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Theoretical Studies on the Reactions of Acetate Esters with Substituted Phenolate Anion Nucleophiles[1]

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Semiempirical MO calculations using the PM3 method are performed on the reactions of acetate esters with substituted phenolate anions. The mechanistic change from rate-limiting formation to breakdown of the anionic intermediate is shown to occur in the gas-phase, especially for meta-nitrophenyl acetate. However the mechanistic change-over takes place at a lower basicity (pK_0) of the anion nucleophile than found for the corresponding formate. This lowering of pK_0 has been ascribed to the electron donating effect of the methyl group in the acetate. For the reactions involving rate-limiting breakdown of the intermediate, the large Brönsted coefficients, β_X (β_{nuc}), are expected in general, but the magnitude increases to a larger value and the pK_0 is lowered accordingly, when an electron-donating nonleaving group, like CH_3, is present. This type of nonleaving group effect provides a necessary condition for the carbonyl addition-elimination mechanism with rate-limiting breakdown of the intermediate.

Introduction

Nucleophilic substitution reactions at a carbonyl carbon can occur through a stepwise mechanism, with a tetrahedral intermediate that has a significant lifetime, or through a concerted, single step mechanism with a transition state (TS) and no addition intermediate. A two-step mechanism for acyl-transfer reactions usually follows a nonlinaer structure-reactivity correlation of log k with the pK_a of the attacking nucleophile showing a break from a large ($\beta = 0.8$-1.0) to a small ($\beta = 0.1$-0.3) slope as the basicity of nucleophile increases.[2] At the breaking point, the pK_a values of the nucleophile and leaving group become equal, $\Delta pK_a = 0$ at pK_0, and there is a change from rate-determining expulsion of the leaving group to rate-determining attack of the nucleophile as the pK_a value of the nucleophile is increased.[2]

Williams and coworkers[3] showed that the reaction of substituted phenolate anions with p-nitrophenyl acetate can proceed by a fully concerted mechanism with no slope change at $\Delta pK_a = 0$ that would be expected for a stepwise mechanism. It was shown that the dependence of log k on the pK_a of the phenolate ion, β_{nuc}, increases with increasing pK_a of the leaving group. However, the β_{nuc} value can also increase with increasing pK_a of the leaving group as a result of a change in the TS structure in a stepwise mechanism through a "Hammond effect" *i.e.*, a later TS for nucleophilic attack on a less reactive ester.

Jencks and coworkers[4] examined the reactions of a series of substituted phenolate anions with substituted phenyl formates and acetates. They concluded that both phenyl formates and acetates react with phenolate anions through a concerted mechanism with no tetrahedral addition intermediate.

In a previous work,[5] we examined theoretically the reactions of a series of substituted (X) phenolate anions with meta-nitro, para-nitro and 3,4-dinitro phenyl formates, *i.e.*, $Z = m$-NO_2, p-NO_2 and 3,4-$(NO_2)_2$, and RY = H in eq. 1 (MNPF, PNPF and DNPF, respectively). We found that the mechanistic change from rate-limiting breakdown to forma-

tion of the tetrahedral intermediate, T^-,
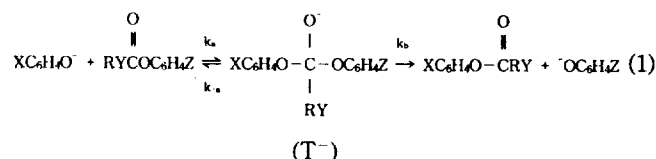
can occur in the gas-phase, especially for MNPF, at approximately equal proton affinity (PA) of the nucleophile and leaving group phenolates *i.e.*, $\Delta PA = 0$, as the PA of the phenolate anion nucleophile is increased. In addition, however, due to the low stability of T^- and a greater stabilization by solvation of the TS for the breakdown step (TS2), all three formate esters are predicted to proceed by a concerted mechanism as Jencks and coworkers found experimentally. The low stability of T^- can be ascribed to the high electron affinity of the phenolate anions.

