free ammonia. From the result, it might be deduced that reaction (14) proceeds very slowly. Consequently, its formation could be interpreted only as a result of the combination of NH_2 and OH radicals as in reaction (7).

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A Mechanistic Study on Reactions of Aryl Benzoates with Ethoxide, Aryloxides and Acetophenone oximates in Absolute Ethanol

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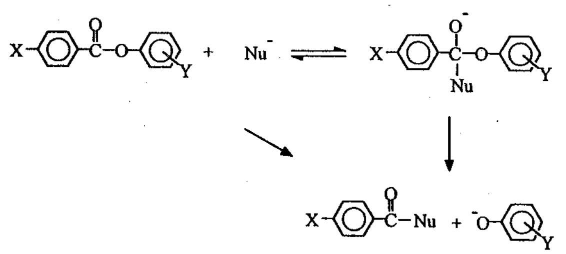
Second-order rate constants have been measured spectrophotometrically for the reactions of aryl benzoates ($X\text{-}C_6H_4CO_2C_6H_4\text{-}Y$) with EtO^-, $Z\text{-}C_6H_4O^-$ and $Z\text{-}C_6H_4C(Me){=}NO^-$ in absolute ethanol at 25.0 ℃. All the reactions have been performed in the presence of excess 18-crown-6 ether in order to eliminate the catalytic effect shown by alkali metal ion. A good Hammett correlation has been obtained with a large ρ^- value (-1.96) when σ^- (Z) constant was used for the reaction of *p*-nitrophenyl benzoate (PNPB) with $Z\text{-}C_6H_4O^-$. Surprisingly, the one for the reaction of PNPB with $Z\text{-}C_6H_4C(Me){=}NO^-$ gives a small but definitely positive ρ^- value ($+0.09$). However, for reactions of $C_6H_5CO_2C_6H_4\text{-}Y$ with EtO^-, correlation of log *k* with σ^- (Y) constant gives very poor Hammett correlation. A significantly improved linearity has been obtained when σ^o (Y) constant was used, indicating that the leaving group departure is little advanced at the TS of the RDS. For reactions of $X\text{-}C_6H_4CO_2C_6H_4\text{-}4\text{-}NO_2$ with EtO^-, $C_6H_5O^-$ and $C_6H_5C(Me){=}NO^-$, correlations of log *k* with σ (X) constants for all the three nucleophile systems give good linearity with large positive ρ values, *e.g.* 2.95, 2.81 and 3.06 for EtO^-, $C_6H_5O^-$ and $C_6H_5C(Me){=}NO^-$, respectively. The large ρ values clearly suggest that the present reaction proceeds *via* a stepwise mechanism in which the formation of the addition intermediate is the RDS.

Introduction

Acyl-transfer reactions have been known to be one of the most important chemical reactions occurring in living bodies, and numerous studies have been performed to investigate the reaction mechanism using many kinds of model systems.[1~5] Two distinct reaction mechanisms have been suggested, *e.g.* one-step concerted and stepwise addition-elimination mechanisms.[1~5] The one-step concerted mechanism has been known to proceed *via* a single transition state (TS) in which nucleophilic attack and leaving group departure occur concertedly.[4,5] On the other hand, the stepwise mechanism has been suggested to proceed *via* a tetrahedral intermediate in which the rate-determining step (RDS) might be either the addition step or the elimination step depending mostly on the basicity of entering and leaving groups.[2,3]

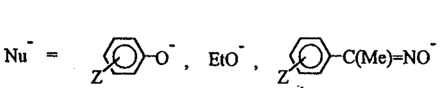
In a previous work, we performed a kinetic study[3b] for the reaction of *p*-nitrophenyl X-substituted benzoates with phenoxide in H_2O containing 20 mole % DMSO, and found that the correlation of log k *vs.* σ(x) constant gives nonlinear Hammett plots as the acyl substituent X becomes a significantly electron withdrawing group (*e.g.* *p*-CN and *p*-NO_2). The nonlinearity was attributed to a change in the RDS, *i.e.* from rate-determining formation to breakdown of the addition intermediate as the acyl substituent X becomes a strong electron withdrawing group.[3b]

We have now expended our study to the following reaction system to get more solid information about the reaction mechanism. The systematic variations of substituent X, Y and Z and the change in the type of nucleophiles would be expected to give us important information about the acyl-transfer reaction mechanism.



X = OMe , Me , H , Cl , CN , NO_2

Y = p-Me, H, p-Cl, m-Cl, p-CHO, p-COMe, p-CN, p-NO_2



Z = p-OMe, p-Me, m-Me, H, p-Cl, p-CN

Experimental

Materials. The aryl substituted benzoates ($X-C_6H_4CO_2C_6H_4-Y$) used in the present study were easily prepared by the method described in literature.[6] Z-substituted acetophenone oximes were prepared from the reaction of Z-substituted acetophenone with hydroxylamine. Their purity was checked by means of their melting point and spectral data such as IR and ^{1}H NMR characteristics. Other chemicals used were of the highest quality available (Aldrich) and were generally recrystallized before use. Absolute ethanol was prepared by the method described in the literature[6] under a nitrogen atmosphere.

