extensively.¹ The reactions are reported to display a variety of mechanisms depending on the substituent (Y) in the substrate, nucleophile and solvent. Tidwell *et al.*^{1b,c} reported that solvolyses of 1-phenylethyl tosylates in protic solvents proceed by a stepwise mechanism in which nucleophilic solvent attack on an ion-pair plays a major role ($\text{S}_{\text{N}}2\text{C}^*$ mechanism), whereas Richard and Jencks^{1a} showed that 1-phenylethyl derivatives react with azide ion through a concerted $\text{S}_{\text{N}}2$ mechanism.

Okamoto *et al.*² observed products with retention of configuration in their phenolysis studies of 1-phenylethyl derivatives, which was rationalized by a mechanism involving a



four center transition state (TS), I, (intermolecular S_Ni mechanism). In our work on the aminolysis of 1-phenylethyl arenesulfonates³ ($YC_6H_4CH(CH_3)OSO_2C_6H_4Z$) with anilines ($XC_6H_4NH_2$) in methanol we found a large negative ρ_{XZ} value⁴ ($\rho_{XZ} = -0.60$, eq 1a), which was interpreted to indicate involvement of such a four center type TS, II, (intermolecular S_Ni mechanism).

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (1a)$$

$$\log(k_{XV}/k_{HV}) = \rho_X\sigma_X + \rho_V\sigma_V + \rho_{XV}\sigma_X\sigma_V \quad (1b)$$

The negative sign of ρ_{XZ} ⁴ is an indicative of a loose, open TS structure, whereas the large magnitude suggests a strong interaction between the nucleophile (X) and leaving group (Z) through an extra interaction route provided by a hydrogen bond in the TS, II.³ In striking contrast, the reactions of 1-phenylethyl chlorides (1-PEC) with anilines in methanol were found to proceed by the ion-pair mechanism in which the nucleophile, aniline, attacks the carbocation within the ion-pair intermediate (S_N2C^+ mechanism).⁵

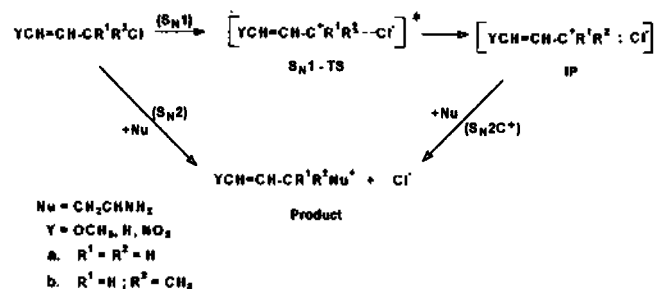
In view of the mechanistic variety exhibited by the nucleophilic substitution reactions of 1-phenylethyl derivatives in solution, it is of interest to investigate the mechanism of such reactions in the gas phase. We report here the results of our MO theoretical studies⁶ on the reactions of 1-PEC with phenoxide and thiophenoxide nucleophiles in the gas phase, eq. 2, using the PM3 method.



where $Nu^- = XC_6H_4O^-$ and $XC_6H_4S^-$
and $X = Y = H, p\text{-Cl}, m\text{-CN}, p\text{-CN}$ and $p\text{-NO}_2$.

Calculations

Because of the complex reaction systems in eq. 2 involving more than 18 heavy atoms, we adopted a semiempirical method, PM3.⁷ All the procedures used in the calculation are the same as described in a previous work.⁶ The mechanistic change-overs in solution were tested with two model systems ($YCH=CHCR^1R^2Cl$ and $CH_2=CHNH_2$ for substrate and nucleophile, respectively), Scheme 1, using



Scheme 1.