On the other hand, it has been shown experimentally[2b,d,e] that as the electron-withdrawing power of the nonleaving group in the addition intermediate, RY, in eq. 1, is decreased, or conversely as the electron-donating power of RY is increased, the higher basicity phenolate group expulsion is favored, *i.e.*,
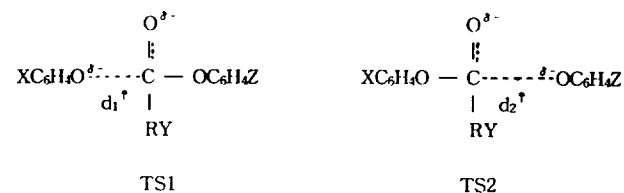
the TS2 is stabilized more than TS1 if $pK_a(Z) > pK_a(X)$. As a result, the pK_0 point at which $\Delta pK_a = 0$ occurs at a lower pK_a value.

In order to examine the effect of RY on pK_0 ($\Delta pK_a = 0$), we carried out PM3 MO calculations on the reactions of phenolate anions with *meta*-nitro, *para*-nitro and 3,4-dinitro

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Table 1. Proton Affinities (PA) Calculated by PM3 Method, in kcal mol^{-1}

Substituent in the Nucleophile	pKa[a]	PA
2-CH$_3$	10.13	330.38
4-CH$_3$	10.09	330.74
H	9.81	331.15
4-Cl	9.26	324.85
3-Cl	8.87	325.01
2-F	8.48	324.42
3,4-Cl$_2$	8.44	320.18
2-Cl	8.32	324.92
3,5-Cl$_2$	8.03	319.60
2,4-Cl$_2$	7.75	319.16
3,4,5-Cl$_3$	7.69	315.95
2,3-Cl$_2$	7.51	320.22
2,6-F$_2$	7.12	318.79
2,4,5-Cl$_3$	6.88	314.95
2,3,5-Cl$_3$	6.58	315.17
2,3,5,6-F$_4$	5.41	305.99

[a] Determined in aqueous solution at 25 °C and ionic strength = 1.0 M, taken from Ref 4.

Figure 1. Energy profile scheme.

phenyl acetates, i.e., Z = m-NO$_2$, p-NO$_2$ and 3,4-(NO$_2$)$_2$ and RY = CH$_3$ in eq. 1(MNPA, PNPA and DNPA, respectively).

Calculations

In this work, a semiempirical MO method, PM3,[6] was used due to the complex reaction systems. The proton affinities calculated by the PM3 method are listed in Table 1 together with the experimental pK$_a$ values in water.

All equilibrium structures including TSs were fully optimized and were characterized by force calculation and identifying all positive or only one negative eigenvalue in the Hessian matrix.[7] Various equilibrium states along the reaction coordinate are schematically shown in Figure 1. The distance between phenoxy oxygen of the nucleophile and the carbonyl carbon was taken as the reaction coordinate.

Table 2. Heats of Formation (ΔH_f, in kcal mol^{-1}) of Various States[a,b] Reactions of meta-Nitrophenyl Acetate (MNPA) with Phenolate Anion Nucleophiles
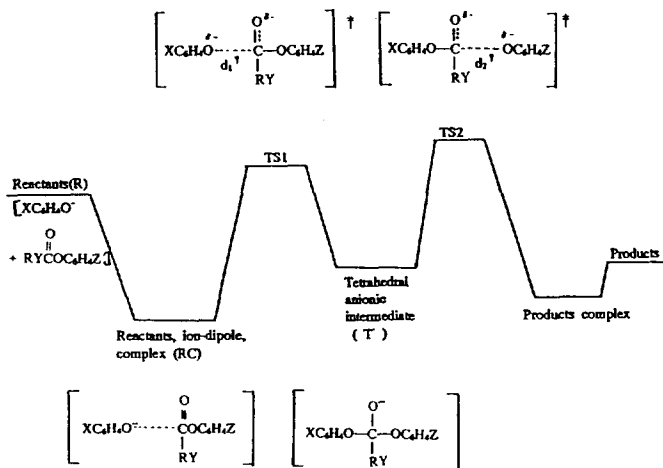
Entry	X	$\delta\Delta H_f$ (R)	$\delta\Delta H_f$ (RC)	$\delta\Delta H_f$ (TS1)	$\delta\Delta H_f$ (T)	$\delta\Delta H_f$ (TS2)	$\delta\Delta H^{\ddagger c}$
1	2-CH$_3$	-118.13	-21	-3	-10	-6	-3
2	4-CH$_3$	-119.39	-20	-2	-10	-6	-3
3	H	-109.74	-21	-3	-10	-6	-3
4	4-Cl	-122.76	-19	-1	-7	-2	-1
5	3-Cl	-122.56	-19	-1	-7	-2	-1
6	2-F	-158.46	-19	-1	-6	-2	-1
7	3,4-Cl$_2$	-132.88	-17	0	-4	0	0
8	2-Cl	-121.29	-19	-1	-6	-1	-1
9	3,5-Cl$_2$	-134.45	-17	1	-3	1	-1
10	2,4-Cl$_2$	-133.50	-17	1	-2	1	0
11	3,4,5-Cl$_3$	-142.52	-16	2	-1	3	1
12	2,3-Cl$_2$	-131.57	-17	1	-3	2	1
13	2,6-F$_2$	-206.46	-17	4	2	6	2
14	2,4,5-Cl$_3$	-143.13	-16	3	0	6	3
15	2,3,5-Cl$_3$	-143.00	-16	3	0	6	3
16	2,3,5,6-F$_4$	-303.66	-14	9	9	15	6

