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Theoretical Studies on the Acyl Transfer Reactions Involving a Tetrahedral Intermediate[†]

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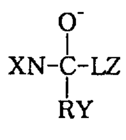
Received August 30, 1995

Theoretical studies of the effect of the nonleaving group (RY) on the breakdown mechanism of the tetrahedral anionic intermediate, T^-, formed by the addition of a less basic phenoxide nucleophile (X) to phenyl benzoates with a more basic phenoxide leaving group (Z) have been carried out using the PM3 MO method. The identity acyl transfer reactions (X=Z) are facilitated by an electron-withdrawing RY whereas they are inhibited by an electron-donating RY group. The results of non-identity acyl transfer reactions indicate that a more electron-donating RY group leads to a greater lowering of the higher barrier, TS2, with a greater degree of bond cleavage, and a greater negative charge development on the phenoxide oxygen atom, whereas the opposite is true for a more electron-withdrawing RY group, *i.e.*, leads to a greater lowering of the lower barrier, TS1. The results provide theoretical basis for the signs of $\rho_{XY}(>0)$ and $\rho_{YZ}(<0)$ observations.

Introduction

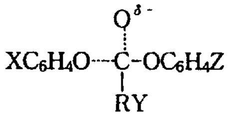
Two distinct reaction pathways have been suggested for nucleophilic substitution at a carbonyl carbon.[1] One step concerted mechanism proceeds through a tetrahedral transition state (TS),[2] whereas two-step addition-elimination processes occur via a tetrahedral intermediate, I.[3] In the step-wise pathway, a mechanistic change-over can take place from rate-limiting breakdown to formation of the intermediate depending on (i) relative basicities (pK_a) of the nucleophile (NX) and nucleofuge (LZ) and (ii) electron-donating or electron-withdrawing power of the nonleaving group (RY).[3]



$$\begin{array}{c} O^- \\ | \\ XN\text{-}C\text{-}LZ \\ | \\ RY \end{array}$$

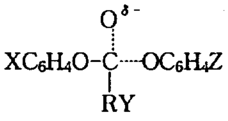
I

In a previous work[4] we examined theoretically the effects of relative basicities (or proton affinities) of the nucleophile and nucleofuge on the acyl transfer mechanism using gas-phase reactions of a series of substituted phenoxide anions ($NX={}^-OC_6H_4X$) with meta-nitro, para-nitro and 3,4-dinitro phenyl formates ($LZ=OC_6H_4Z$ with $Z=m\text{-}NO_2$, $p\text{-}NO_2$ and $3,4\text{-}(NO_2)_2$ for RY=H). The results suggested that whichever is the lower basicity phenoxide anion the TS level involving partial bond cleavage of that lower basicity phenoxide gives the lower TS. Thus the depression of the TS1 level due to a decrease in the basicity of the phenoxide anion nucleophile with a constant nucleofuge may lead to a lower TS1 level than TS2 and the mechanistic change from rate-limiting formation to breakdown of the tetrahedral intermediate, T^-, can take place. It was also found that solvation by one water molecule leads to a greater degree of depression of the second barrier, TS2, than that of TS1 and the reaction is expected to change to rate-limiting formation of T^- (or to a concerted process when T^- becomes extremely unstable) as experimentally observed in solution for all the compounds studied.[5]



$$\begin{array}{c} O^{\delta-} \\ \vdots \\ XC_6H_4O\cdots C\text{-}OC_6H_4Z \\ | \\ RY \end{array}$$

TS1



$$\begin{array}{c} O^{\delta-} \\ \vdots \\ XC_6H_4O\text{-}C\cdots OC_6H_4Z \\ | \\ RY \end{array}$$

TS2

On the other hand, it has been shown experimentally that as the electron withdrawing power of the nonleaving group in the addition intermediate, RY, is decreased, or conversely as the electron donating power of RY is increased, the higher basicity phenoxide group expulsion is favored *i.e.*, the TS2 is stabilized more than TS1 if $pK_a(Z)>pK_a(X)$.[4]

Since the effect of RY on the degree of bond cleavage in TS1 (d_1^*) and TS2 (d_2^*) is important in determinig the sign of ρ_{XY} and ρ_{YZ} in Eq. (1),(6,7) which in turn is important as a mechanistic criteria, we decided to study the effect of RY on the mechnism of the acyl transfer reactions involving a tetrahedral intermediate in a greater detail.