Table 1. Heats of formation (ΔH_f) of reactants, activation energies (ΔG^\ddagger) and reaction energies (ΔG°) for the reactions of 1-PEC with X-phenoxides (in kcal mol⁻¹)

Y	X	ΔH_f	Activation parameter			Reaction parameter		
		Reactants	ΔH^\ddagger	$-T\Delta S^\ddagger$	ΔG^\ddagger	ΔH°	$-T\Delta S^\circ$	ΔG°
H	H	-39.53	21.32	12.01	33.33	-1.30	4.53	3.23
	p-Cl	52.55	24.04	12.02	36.06	4.85	4.61	9.46
	m-CN	-15.68	25.70	11.99	37.69	9.71	4.61	14.32
	p-CN	-21.2	28.40	12.01	40.41	14.73	4.68	19.41
	p-NO ₂	76.96	33.11	11.83	44.94	25.43	4.25	29.68
p-Cl	H	-46.17	19.53	12.04	31.57	-1.32	4.54	3.22
	p-Cl	-59.19	22.36	12.02	34.38	4.89	4.60	9.49
	m-CN	22.32	24.09	12.03	36.12	9.83	4.60	14.43
	p-CN	-27.84	26.88	12.04	38.92	14.86	4.65	19.51
	p-NO ₂	-83.60	31.74	11.90	43.64	25.65	4.27	29.92
m-CN	H	-4.11	16.69	12.03	28.72	-1.40	4.52	3.12
	p-Cl	-17.13	19.68	12.06	31.74	4.93	4.61	9.54
	m-CN	19.74	21.45	12.11	33.56	10.11	4.57	14.68
	p-CN	14.22	24.40	12.16	36.56	15.08	4.69	19.77
	p-NO ₂	41.54	29.54	12.01	41.55	26.13	4.24	30.37
p-NO ₂	H	-4.13	16.26	12.03	28.29	-1.35	4.51	3.16
	p-Cl	-17.15	19.25	12.09	31.34	4.96	4.60	9.56
	m-CN	19.72	21.20	12.11	33.21	10.04	4.61	14.65
	p-CN	14.20	23.98	12.18	36.16	15.12	4.66	19.78
	p-NO ₂	-41.56	29.07	12.05	41.12	26.09	4.24	30.33
p-NO ₂	H	-47.82	13.11	12.44	25.55	-1.40	4.57	3.17
	p-Cl	-60.84	16.24	12.50	28.74	5.01	4.65	9.66
	m-CN	-23.97	18.19	12.53	30.72	10.29	4.63	14.92
	p-CN	-29.49	21.18	12.62	33.80	15.35	4.68	20.03
	p-NO ₂	-85.25	26.47	12.45	38.92	26.51	4.25	30.76

the Cramer-Truhlar solvation model, PM3-SM3.⁸ Due to difficulties of locating an ion-pair (IP) in the gas phase with the present PM3 method, we located S_N1 -TS and S_N2 -TS only, and hence we were unable to differentiate between the S_N1 and S_N2C^+ mechanisms. Detailed studies using *ab initio* MO method on such mechanistic differences between S_N1 and S_N2C^+ are presently in progress.

Results and Discussion

Gas-Phase S_N2 Reactions. The nucleophilic substitution reactions of 1-PEC with phenoxide and thiophenoxide nucleophiles in the gas phase, eq. 2, were found to proceed by a simple, concerted S_N2 mechanism. The potential energy surface is of a double-well type with a TS in between two stable ion-dipole (reactant and product) complexes, which is a typical energy profile for the S_N2 processes.⁹ We have determined activation parameters measured from the separated reactants level. Examination of the results in Tables 1 and 2 reveals that the barrier heights, ΔG^\ddagger , and reaction energies, ΔG° , are higher by *ca.* 4-6 kcal mol⁻¹ than the corresponding values for the gas phase S_N2 reactions of benzyl chlorides.⁹ This can be attributed to the destabilization of the TS and product by the α -Me group of 1-PEC; the α -Me group is expected to exert unfavorable effects due to steric crowding and electron donation. This latter effect suggests that the TS is a rather tight, associative