[a] R = Reactant; RC = Reactant (ion-dipole) complex; TS1 and TS2 = Transition states for the formation and breakdown steps of the intermediate, respectively; T$^-$ = Tetrahedral anionic intermediate. [b] $\delta\Delta H_f$ (Y) = ΔH_f (Y)-ΔH_f (R). [c] $\delta\Delta H^{\ddagger}$ = ΔH_f (TS2)-ΔH_f (TS 1).

Table 3. Heats of Formation (ΔH_f, in kcal mol^{-1}) of Various States[a,b] Reactions of para-Nitrophenyl Acetate (PNPA) with Phenolate Anion Nucleophiles

Entry	X	$\delta\Delta H_f$ (R)	$\delta\Delta H_f$ (RC)	$\delta\Delta H_f$ (TS1)	$\delta\Delta H_f$ (T$^-$)	$\delta\Delta H_f$ (TS2)	$\delta\Delta H^{\ddagger c}$
1	2-CH$_3$	-118.83	-23	-5	-13	-12	-8
2	4-CH$_3$	-120.09	-26	-5	-13	-13	-8
3	H	-111.44	-23	-4	-13	-12	-8
4	4-Cl	-123.45	-19	-3	-10	-9	-6
5	3-Cl	-123.25	-24	-3	-10	-9	-6
6	2-F	-159.15	-24	-3	-10	-9	-6
7	3,4-Cl$_2$	-133.57	-17	-1	-7	-9	-6
8	2-Cl	-121.98	-24	-3	-10	-8	-4
9	3,5-Cl$_2$	-135.14	-17	-1	-7	-5	-5
10	2,4-Cl$_2$	-134.19	-23	-1	-6	-4	-4
11	3,4,5-Cl$_3$	-143.21	-16	0	-4	-2	-3
12	2,3-Cl$_2$	-132.26	-18	0	-7	-5	-4
13	2,6-F$_2$	-207.75	-22	2	-2	-1	-3
14	2,4,5-Cl$_3$	-143.82	-16	1	-3	-1	-2
15	2,3,5-Cl$_3$	-143.69	-18	1	-3	-1	-2
16	2,3,5,6-F$_4$	-304.35	-16	7	6	7	1

[a] R = Reactant; RC = Reactant (ion-dipole) complex; TS1 and TS2 = Transition states for the formation and breakdown steps of the intermediate, respectively; T$^-$ = Tetrahedral anionic intermediate. [b] $\delta\Delta H_f$(Y) = ΔH_f(Y)-ΔH_f(R). [c] $\delta\Delta H^{\ddagger}$ = ΔH_f(TS2)-ΔH_f(TS1).