[†] Determination of Reactivity by MO theory. Part 94. Part 93, Lim, W. M.; Kim, W. K.; Jung, H. J.; Lee, I. *Bull. Korean Chem. Soc.*, **1995**, *16*, 252.

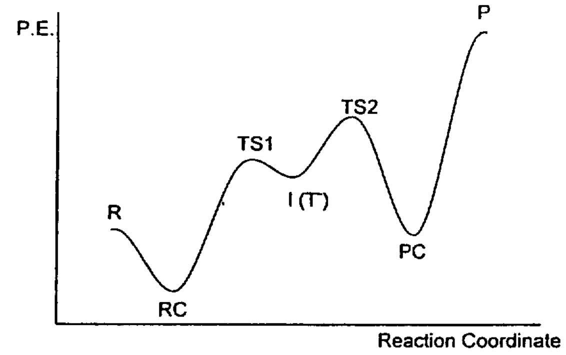


Figure 1. Various equilibrium states along the reaction coordinate for the reactions of phenyl benzoate with phenoxide.

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

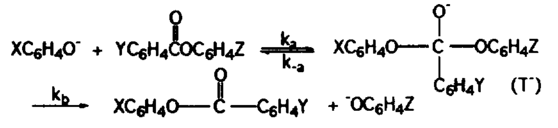
where i, j=X, Y or Z in TS1 and TS2. It has been shown that ρ_{XY} and ρ_{YZ} can be alternatively defined as Eqs. (2a) and (2b), and the signs provide useful mechanistic

$$\rho_{XY} = \frac{\partial^2 \log k_{XY}}{\partial\sigma_X \partial\sigma_Y} = \frac{\partial\rho_X}{\partial\sigma_Y} \qquad (2a)$$

$$\rho_{YZ} = \frac{\partial^2 \log k_{YZ}}{\partial\sigma_Y \partial\sigma_Z} = \frac{\partial\rho_Z}{\partial\sigma_Y} \qquad (2b)$$

criteria : $\rho_{XY}>0$ and $\rho_{YZ}<0$ for rate-limiting breakdown of T^-, and the signs reverse to $\rho_{XY}<0$ and $\rho_{YZ}>0$ for rate-limiting formation of T^-, which may become concerted one-step mechanism when the lifetime of the T^- becomes insignificant.(6,7)

In this work, we examined the effect of RY group on the acyl transfer mechanism using three sets of nucleophile-nucleofuge combinations (X : Z), Eq. (3).



(3)

X : Z = NO_2 : H, NO_2 : CH_3, NO_2 : OCH_3
Y = OCH_3, H or NO_2

Calculations

The reaction systems we investigated in this work contain 22-31 heavy atoms so that the use of *ab initio* method is out of the question and a semiempirical MO method, PM3,[8] was used throughout. All equilibrium structures including TSs were fully optimized and were characterized by force calculation and identifying all positive and only one negative eigenvalue in the Hessian matrix.[9] The distance between phenoxy oxygen of the nucleophile and the carbonyl carbon was taken as the reaction coordinate. The TSs were located by the reaction coordinate method and refined by the use of NLLSQ[10] or TS[11] option in the MOPAC program.[12]

Various equilibrium states along the reaction coordinate are schematically shown in Figure 1. The results and discussions are presented in terms of energy changes, ΔE_C, $\Delta E_R^{\neq}$ and $\Delta E_I^{\neq}$, by converting the corresponding enthalpy changes. For example, activation enthalpies from the reactants and the intermediate, $\Delta H_R^{\neq}$ and $\Delta H_I^{\neq}$ are converted to the corresspoonding activation energies (at T=298 K) by taking into account the changes in molecularity involved in the activation processes,