type with negative charge development on the α -carbon¹⁰ (*vide infra*, $\rho_Y > 0$). The entropy terms are practically constant irrespective of the substituents X or Y (Tables 1 and 2) and the magnitudes differ little from those corresponding values for the reactions of benzyl chlorides.⁶ The trends of changes in ΔG^\ddagger and ΔG° are quite similar to those for the benzyl chloride reactions⁶: a stronger electron acceptor X in the nucleophile leads to higher values in both ΔG^\ddagger and ΔG° , whereas a stronger electron acceptor Y in the ring lowers ΔG^\ddagger but has insignificant effect on ΔG° . Since the reactions have high activation barriers and are all endothermic with highly structured TSs (low entropies), gas-phase experimental studies will not be feasible. Linearities of the rate-equilibrium plots,¹¹ eq. 3, were good (regression coefficients $r \geq 0.99$) with the slopes, α , ranging from 0.44 (Y=

$$\delta \Delta G^\ddagger = \alpha \delta \Delta G^\circ \quad (3)$$

H) to 0.49 (Y=p-NO₂) for phenoxides and from 0.39 (Y=H) to 0.44 (Y=NO₂) for thiophenoxides. These values are similar to those corresponding values for the reactions of benzyl chlorides.⁶ Somewhat greater α values for the reactions of phenoxide series suggest that the TS occurs at a later position on the reaction coordinate for the phenoxides than for thiophenoxides. This is consistent with Bell-Evans-Polanyi principle,¹² since the more endothermic reactions of phenoxides lead to a later TS than the less endothermic reactions

Table 2. Heats of formation (ΔH_f) of reactants, activation energies (ΔG^\ddagger) and reaction energies (ΔG°) for the reactions 1-PES with X-thiophenoxides (in kcal mol⁻¹)

Y	X	H_f	Activation parameter			Reaction parameter		
		Reaction	ΔH^\ddagger	-TAS	ΔG^\ddagger	ΔH°	-TAS	ΔG°
H	H	2.58	11.11	11.87	22.98	-3.82	3.87	0.05
	Cl	-8.12	12.62	11.90	24.51	0.22	3.89	4.11
	m-CN	29.54	13.77	11.90	25.67	4.62	3.89	8.51
	p-CN	27.29	14.91	12.02	26.93	6.66	3.92	10.58
	p-NO ₂	-23.99	17.75	11.93	29.68	13.81	3.53	17.34
Cl	H	-4.06	9.22	11.88	21.10	-3.86	3.87	0.01
	Cl	-14.76	10.83	11.91	22.74	0.23	3.89	4.12
	m-CN	22.90	12.07	11.93	24.00	4.70	3.90	8.60
	p-CN	20.65	13.25	11.98	25.23	6.75	3.94	10.69
	p-NO ₂	-30.63	16.23	11.96	28.19	13.99	3.55	17.54
m-CN	H	38.01	6.25	11.89	18.14	-3.94	3.90	-0.04
	Cl	27.31	7.96	11.92	19.88	0.26	3.93	4.19
	m-CN	64.97	9.37	11.99	21.36	4.96	3.92	8.88
	p-CN	62.72	10.54	12.07	22.61	6.95	3.97	10.92
	p-NO ₂	11.44	13.64	12.00	25.64	14.43	3.55	17.98
p-CN	H	37.98	5.76	11.93	17.69	-3.98	3.88	-0.10
	Cl	27.28	7.50	12.01	19.51	0.19	3.92	4.11
	m-CN	64.94	8.89	12.00	20.89	4.79	3.90	8.69
	p-CN	62.69	10.13	12.05	22.18	6.88	3.96	10.84
	p-NO ₂	11.41	13.30	12.00	25.30	14.28	3.55	17.83
p-NO ₂	H	-5.71	2.30	12.33	14.63	-4.20	3.98	-0.22
	Cl	-16.41	4.19	12.39	16.58	0.06	3.99	4.05
	m-CN	21.25	5.70	12.39	18.09	4.84	3.95	8.79
	p-CN	19.00	7.02	12.47	19.49	6.91	3.02	10.93
	p-NO ₂	-32.28	10.40	12.36	22.76	14.49	3.61	18.10

of thiophenoxides (Tables 1 and 2).