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Table 4. Heats of Formation (ΔH_f, in kcal mol^{-1}) of Various States[a,b] Reactions of *meta, para*-Dinitrophenyl Acetate (DNPA) with Phenolate Anion Nucleophiles

Entry	X	$\delta\Delta H_f$ (R)	$\delta\Delta H_f$ (RC)	$\delta\Delta H_f$ (TS1)	$\delta\Delta H_f$ (T$^-$)	$\delta\Delta H_f$ (TS2)	$\delta\Delta H^{\dagger c}$
1	2-CH$_3$	−117.23	−29	−11	−22	−	−
2	4-CH$_3$	−118.49	−32	−10	−22	−	−
3	H	−108.84	−50	−11	−23	−	−
4	4-Cl	−121.86	−23	−9	−19	−	−
5	3-Cl	−121.66	−28	−9	−19	−	−
6	2-F	−157.56	−26	−9	−18	−	−
7	3,4-Cl$_2$	−131.98	−22	−7	−15	−	−
8	2-Cl	−120.39	−29	−9	−18	−	−
9	3,5-Cl$_2$	−133.55	−22	−7	−15	−	−
10	2,4-Cl$_2$	−132.60	−29	−7	−14	−	−
11	3,4,5-Cl$_3$	−141.62	−21	−6	−12	−	−
12	2,3-Cl$_2$	−130.67	−23	−7	−15	−	−
13	2,6-F$_2$	−205.56	−28	−5	−10	−	−
14	2,4,5-Cl$_3$	−142.23	−23	−5	−11	−11	−6
15	2,3,5-Cl$_3$	−142.10	−26	−5	−11	−11	−6
16	2,3,5,6-F$_4$	−302.76	−21	0	−3	−2	−2

[a] R = Reactant; RC = Reactant (ion-dipole) complex; TS1 and TS2 = Transition states for the formation and breakdown steps of the intermediate, respectively; T$^-$ = Tetrahedral anionic intermediate. [b]$\delta\Delta H_f(Y) = \Delta H_f(Y)$-$\Delta H_f(R)$. [c]$\delta\Delta H^{\dagger} = \Delta H_f(TS2)$-$\Delta H_f(TS1)$.

TSs were located by the reaction coordinate (RC) method and refined by the use of NLLSQ or TS option.

Results and Disscussion

The calculated heats of formation, ΔH_f in kcal mol^{-1}, for the reactions of MNPA, PNPA and DNPA with phenolate anion nucleophiles are summarized in Tables 2, 3 and 4, respectively.

Reaction of meta-nitrophenyl acetate (MNPA). The binding energies of the reactant ion-dipole complexes (RC) are between 14 and 21 kcal mol^{-1}, which are *ca.* 5 kcal mol^{-1} lower values than those for the formate (MNPF).[5] We note that for the phenolate nucleophiles with the relatively high pK_a values (for entries 1-10), the TS2 level is lower than the TS1 level indicating that the rate-limiting step is formation of the tetrahedral intermedaite, T$^-$. In contrast, for the nucleophiles with the lower pK_a values (entries 11-16), the level of TS2 is higher than that of TS1 leading to rate-limiting breakdown of T$^-$. This level order change indicates that for the gas-phase reactions of MNPA the mechanistic change occurs at $pK_a \cong 7.7$, which is somewhat lower than the pK_0 (where $\Delta pK_a = pK_a(X) - pK_a(Z) = 0$) at which the mechanistic change-over is expected to take place. This is lower by *ca.* 0.5 pK_a unit than that found for the formate (MNPF), demonstrating that substitution of RY = H by a more electron donating group, RY = CH$_3$ in eq. 1, lowers the pK_0 point. This shows that a more electron-donating RY group lowers the TS2 level relative to TS1, *i.e.*, the leaving group, $^-$OC$_6$H$_4$Z which has higher pK_a, expulsion is favored more than the nucleophile, $^-$OC$_6$H$_4$X which has lower pK_a, expulsion. This

Table 5. Bond Lengths (Å) of the Partial Bonds between C_α and O in TS1 ($d_1^{\dagger}$) and TS2 ($d_2^{\dagger}$)