$$\Delta E_R^{\neq} = \Delta H_R^{\neq} + RT \qquad (4a)$$

$$\Delta E_I^{\neq} = \Delta H_I^{\neq} \qquad (4b)$$

Eqs. (4a) and (4b).[13] The bond length changes in going from the intermediate to the TS ($d^{\neq}$-d_I) are denoted as $\Delta d^{\neq}$. Symbols Δ and δ are used to represent differences between equilibrium states and between different Y substituents which are all at para position, respectively. The energy changes used are defined in Eqs. (5), where subscripts RC, R, and I denote reactant complex, reactant, and intermediate, respectively. The basicities in water, pK_a, of phenols (in water at 25.0 ℃)[14] and the basicities in the gas-phase, proton affinities, of phenoxide anion, PA, (PM3) used

$$\Delta E_C = E_{RC} - E_R \qquad (5a)$$

$$\Delta E_R^{\neq} = E^{\neq} - E_R \qquad (5b)$$

$$\Delta E_I^{\neq} = E^{\neq} - E_I \qquad (5c)$$

in this work are listed in Table 1. The two measures of the basicity, pK_a and PA, vary in parallel so that the effects of relative basicity on the TS structure can be discussed in terms of PA or pK_a.

Table 1. The pK_a values (in water at 25.0 ℃) and proton affinities (PA, PM3) for phenols and phenoxides, respectively

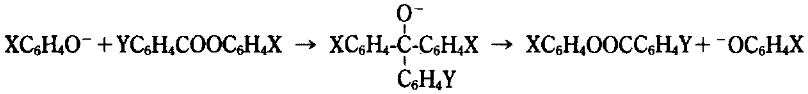
X	pK_a	PA (kcal/mol)
p-CH_3	10.23	−376.5
p-CH_3O	10.20	−379.4
H	9.99	−376.0
p-NO_2	7.15	−303.6

Results and Discussion

Identity Acyl Transfer Reactions. In this type of reaction, the phenoxide anion nucleophile and nucleofuge are identical so that there is no thermodynamic driving force, $\Delta E^{\circ}=0$, and the activation barrier represents an intrinsic barrier, $\Delta E_o^{\neq}$.[15] Three cases, X=Z=H, CH_3O and NO_2, are studied for Y=H, CH_3O and NO_2. The energetics and bond length changes are summarized in Tables 2 and 3, respectively. Examination of Table 2 indicates that the methoxy group invariably (X=Z=OCH_3 as well as Y=OCH_3) elevates the barrier height, $\Delta E_R^{\neq}$. On the other hand, the nitro group depresses the barrier height only when it is at Y (Y=NO_2). These trends are in line with the experimental results of the faster rate for *p*-nitro benzoate and the lower rate for p-methoxy benzoate,(7c,16) which are also in agreement with the stabilizing and destabilizing effects of Y=p-NO_2 and p-CH_3O group on the anionic TS and intermediate, T^-.

The stability of intermediates, $\Delta E_I^{\neq}$, is similar for X=Z=H and X=Z=OCH_3 as well as for Y=H and Y=CH_3O. The well-depth of intermediates is the shallowest for X=

Table 2. The energetics for identity acyl transfer reactions (X=Z) with three different Y groups.[a]



$$XC_6H_4O^- + YC_6H_4COOC_6H_4X \rightarrow XC_6H_4\text{-}\overset{\overset{O^-}{|}}{\underset{\underset{C_6H_4Y}{|}}{C}}\text{-}C_6H_4X \rightarrow XC_6H_4OOCC_6H_4Y + {}^-OC_6H_4X$$

	X=Z=H			X=Z=OCH_3			X=Z=NO_2		
	Y=H	CH_3O	NO_2	H	CH_3O	NO_2	H	CH_3O	NO_2
ΔH_f	−66.10	−104.45	−79.81	−144.04	−122.35	−150.97	−111.66	−150.12	−117.24
$\Delta H_f(I)$	−64.83	−102.91	−81.82	−140.87	−178.71	−157.46	−106.75	−144.25	−120.61
$\Delta E_C{}^b$	−17.2	−18.1	−23.7	−17.2	−18.0	−23.2	−15.8	−16.4	−20.8
$\Delta E_R{}^{*b}$	6.7	7.0	−4.1	8.4	8.8	−1.9	7.7	8.0	0.7
$\Delta E_I{}^{*b}$	4.9	4.2	4.2	4.6	4.5	4.0	2.1	1.4	3.4

[a] Energies in kcal/mol. [b] $\Delta E_C = E_{RC} - E_R$, $\Delta E_R{}^* = E^* - E_R$ and $\Delta EI^* = E^* - E_I$ where R, RC and I denote reactant, reactant complex and intermediate, respectively.