The slope β in the Brønsted type plots^{11c,13} of ΔG^\ddagger vs proton affinities (PA) of the nucleophiles, eq. 4, provides a measure of bond making by the nucleophile in the TS.

$$\delta\Delta G^\ddagger_x = \beta\delta(\text{PA}_x) \quad (4)$$

Comparison of the β values with the corresponding values of α , eq. 3, in Table 3 shows good agreements between the two. We have also included in Table 3 the calculated percentage bond order changes, $\% \Delta n^\ddagger$ shown in eq. 5 where r^\ddagger , r_R and r_P denote bond length in the TS, reactant and product and a is the Pauling parameter, for bond making ($\% \Delta n^\ddagger_{\text{C-Nu}}$) and bond cleavage ($\% \Delta n^\ddagger_{\text{C-Cl}}$)^{6,14} using the parameter $a=0.7$.^{14c}

$$\% \Delta n^\ddagger = \frac{[\exp(-r^\ddagger/a) - \exp(-r_R/a)]}{[\exp(-r_P/a) - \exp(-r_R/a)]} \times 100 \quad (5)$$

We note in Table 3 that the extent of bond making as expressed by $\% \Delta n^\ddagger_{\text{C-Nu}}$ is rather greater than that by β for $Y=H$ (e.g. 49% vs 43% for $\text{XC}_6\text{H}_4\text{O}$ series) and this divergence is much greater for the reactions of thiophenoxides series (48% vs 37%). In view of the good agreement between α and β , the $\% \Delta n^\ddagger_{\text{C-Nu}}$ values may be considered a less reliable measure of the degree of bond making. The extents of bond-making and -breaking represented by $\% \Delta n^\ddagger$ are similar for the phenoxide series but the extent of bond making is ahead of bond cleavage for the thiophenoxide series. This means that the TSs for the phenoxide series are more symmetric than those for the thiophenoxides.

Overall, the TSs for the thiophenoxides are earlier on the reaction coordinate than for the phenoxides (*vide supra*), and the TS becomes tighter with a stronger electron acceptor substituent Y in the substrate, which is in agreement with the experimental results of S_N2 reactions at benzylic carbon in the gas phase,¹⁵ in MeOH ,¹⁶ and in 20% aqueous acetonitrile.^{18,17}

The Hammett coefficients, ρ_X and ρ_Y in eq. 6, and the cross-interaction constants, ρ_{XY} in eq. 1b,⁴ are collected in

$$\delta\Delta G^\ddagger / (-2.303RT) = \rho \sigma \quad (6)$$

Table 4. Reference to this Table reveals that the magnitude of ρ_X for the phenoxides is greater ($\rho_X = -6.5 \sim -7.4$) sug-

Table 3. The TS structures represented by various parameters for progress of the reaction

Nu	Y	X	α	β	$\% \Delta n^\ddagger_{\text{C-Nu}}$	$\% \Delta n^\ddagger_{\text{C-Cl}}$
$\text{XC}_6\text{H}_4\text{O}$	H	H	0.44	0.43	49	49(0.51) ^a
		p-NO ₂			54	55
	p-NO ₂	H	0.49	0.50	48	46
		p-NO ₂			54	51(0.49)
$\text{XC}_6\text{H}_4\text{S}$	H	H	0.39	0.37	48	42(0.58)
		p-NO ₂			53	46
	p-NO ₂	H	0.44	0.45	49	40
		p-NO ₂			54	43(0.57)

^a Values in parenthesis are bond orders, n^\ddagger .