Kinetics. The kinetic studies for relative slow reactions ($t_{1/2}$>10 seconds) were performed with a Hitachi U-2000 Model UV-Vis spectrophotometer equipped with a Neslab RTE-110 Model constant temperature circulating bath to keep the temperature in the UV-cell at 25± 0.1 ℃. The reactions were followed by monitoring the appearance of the leaving phenoxide at a fixed wavelength corresponding to the maximum absorption (λ_{max}) of $Y-C_6H_4O^-$. All the reactions were carried out under pseudo-first-order condition in which the concentration of nucleophiles was generally 20 times greater than the substrate concentration. The stock solution of aryloxides (Z-PhO^-) and acetophenone oximates (Z-Ox^-) were made up with EtO^-K^+ solution and 2 equivalent corresponding phenol or oxime to suppress formation of EtO^- ion by solvolysis and to ensure a self-buffer solution as described previously.[3c] Potassium ethoxide solution was prepared by dissolving potassium metal in absolute ethanol under a nitrogen atmosphere and titrated against potassium hydrogen phthalate. All the kinetics were performed in the presence of 18-crown-6 ether in excess in order to eliminate alkali metal ion catalysis.

Results

All the reactions studied here obeyed pseudo-first-order kinetics up to over 90% of the total reaction. Pseudo-first-order rate constants (k_{obs}) were obtained from the equation, $\ln(A_\infty - A_t) = -k_{obs} \cdot t + c$. Generally, five different concentrations of a nucleophile were used to obtain second-order rate constants from the plots of k_{obs} *vs.* the concentration of a nucleophile.

In Table 1 are summarized second-order rate constants for the reaction of *p*-nitrophenyl benzoate with various substituted phenoxides (Z-PhO^-) and acetophenone oximates (Z-Ox^-) in absolute EtOH at 25.0 ℃, together with σ^- constants for the substituent Z. Hammett plots have been demonstrated in Figure 1. In Table 2 are summarized second-order rate constants for the reaction of Y-substituted phenyl benzoates with EtO^-, and Brönsted and Hammett plots are shown in Figures 2 and 3. Second-order rate constants for the reaction of *p*-nitrophenyl X-substituted benzoates with PhO^-, EtO^- and Ox^- are summarized in Table 3, and demonstrated graphically in Figures 4-6 against σ constant for the acyl substituent X.

Discussion

The Effect of Substituent in the Entering Group (Z). As shown in Table 1, the reactivity of aryloxides (Z-PhO^-) toward *p*-nitrophenyl benzoate (PNPB) decreases as the electron withdrawing ability of the substituent Z increases. A good linear correlation has been obtained in the plot of log k *vs.* σ^- (Z) constant as shown in Figure 1. Since the negative charge on the oxygen atom of cyanophenoxide ($CNPhO^-$) can be delocalized onto the substituent by direct resonance, $CNPhO^-$ is expected to exhibit extra rate retardation. Therefore, the finding of good correlation of log k with σ^- constant is consistent with the expectation for the reaction of PNPB with Z substituted aryloxides.

Since ethanol is less polar than H_2O, the effect of substituent on reaction rates would be more significant in EtOH. In fact, the magnitude of ρ^- value in Figure 1 is calculated to be -1.96. This appears to be much larger than the one obtained from the corresponding reaction run in H_2O (*e.g.* ρ^- in $H_2O = -1.04$).[3b] This is also consistent with the fact

Table 1. Summary of Second-order Rate Constants (k_2, $M^{-1}s^{-1}$) for the reaction of *p*-Nitrophenyl Benzoate with Z-Substituted Phenoxides (Z-PhO$^-$) and Acetophenone oximates (Z-Ox$^-$) in Absolute EtOH at 25.0 ℃

		k_2, $M^{-1}s^{-1}$	
Z	σ^{-a}	Z-PhO$^-$	Z-Ox$^-$
1 *p*-CN	1.00	0.00166	23.5
2 *p*-Cl	0.23	0.0590	19.1
3 H	0	0.146	18.0
4 *m*-CH_3	−0.07	0.183	18.8
5 *p*-CH_3	−0.17	0.304	18.7
6 *p*-OCH_3	−0.27	0.589	18.2

[a]Data from reference 15.