Table 3. The bond length (Å) for identity acyl transfer reactions (X=Z) with three different Y groups

		Y=H			OCH_3			NO_2		
X=Z		TS	I	$\Delta d_I{}^{*a}$	TS	I	$\Delta d_I{}^*$	TS	I	Δd_I
	d(C-Nu)	1.825		0.362	1.821		0.359	1.815		0.349
H			1.463			1.462			1.466	
	d(C-L)	1.417		−0.046	1.461		−0.001	1.411		−0.055
	d(C-Nu)	1.799		0.336	1.796		0.334	1.789		0.332
OCH_3			1.463			1.462			1.457	
	d(C-L)	1.419		−0.044	1.419		−0.043	1.414		−0.043
	d(C-Nu)	1.750		0.270	1.742		0.264	1.797		0.325
NO_2			1.480			1.478			1.472	
	d(C-L)	1.428		−0.052	1.429		−0.049	1.417		−0.055

[a] $\Delta d_I{}^* = d^* - d_I$.

Table 4. Relative barrier heights ($\Delta E_{II}{}^*$) and bond stretching (Δd^*) relative to the tetrahedral intermediates.[a]

	X=NO_2 : Z=H				X=NO_2 : Z=CH_3				X=NO_2 : Z=OCH_3			
Y	$\delta\Delta E_{I1}{}^{*c}$	$\delta\Delta E_{I2}{}^*$	$\delta\Delta d_1{}^*$	$\delta\Delta d_2{}^*$	$\delta\Delta E_{I1}{}^*$	$\delta\Delta E_{I2}{}^*$	$\delta\Delta d_1{}^*$	$\delta\Delta d_2{}^*$	$\delta\Delta E_{I1}{}^*$	$\delta\Delta E_{I2}{}^*$	$\delta\Delta d_1{}^*$	$\delta\Delta d_2{}^*$
OCH_3	−0.18	−1.63	−0.002	0.006	−0.09	−0.10	−0.004	0.010	−0.22	−0.28	0.004	0.068
H[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	(0.62)	(7.36)	(0.178)	(0.383)	(0.66)	(6.31)	(0.177)	(0.393)	(0.85)	(7.02)	(0.196)	(0.358)
NO_2	0.71	1.02	0.067	0.058	0.67	0.73	0.068	0.061	0.74	0.97	0.065	0.055

[a] Δ denotes changes relative to the value for the intermediate (T^-) and δ denotes changes relative to the value for Y-H. [b] The $\Delta E_i{}^*$ and $\Delta d_i{}^*$ values where $i=1$ or 2 for Y=H are shown in parenthesis. [c] Energies are in kcal/mol and bond lengths are in Å.

Z=NO_2, but is the deepest when X=Z=NO_2 and Y=NO_2 as well. The three nitro groups within an intermediates, T^-, seems to effectively delocalize the anionic charge within the tetrahedral intermediate, T^-, and the breakdown of T^- becomes more difficult, *i.e.*, the barrier becomes higher relative to the stabilized intermediate.

The bond length changes, Δd^* in Table 3, reveal that they vary proportionally with the changes in the well-depth of T^- as X=Z is varied from H to NO_2. This is again a manifestation of the well-known proportionality between the intrinsic barrier ($\Delta E_o{}^*$) and the deformation energy, the major part of which is the bond stretching energy, $\Delta E_{str}{}^*$.[17]

Non-Identity Acyl Transfer Reactions. We have varied three phenoxide nucleofuges in the increasing order of basicity, Z=H, CH_3 and OCH_3, with a fixed phenoxide nucleophile of the lowest basicity, X=NO_2 (Table 1). The reactions are therefore all endothermic ($\Delta E_o > 0$) and, as the energetics in Table 4 (for Y=H) and the energy profile along the reaction coordinate in Figure 1 show, the reactions proceed by a triple-well type of potential energy surface with a higher second barrier so that all the reactions proceed by a step-wise mechanism with rate-limiting breakdown of