Table 4. Simple Hammett ρ -values^a and cross-interaction constants, ρ_{XY} ^a

	X or Y	H	p-Cl	m-CN	p-CN	p-NO ₂	
$\text{XC}_6\text{H}_5\text{O}$	ρ_X	-6.45	-6.70	-7.13	-7.13	-7.44	$\rho_{XY} = 0.76$
	ρ_Y	4.39	4.11	3.92	3.72	3.39	$(-0.60)^b$
$\text{XC}_6\text{H}_5\text{S}^-$	ρ_X	-3.70	-3.89	-4.14	-4.18	-4.48	$\rho_{XY} = -0.69$
	ρ_Y	4.49	4.44	4.26	4.18	3.90	$(-0.59)^b$

^a Regression coefficients were better than 0.97 in all cases. ^b The ρ_{XY} values for the reactions of benzyl chlorides.

gesting a greater degree of bond making in the TS than that for the thiophenoxides ($\rho_X = -3.7 \sim -4.5$) in agreement with the prediction of progress of reaction based on the larger α and β values for the former.

In contrast, the magnitude of the ρ_Y values are quite similar for the two series of nucleophiles. Since ρ_Y is positive and the magnitude is similar, the negative charge developed on the α -carbon in the TS may be considered to be similar in the two reaction series of phenoxide and thiophenoxide. This is contrary to the trends shown by the extents of bond-making and -breaking reflected in the $\% \Delta n^\ddagger$ values; the $\% \Delta n^\ddagger_{\text{C-Nu}}$ values are similar for the two series of nucleophiles but the $\% \Delta n^\ddagger_{\text{C-Cl}}$ values are smaller for the thiophenoxides than for the phenoxides suggesting that the TSs are somewhat tighter and hence the negative charge developed in the TS should be greater for the thiophenoxides than for the phenoxides. Thus the similar extent of bond making predicted by the similar magnitude of $\% \Delta n^\ddagger_{\text{C-Nu}}$ for the two series of nucleophiles does not seem plausible, especially in view of a lower degree of bond making predicted for the thiophenoxides by both α and β parameters.

Finally the magnitude of ρ_{XY} is greater for the phenoxides than that of the thiophenoxides. This is again in agreement with the predictions based on α and β , since a greater magnitude of ρ_{XY} is believed to indicate a greater extent of bond making in the TS.⁴ The sign and magnitude of the ρ_{XY} values are consistent with those expected for a normal, concerted S_N2 reaction.⁴ The magnitudes of the ρ_{XY} values are however slightly greater than those for the corresponding values of the benzyl chloride reaction series.⁶ This could be an indication of slightly greater extent of bond making for the reactions of 1-PEC than for the reactions of benzyl chlorides, which is in line with a later TS, *i.e.*, a tighter bond formation, for the reactions at a sterically more hindered reaction center.¹⁸ This is reasonable and, as has already noted above, is consistent with the prediction based on the Bell-Evans-Polanyi principle¹² (*vide supra*) since a sterically crowded TS will lead to a greater activation barrier and also a more endothermic reaction due to formation of a higher energy product.

We have determined α -($\text{YC}_6\text{H}_4\text{CD}(\text{CH}_3)\text{Cl}$) and β -secondary deuterium ($\text{YC}_6\text{H}_4\text{CH}(\text{CD}_3)\text{Cl}$) kinetic isotope effects (KIE) for the two extreme cases of $X=Y=H$ (for the lowest degree of bond making) and $X=Y=\text{NO}_2$ (for the highest extent of bond making). The results in Table 5 reveal that the β -deuterium KIEs are consistent with those predicted for the normal S_N2 reactions.¹⁹ The α -deuterium KIEs are all of an inverse type,^{4c} $k_H/k_D < 1.0$; for the thiophenoxide series the k_H/k_D values are unusually small, most probably due to a re-