X	MNPA		PNPA		DNPA	
	$d_1^{\dagger}$	$d_2^{\dagger}$	$d_1^{\dagger}$	$d_2^{\dagger}$	$d_1^{\dagger}$	$d_2^{\dagger}$
2-CH$_3$	1.982	1.764	2.050	1.736	2.111	−
4-CH$_3$	1.998	1.860	2.050	1.736	2.111	−
H	2.008	1.860	2.050	1.736	2.111	−
4-Cl	1.944	1.885	1.987	1.760	2.060	−
3-Cl	1.944	1.885	1.986	1.735	2.060	−
2-F	1.929	1.880	1.974	1.757	2.042	−
3,4-Cl$_2$	1.888	1.868	1.944	1.777	2.001	−
2-Cl	1.929	1.880	1.974	1.757	2.041	−
3,5-Cl$_2$	1.900	1.868	1.944	1.777	2.001	−
2,4-Cl$_2$	1.875	1.844	1.920	1.757	1.998	−
3,4,5-Cl$_3$	1.861	1.868	1.906	1.777	1.971	−
2,3-Cl$_2$	1.900	1.903	1.920	1.757	1.998	−
2,6-F$_2$	1.796	1.850	1.842	1.687	1.898	−
2,4,5-Cl$_3$	1.845	1.903	1.906	1.799	1.971	1.694
2,3,5-Cl$_3$	1.853	1.903	1.906	1.799	1.957	1.694
2,3,5,6-F$_4$	1.673	1.905	1.710	1.751	1.772	1.699

is in good agreement with the solution-phase experimental results reported.[2b,d,e]

The two critical bond lengths, $d_1^{\dagger}$ and $d_2^{\dagger}$ in TS1 and TS2, respectively, listed in Table 5 reveal that the rate-determining step is characterized by a TS formed with the partial bond of a phenolate anion of a longer $d^{\dagger}$; at pK_0 the two becomes approximately equal, $d_1^{\dagger} \cong d_2^{\dagger}$. The breakdown of T$^-$ takes place in the direction of producing a lower pK_a phenolate anion in eq. 1. This means that when an electron donating RY group is present the higher pK_a phenolate, $^-$OC$_6$H$_4$Z, in T$^-$ becomes lowered relative to the lower pK_a phenolate, $^-$OC$_6$H$_4$Z.

As has been shown previously, this disagreement with the concerted mechanism found for all the phenolate nucleophile in solution[4] is due to the neglect of solvent effect in our MO theoretical calculation. In solution, TS2 is lowered much more than TS1 and leads to a lowering of the barrier to breakdown of the intermediate and the process should then corresponds to an enforced concerted mechanism[8] in agreement with the mechanism proposed in solution.

Reaction of para-nitrophenyl acetate (PNPA). For the formate, PNPF, *ca.* 1.0 unit lowering of the leaving group pK_a (pK_a's are 8.19 and 7.15 for *m*-NO$_2$ and *p*-NO$_2$-phenols respectively) resulted in a nearly uniform lowering of TS1, T$^-$ and TS2 by *ca.* 4 kcal mol^{-1}. However, comparison of ΔH_f values in Tables 2 and 3 indicates that the *ca.* 1.0 pK_a unit lowering of the leaving group brings *ca.* 3 kcal mol^{-1} lowering for TS1 and T$^-$, but the level lowering of TS2 is over two times, 6-7 kcal mol^{-1}. Much greater lowering of TS2 relative to TS1 is again consistent with the electron-donating effect of RY = CH$_3$.

In this case, the levels of TS2 is lower than those of TS1 for all phenloate nucleophiles except for the least basic X = 2, 3,5,6-F$_4$. This is the same trend as we found for the formate, PNPF,[5] but pK_a for 2,3,5,6-F$_4$-phenol is much lower than that

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Figure 2. Schematic energy profile for the mechanism involving rate determining breakdown of the tetrahedral intermediate, T^-.
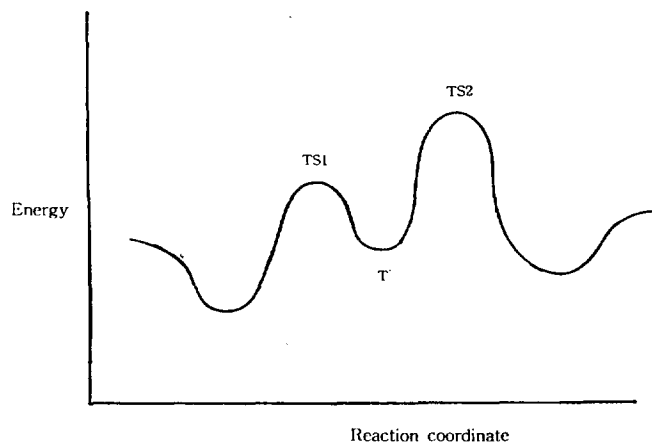

Figure 3. Schematic energy profile for the mechanism involving rate determining formation of the tetrahedral intermediate, T^-.

for the conjugate acid of the leaving group, p-NO$_2$-phenol, so that lowering of pK_0 due to substitution by RY=CH$_3$ cannot be seen clearly. Here again the level change of $d^{\dagger}$ takes place at 2,3,5,6-F$_4$-C$_6$H$_1$O$^-$ from $d_1^{\dagger}>d_2^{\dagger}$ to $d_1^{\dagger}<d_2^{\dagger}$ (Table 5).