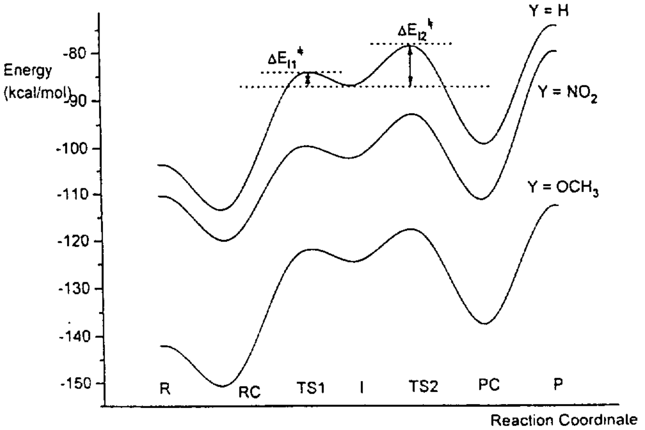
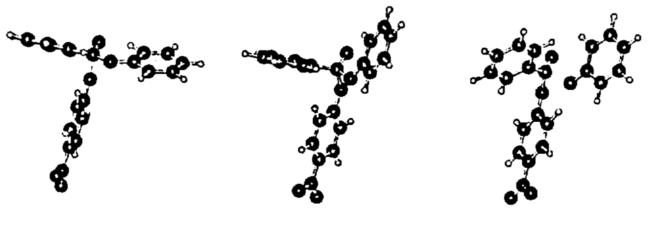


Figure 2. Energy profile for the reactions of phenyl benzoates with *p*-nitrophenoxide ion ($X=NO_2:Z=H$).



TS1 Intermediate (T^-) TS2

Figure 3. Transition state and intermediate (T^-) structures for the reaction of phenyl benzoate with phenoxide anion. ($X=NO_2$, $Y=Z=H$).

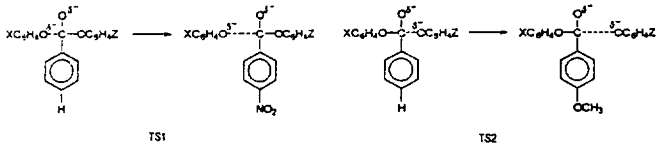
the anionic tetrahedral intermediate, T^-.

The main objective of this work is the analysis of the effects of the nonleaving group, RY in **I**, on the relative energy barriers, $\Delta E_{I1}^{\neq}$ and $\Delta E_{I2}^{\neq}$, as we noted in the Introduction. Thus the forward reactions of those investigated in this work are well suited for our purpose. Obviously the reverse processes should provide examples of the step-wise mechanism with rate-limiting formation, and the reverse applications of the present results should provide informations readily for such type of reactions.

Energy profiles for the reactions of phenyl benzoates with *p*-nitrophenoxide anion nucleophile ($Z=H$; $X=NO_2$) and the typical TS structures (for $Y=H$) are shown in Figures. 2 and 3, respectively.

The relative barrier heights, $\Delta E_I^{\neq}$, and bond stretching, $\Delta d^{\neq}$, relative to the anionic intermediate, T^-, summarized in Table 4, disclose very important and interesting trends of the effects of the nonleaving group, RY in **I**, on the energetic and structural changes of the two TSs, TS1 and TS2.

(i) Both barriers, TS1 and TS2, are depressed by an electron-donating Y whereas they are elevated by an electron-withdrawing Y group. However, the higher barrier (TS2) corresponding to the rate-limiting step, which is in these cases the expulsion of a more basic phenoxide group (Z), is depressed more when Y is electron-donating, whereas it is elevated when Y is electron-withdrawing than the other lower barrier, TS1. The net effects are therefore expulsion of the more basic pheoxide is favored by an electron-donating Y whereas expulsion of the less basic phenoxide is favored by an electron-withdrawing Y from T^-.