Table 5. α - and β -deuterium secondary kinetic isotope effects (KIE) for the reactions of 1-PEC ($\text{YC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{Cl}$) with phenoxides and thiophenoxides

	Substituents		$k_{\text{H}}/k_{\text{D}}$	
	X	Y	$\text{XC}_6\text{H}_5\text{O}^-$	$\text{XC}_6\text{H}_5\text{S}^-$
α -KIE	H	H	0.877	0.586
	NO_2	NO_2	0.934	0.556
β -KIE	H	H	1.013	1.030
	NO_2	NO_2	1.013	1.017

lately tight TS with a bulky reaction center of the nucleophile with a second row element, S.

Analyses of the changes in the $k_{\text{H}}/k_{\text{D}}$ values with changes in the substituents ($X=Y$) are instructive. In a recent paper, Westaway *et al.*²⁰ reported that the change in the $k_{\text{H}}/k_{\text{D}}$ value with changes in the substituents in the nucleophile and the substrate is greater when the $S_{\text{N}}2$ TS is more symmetrical, i.e., $\% \Delta n^{\ddagger}_{\text{C-Nu}}$ $\% \Delta n^{\ddagger}_{\text{C-Cl}}$ in Table 3. The results in Table 5 are in line with this expectation, since a more symmetrical TS with the phenoxides leads to a slightly larger variation of $k_{\text{H}}/k_{\text{D}}$ when substituents are varied from $X=Y=\text{H}$ to $X=Y=\text{NO}_2$. Westaway *et al.*²⁰ have also suggested based on their kinetic isotope effect studies that a significant change only occurs in the weaker reacting bond in the $S_{\text{N}}2$ TS when substituents are varied and the variation of $k_{\text{H}}/k_{\text{D}}$ arises mostly from the reacting bond change of a stronger bond. The bond energies (BEs) of the C-O, C-S and C-Cl bonds are 85, 65 and 81 kcal mol⁻¹ respectively. Since the BEs for C-O and C-Cl are similar, we expect a more symmetrical $S_{\text{N}}2$ TS for the phenoxides. For the thiophenoxides, the C-Cl bond is much stronger than the C-S bond so that there will be a significant change in the C-S bond but little change in the C-Cl bond in the $S_{\text{N}}2$ TS when substituents are varied. This is in agreement with the smaller variation of $\% \Delta n^{\ddagger}_{\text{C-Cl}}$ (42→43) than that of $\% \Delta n^{\ddagger}_{\text{C-Nu}}$ (48→54) for the thiophenoxide when substituents are changed from $X=Y=\text{H}$ to $X=Y=\text{NO}_2$. They also predicted that the stronger bond (C-Cl) will be shorter (bond order is greater) than the weaker bond (C-S) (bond order is smaller) in the reactant-like, unsymmetrical, $S_{\text{N}}2$ TS, which is also in agreement with our results in Table 3. In this connection, it should be noted that bond orders in the TS, n^{\ddagger} , are related to the $\% \Delta n^{\ddagger}$ values by eqs. 7.

$$n^{\ddagger}_{\text{C-Cl}} = 1 - \% \Delta n^{\ddagger}_{\text{C-Cl}} \quad (7a)$$

$$n^{\ddagger}_{\text{C-Nu}} = \% \Delta n^{\ddagger}_{\text{C-Nu}} \quad (7b)$$

The detailed analysis of reacting bond changes in the $S_{\text{N}}2$ TS when substituents are changed can not be applied based on our $\% \Delta n^{\ddagger}$ data in Table 3, since the conservation of bond orders, eq. 8, is not strictly held in our results.

$$\sum n_i^{\ddagger} = n^{\ddagger}_{\text{(C-Cl)}} + n^{\ddagger}_{\text{(C-Nu)}} = 1.0 \quad (8)$$

Nucleophilic Reactions of 1-PEC in Solution.