The differences between the levels of TS2 and T^- are in general small and T^- has a property of transient equilibrium point on the potential energy surface so that passage through T^- should experience negligible barrier to decomposition especially when the solvent effect is accounted for[5]; thus the process becomes an enforced concerted mechanism[8] as experimentally found in solution.[4]

Reaction of 3,4-dinitrophenyl acetate (DNPA). As has been found for the formate, the levels of TS2 for this series are all lower than those of the corresponding TS1; the reactions of DNPA with all phenolate nucleophiles should therefore proceed concertedly in the gas phase in agreement with the proposal based on the results in solution. The $d_1^{\dagger}$ values are all greater than the $d_2^{\dagger}$ values in Table 5, in agreement with a single concerted mechanism for all the nucleophiles.

In summary, the gas-phase reactions of MNPA show a mechanistic change as the pK_a value of the nucleophile is decreased from rate-limiting formation to breakdown of T^- at a pK_a value which is lower by 0.5 pK_a unit than the corresponding point for the formate, MNPF. This effect is not clearly shown for the reactions of PNPA and also of DNPA due to the lack of nucleophiles whose pK_a's are near enough to the pK_a value at which mechanistic change occurs. However, the level order changes, especially the greater lowering of TS2, in Tables 3 and 4 point to the similar lowering of the pK_a (pK_0) at which the mechanistic change takes place due to the electron-donating effect of RY=CH$_3$.

The effect of the nonleaving group, RY, in the nucleophilic substitution reactions at a carbonyl carbon has long been a subject of intensive study experimentally.[2b,d,e] When the pK_a value of ZC$_6$H$_4$O$^-$ group is higher than that of XC$_6$H$_4$O$^-$ in eq. 1, i.e., $pK_a(Z)>pK_a(X)$, the level of TS2 is higher than TS1 so that the reaction proceed by a rate-limiting breakdown of T^-, Figure 2. In this case, the macroscopic rate constant observed, k_2, is given by eq. 2, since $k_{-a}>k_b$.
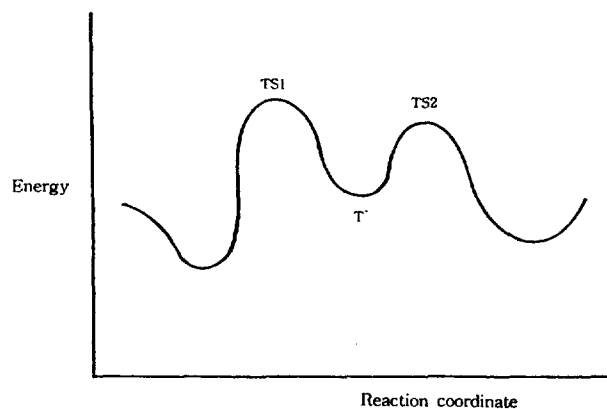
$$k_2 = \frac{k_a \cdot k_b}{k_{-a}+k_b} \cong \frac{k_a}{k_{-a}} \cdot k_b = Kk_b \qquad (2)$$

The observed Brönsted coefficient, β_X (or β_{nuc}), is then

$$\beta_X(\text{obsd}) = \frac{\partial \log k_2}{\partial pKa(X)} = \frac{\partial \log k_a}{\partial pKa(X)} - \frac{\partial \log k_{-a}}{\partial pKa(X)} + \frac{\partial \log k_b}{\partial pKa(X)}$$

$$= \beta_X(k_a) - \beta_X(k_{-a}) + \beta_X(k_b) \qquad (3)$$

a complex quantity.[9] Consideration of signs of each component term, eq. 4, should lead to a large observed $\beta_X(\text{obsd})$ since all three terms contribute additively.

$$\beta_X(\text{obsd}) = (+) - (-) + (+) \qquad (4)$$

This is why the reactions which proceed by the rate-limiting breakdown actually exhibit a large β_X (0.8-1.0) for experimental studies carried out in solution.[2] We should note here that the actual species of nucleophile and leaving group do not matter but only their basicities i.e., pK_a values are important. For exmple, the nucleophile can be an amine, in which case the tetrahedral intermediate is a zwitterionic form, $T^{\pm}$.