$\delta\sigma_Y(=\sigma(Y=NO_2)-\sigma(Y=H))>0$
$\delta\Delta d_1^{\neq}>0$
$\delta\Delta q^{\neq}(O^1)<0$
$\delta\rho_X>0\ (\delta\beta_X<0)$

$\delta\sigma_Y(=\sigma(Y=OCH_3)-\sigma(Y=H))<0$
$\delta\Delta d_2^{\neq}>0$
$\delta\Delta q^{\neq}(O^3)<0$
$\delta\rho_Z>0\ (\delta\beta_Z<0)$

$$\rho_{XY}=\frac{\partial\rho_X}{\partial\sigma_Y}=\frac{(+)}{(+)}>0 \qquad \rho_{YZ}=\frac{\partial\rho_Z}{\partial\sigma_Y}=\frac{(+)}{(-)}<0$$

Scheme 1.

(ii) Bond cleavage increases in TS2 ($\delta\Delta d_2^{\neq}>0$), whereas it decreases in TS1 ($\delta\Delta d_1^{\neq}<0$), when Y is a more electron-donating group ($\delta\sigma_Y<0$). In terms of ρ_Z (ρ_{lg}) and ρ_X (ρ_{nuc}) these correspond to a more positive ρ_Z and a more negative ρ_X, $\delta\rho_Z>0$ and $\delta\rho_X<0$, respectively, Scheme 1. According to the definition of ρ_{XY} and ρ_{YZ}, Eqs. (2a) and (2b), the signs are thus given by Eqs. (6a) and (6b).

$$\rho_{XY}=\frac{\partial\rho_X}{\partial\sigma_Y}=\frac{(-)}{(-)}>0 \tag{6a}$$

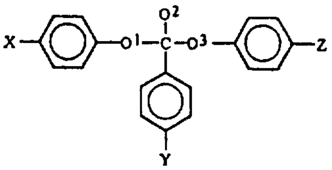
$$\rho_{YZ}=\frac{\partial\rho_Z}{\partial\sigma_Y}=\frac{(+)}{(-)}<0 \tag{6b}$$

For nucleofuges $Z=OCH_3$, $\delta\Delta d_1^{\neq}$ is slightly positive but the relative trends are similar in Table 4. Likewise, when Y is a more electron withdrawing group ($\delta\sigma_Y>0$) bond cleavage increases more in TS1 ($\delta\rho_X>0$) than that in TS2. In this case $\delta\Delta d_2^{\neq}$ is also positive so that ρ_Z also increases, $\delta\rho_Z>0$, but the magnitude of the increase in ρ_X is greater than that in ρ_Z.

Changes in the atomic charges, $\Delta q^{\neq}=q^{\neq}-q_I$, of the three oxygen atoms involved on going from the intermediate to TS1 and TS2 are summarized in Table 5.

Examination of Table 5 reveals that as we change substituent Y from H to OCH_3, the oxygen atom on the more basic phenoxide, O^3 on the nucleofuge in TS2, is seen to become more negative ($\delta\Delta q_3^{\neq}<0$), whereas that on the less-basic pheoxide, O^1 on the nucleophile in TS1, becomes less negative ($\delta\Delta q_1^{\neq}>0$), for all nucleofuges, $Z=H$, CH_3 and OCH_3. This provides a strong support for an increased bond cleavage, and hence a greater positive ρ_Z, ($\delta\Delta d_2^{\neq}>0$ and $\delta\rho_Z>0$) in TS2 and an increased bond formation, and hence a greater negative ρ_X ($\delta\Delta d_1^{\neq}<0$ and $\delta\rho_X<0$) in TS1 for $Y=OCH_3$ compared to those for $Y=H$; in effect an electron-donor Y substituent leads to later TSs for both TS1 and TS2. In constrast, when Y is changed to an electron-acceptor, $Y=NO_2$, a greater increase in the negative charge on O^1 (TS1) than on O^3 (TS2) is obtained, indicating that the decrease in the extent of bond making, *i.e.*, the decrease in the negative ρ_X value ($\delta\rho_X>0$) is greater than the increase in the positive ρ_Z ($\delta\rho_Z>0$); thus $\delta\Delta d_1^{\neq}>0$ and $\delta\rho_X>0$ but $|\delta\rho_X|>|\delta\rho_Z|$. These trends are consistent with those expected from the results of energy changes (Table 2) and bond length changes (Table 3) discussed above.