The enthalpies of activation, ΔH^{\ddagger} , are calculated for model reaction systems of $S_{\text{N}}1$ and $S_{\text{N}}2$ processes (shown in Scheme 1) in water using the Cramer-Truhlar solvation model⁸ with the PM3-SM3 method. The results are sum-

Table 6. Activation enthalpies in water, ΔH^{\ddagger} , calculated using the Cramer-Truhlar solvation model (PM3-SM3) on $S_{\text{N}}1$ and $S_{\text{N}}2$ reactions with model systems of $\text{YCH}=\text{CHCR}^1\text{R}^2\text{Cl}$ with $\text{NH}_2\text{CH}=\text{CH}_2$

R ¹	R ²	Y	ΔH^{\ddagger} (kcal mol ⁻¹)	
			$S_{\text{N}}1$	$S_{\text{N}}2$
H	H	H	40.4	30.4
H	H	NO_2	50.2	30.9
H	H	OCH_3	23.0	28.9
H	CH_3	H	33.1	34.3
H	CH_3	NO_2	-	34.2
H	CH_3	OCH_3	20.7	-

marized in Table 6. The competitive nature of $S_{\text{N}}1$ and $S_{\text{N}}2$ processes of the reactions of benzyl chlorides (modeled with $\text{YCH}=\text{CHCH}_2\text{Cl}$, III) in water is well reproduced in the results shown; for the reaction of III with a strong electron acceptor Y ($Y=\text{NO}_2$), the concerted $S_{\text{N}}2$ process is much more favorable, by ca. 20 kcal mol⁻¹, whereas for III with a strong donor Y ($Y=\text{OCH}_3$), the $S_{\text{N}}1$ process becomes more favored (by 6 kcal mol⁻¹). The barrier height difference is reduced to ca. 10 kcal mol⁻¹ in favor of the $S_{\text{N}}2$ process when there is no substituent ($Y=\text{H}$).

In contrast, however, for the reactions of 1-PEC (modeled with $\text{YCH}=\text{CH}(\text{CH}_3)\text{Cl}$, IV) two extreme situations are obtained; when Y is a strong acceptor ($Y=\text{NO}_2$) only the $S_{\text{N}}2$ TS was obtained, whereas when Y is a strong donor ($Y=\text{OCH}_3$) only the $S_{\text{N}}1$ process was found to be possible. In between these two extreme cases, for $Y=\text{H}$ the two processes become competitive with similar activation barriers for the $S_{\text{N}}1$ and $S_{\text{N}}2$ pathways. These are consistent with the experimentally observed mechanistic change-overs in solution. As we noted above, it is difficult to characterize the ion-pair intermediate with our method so that the $S_{\text{N}}1$ process in Table 6 can be either a classical $S_{\text{N}}1$ mechanism with rate-limiting bond cleavage, or a $S_{\text{N}}2\text{C}^{\ddagger}$ mechanism^{5b} with rate-limiting nucleophilic attack on the carbocation within the ion-pair (IP) in Scheme 1. The differences in the mechanistic behaviors between the reactions of III and IV are due to substitution of CH_3 for one of the hydrogen atom on C_{α} in III. Since in water the partially charge separated state (TS) is strongly stabilized, the TSs in the reactions of both III and IV in water have a loose, open structure with cationic charge on the reaction center carbon. This positive charge is stabilized by both α -methyl group in IV and by a strong electron donor Y in both III and IV.

The enhanced stabilization of the cationic charge by the α -Me group in IV leads to much more $S_{\text{N}}1$ -like TS for IV than III in water. This is in contrast to the gas-phase reactions of 1-PEC, which reacts by a concerted displacement ($S_{\text{N}}2$) mechanism irrespective of the substituent Y involving a tight TS with negative charge development on the α -carbon. We conclude that the mechanism of the nucleophilic substitution reactions of 1-PEC is strongly dependent on the substituent (Y) in the substrate, the nucleophile and the reaction medium.

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