As we raise the pK_a value of the nucleophile, the situation reverses to $pK_a(X)>pK_a(Z)$ and now mechanistic change takes place to the rate-limiting formation of T^- (Figure 3). For this case, k_b becomes greater than k_{-a} ($k_{-a}<k_b$) leading to $k_2 \cong k_a$, and β_X now decreases to ca. 1/3 (β_X=0.1-0.3) of the value for the rate-limiting breakdown case as observed experimentally.[2]

$$\beta_X(\text{obsd}) = \frac{\partial \log k_2}{\partial pKa(X)} \cong \frac{\partial \log k_a}{\partial pKa(X)} = \beta_X(k_a) \qquad (5)$$

When the RY group is changed to a stronger electron-donating group, the equilibrium shifts to the right in eq. 1 and TS2 is stabilized more than TS1. Now for the rate-limiting elimination mechanism, k_{-a}/k_b decreases and as a result k_{-a} decreases relative to k_b. This type of situation is also encountered when the reaction of a neutral nucleophile (amines) is involved in a more polar solvent. Now in eq. 3, the second term, $\beta_X(k_{-a})$ increases due to the well-known reactivity-selectivity principle,[9,10] which states that a lower reactivity (k_{-a}) is accompanied by a greater selectivity, ($\beta_X(k_{-a})$),

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consequently, the magnitude of β_X is increased as indeed observed experimentally.[9] We should note here that the effect of nucleophile (X) on k_b is always much smaller than on k_{-a} and/or k_a.

As we increase the electron-donating power of RY (which can be expressed as $\delta\sigma_Y<0$ if Y is considered as a substituent on the substrate), TS2 is stabilized more and bond cleavage is facilitated so that the Hammett coefficient of the leaving group, ρ_Z (ρ_{lg}) increases $\delta\rho_z>0$. Thus $\partial\rho_Z/\partial\rho_Y$ ($=\rho_{YZ}$)< 0.[11] The negative sign of ρ_{YZ} is therefore a necessary condition for the rate-limiting breakdown of T[-].[11b] This is of course true only in the gas-phase, in solution solvent effect can change the mechanism to a concerted one.

The lowering of pK_0 due to an electron-donating RY(CH$_3$ versus H) is a consequence of this negative ρ_{YZ}, since an electron-donating RY, $\delta\rho_Y<0$, leads to an increase in bond cleavage, $\delta\rho_Z>0$, which brings down the pK_0 point to a lower pK_a than that expected from a more electron-withdrawing RY group. This is what we obtained theoretically in this work on the gas-phase reactions of MNPA.

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Photodissociation Dynamics of H₂O₂ at 280-290 nm

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Laser induced fluorescence spectra of OH produced from photodissociation of H₂O₂ at 280-290 nm in the gas phase have been observed. By analyzing the Doppler profiles, the anisotropy parameter ($\beta=-0.7$) and the center of mass translational energy of the fragments have been measured. The measured energy distribution is well described by an impulsive model. The excited state leading to dissociation is found to be of ^1A_u symmetry. The dissociation from this state is prompt and direct with the fragment OH rotating in the plane perpendicular to the O-O bond axis.

Introduction

Doppler profiles in absorption or emission spectra of molecules in a chemically or photochemically changing system can provide valuable information on the dynamics of the process. In order to study the dynamics of such a process, it requires measurements of certain physical properties of the system such as energy distribution, angular distribution of the final products, and so forth. Especially, vector properties such as recoil velocities and angular momenta of the final products are of great importance. These can be measured by translational spectroscopy using molecular beams and a mass spectrometer. However, in certain circumstances that the molecules or atoms in the system can absorb or emit radiation of an easily accesible spectral region, not only the energies distributed among quantum states of the product