Table 5. $\Delta q^{\neq}$ $(=q^{\neq}-q_I)$ values (in electronic unit) for carbonyl carbon and oxygen atoms



	$X=NO_2:Z=H$											
	TS1				Intermediate[a]				TS2			
Y	C	O^1	O^2	O^3	C	O^1	O^2	O^3	C	O^1	O^2	O^3
OCH_3	0.022	−0.116	0.066	0.025	0.0 (0.513)	0.0 (−0.239)	0.0 (−0.634)	0.0 (−0.297)	0.028	0.009	0.151	−0.242
H	0.021	−0.117	0.065	0.026	0.0 (0.513)	0.0 (−0.240)	0.0 (−0.631)	0.0 (−0.297)	0.033	0.015	0.149	−0.223
NO_2	0.023	−0.155	0.094	0.034	0.0 (0.504)	0.0 (−0.236)	0.0 (−0.631)	0.0 (−0.296)	0.029	0.020	0.178	−0.255
	$X=NO_2:Z=CH_3$											
OCH_3	0.021	−0.114	0.063	0.025	0.0 (0.517)	0.0 (−0.241)	0.0 (−0.633)	0.0 (−0.296)	0.026	0.013	0.161	−0.251
H	0.021	−0.116	0.065	0.026	0.0 (0.513)	0.0 (−0.240)	0.0 (−0.632)	0.0 (−0.297)	0.026	0.010	0.155	−0.245
NO_2	0.023	−0.154	0.093	0.034	0.0 (0.504)	0.0 (−0.236)	0.0 (−0.631)	0.0 (−0.296)	0.0189	0.013	0.184	−0.277
	$X=NO_2:Z=OCH_3$											
OCH_3	0.023	−0.126	0.073	0.023	0.0 (0.513)	0.0 (−0.237)	0.0 (−0.635)	0.0 (−0.297)	0.038	0.001	0.177	−0.239
H	0.023	−0.127	0.071	0.029	0.0 (0.512)	0.0 (−0.238)	0.0 (−0.633)	0.0 (−0.297)	0.033	0.013	0.143	−0.210
NO_2	0.024	−0.164	0.100	0.036	0.0 (0.504)	0.0 (−0.235)	0.0 (−0.632)	0.0 (−0.296)	0.030	0.017	0.169	−0.241

[a] The atomic charges in the intermediate, q_I, are shown in parenthesis.

In effect an electron donating RY group leads to later TSs whereas an electron withdrawing RY group leads to an earlier TS for TS1 but a later TS for TS2. These results of the present work therefore provide a theoretical basis for the positive ρ_{XY} for an electron-withdrawing RY group and negative ρ_{YZ} for an electron donating RY group established qualitatively based on experimental trends for the step-wise mechanism with rate-limiting breakdown of the tetrahedral intermediate.(7a)

Now for the reverse reactions listed in Table 4, the roles of nucleophile and nucleofuge are interchanged; for example the first reaction now becomes $X=H$ and $Z=NO_2$ and the reaction proceeds *via* rate-limiting formation of T^-. For such processes the changes in $\Delta E_I^{\neq}$ and $\Delta d^{\neq}$ for $Y=OCH_3$ relative to $Y=H$ should lead to the reversed signs for ρ_{XY} (<0) and ρ_{YZ} (>0) from those of the processes with rate-limiting breakdown of T^-. If the intermediate, T^-, becomes less and less stable, the second barrier (TS2) in this type of reaction will eventually disappear and the reaction should become a concerted one, *i.e.*, an S_N2 type process. Indeed, we observed the signs of ρ_{XY} (<0) and ρ_{YZ} (>0) for S_N2 processes as expected from this argument.[6]

Besides the reversed sign assignments of ρ_{XY} and ρ_{YZ} for the rate-limiting breakdown and formation mechanisms, there is large difference in the magnitude of ρ_X (ρ_{nuc}) or β_X (β_{nuc}) and ρ_Z (ρ_{lg}) or β_Z (β_{lg}). The magnitude of ρ_X (β_X) and ρ_Z (β_Z) values are much greater for the rate-limiting breakdown mechanism, as have been experimentally observed.(3,16) For this mechanism, application of steady-state approximation to T^- with the assumption of $k_{-a} \gg k_b$ in Eq. (3) leads to the complex macroscopic rate constant, $k_2=(k_a/k_{-a})k_b=K\cdot k_b$. For example, it can be shown that the magnitude of ρ_X (k_2) is much greater than that of ρ_X (k_a), which is the value expected for the rate-limiting formation processes.

$$\rho_X(k_2)=\frac{\partial \log k_2}{\partial \sigma_X}=\frac{\partial \log k_a}{\partial \sigma_X}-\frac{\partial \log k_{-a}}{\partial \sigma_X}+\frac{\partial \log k_b}{\partial \sigma_X}$$
$$=(-)-(+)+(-) \tag{7}$$

Eq. (7) indicates that the magnitude of $\rho_X(k_2)$ for the rate-limiting breakdown processes is larger by approximately three times than that for $\rho_X(k_a)$ for the rate-limiting formation processes, since the three terms in Eq. (7) are additive to give a greater negative value for $\rho_X(k_2)$ derived from the experimentally observed macroscopic rate constant, k_2. Similar arguments lead to much larger magnitude also for β_X, ρ_Z as well as β_Z for the rate-limiting breakdown processes.(3,16) Thus in the acyl transfer with basic nucleophiles and good leaving groups the rate-determining step is attack of the nucleophile for which the magnitude of ρ_X (β_X) and ρ_Z (β_Z) is small, whereas in the acyl transfer with weakly basic nucleophiles and basic leaving groups it is expulsion of the leaving group for which the magnitude of ρ_X (β_X) and ρ_Z (β_Z) is large. Since no kinetic mechanistic criteria can be sufficient,[16,18] one should endeavor to provide as many supporting evidence as possible to increase the possibility of predicting a correct mechanism. In this sense, the signs of ρ_{XY} (>0) and ρ_{YZ} (<0) supplemented by a much greater magnitude of ρ_X, β_X, ρ_Z and/or β_Z values as well as ρ_{XY} (relative to ρ_{YZ}) will provide a good possibility of predicting a correct acyl transfer mechanism with rate-limiting breakdown of the intermediate, T^-.

In summary, the results provide theoretical basis for the qualitative experimental observations that an electron-donating nonleaving group, RY, favors expulsion of the more basic phenoxide by depressing the higher barrier, TS2, more than TS1 with a greater extent of bond cleavage, whereas the opposite holds for an electron-withdrawing RY, *i.e.*, favors expulsion of the less basic phenoxide by depressing the lower barrier, TS1, more than TS2 with a greater extent of bond cleavage in TS1 than that in TS2. These trends are also in agreement with the signs of ρ_{XY} (>0) and ρ_{YZ} (<0) established qualitatively based on the experimental results.

Acknowledgment. We thank the Ministry of Education of Korea for a Basic Science Research Grant (BSRI-94-3428) and Inha University for support of this work.

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Regioselective Friedel-Crafts Reaction of Allyldichlorosilane with 3,4-Benzo-1,1-dichloro-1-silacyclopentene

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Received September 5, 1995

A 86 : 14 isomeric mixture of 3,4-[3′-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene and 3,4-[2′-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene was prepared by the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene catalyzed by Lewis acid $AlCl_3$. The structure of the products was confirmed by methylation with methylmagnesium bromide and by methoxylation with trimethylorthoformate.

Introduction

There has been considerable interest in the chemistry of 3,4-benzo-1,1-dichloro-1-silacyclopentene (*i.e.*, 2,2-dichloro-2-silaindan) **I** and allyldichlorosilane **II**. The dimethyl derivative of **I**, 3,4-benzo-1,1-dimethyl-1-silacyclopentene undergoes an anionic ring-opening polymerization to give a thermally stable polycarbosilane.[1,2] Allyldichlosilane was also found to undergo Friedel-Crafts reactions with aromatic compounds to produce (2-arylpropyl)chlorosilanes.[3,4] Friedel-Crafts reac-

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