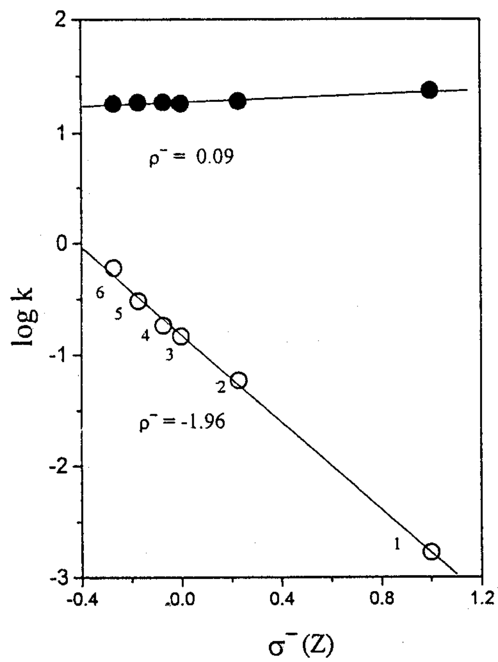


Figure 1. Hammett plots for the reaction of *p*-nitrophenyl benzoate (PNPB) with Z-substituted phenoxides (○) and acetophenone oximates (●) in absolute EtOH at 25.0 ℃. The numbers refer to the nucleophile in Table 1.

Table 2. Summary of Second-order Rate Constants (k_2, $M^{-1}s^{-1}$) for the reaction of Y-Substituted Phenyl Benzoates ($C_6H_5CO_2C_6H_4$-Y) with EtO$^-$ in Absolute EtOH at 25.0 ℃

Y	σ^{-a}	σ^{oa}	pK_a^b	k_2, $M^{-1}s^{-1}$
1 *p*-NO_2	1.27	0.82	7.14	11.8
2 *p*-CN	1.00	0.69	7.95	6.98
3 *p*-$COCH_3$	0.87	0.46	8.05	1.70
4 *p*-CHO	1.13	0.42	7.66	2.70
5 *m*-Cl	0.37	0.37	9.02	1.16
6 *p*-Cl	0.23	0.27	9.38	0.81
7 H	0	0	9.95	0.12
8 *p*-CH_3	−0.17	−0.12	10.19	0.074

[a]Data from reference 15. [b]Data from reference 10.

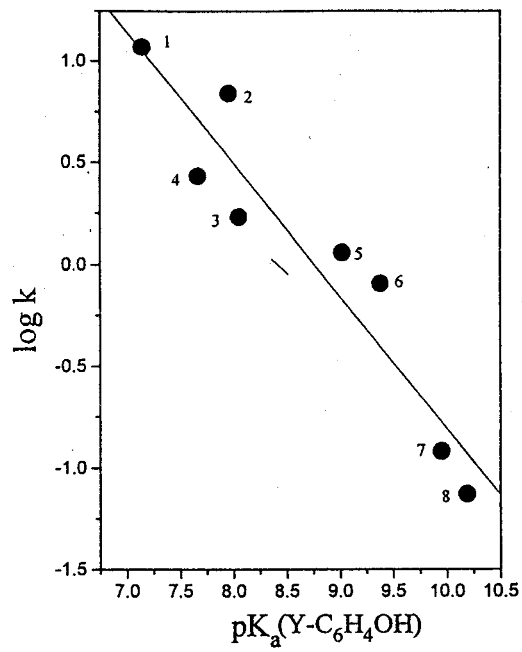


Figure 2. Brönsted plot for the reaction of Y-substituted phenyl benzoates ($C_6H_5CO_2C_6H_4$-Y) with EtO$^-$ in absolute EtOH at 25.0 ℃. The numbers refer to the substrate in Table 2.

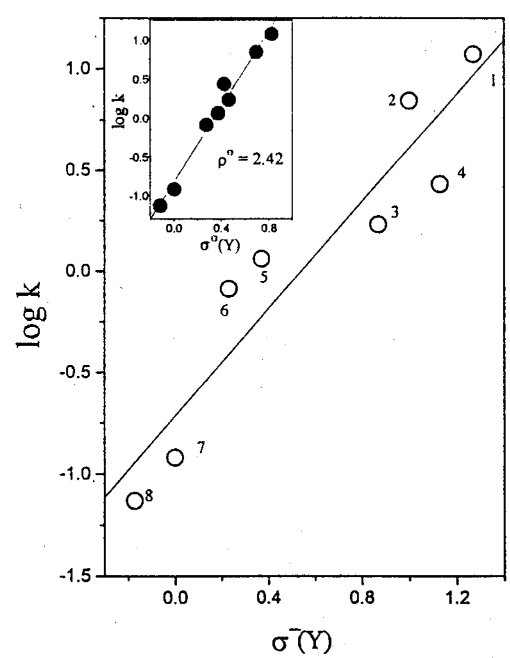


Figure 3. Hammett plots for the reaction of Y-substituted phenyl benzoates ($C_6H_5CO_2C_6H_4$-Y) in absolute EtOH at 25.0 ℃. The numbers refer to the substrate in Table 2.

that the ρ value for dissociation of phenols at 25 ℃ is larger in EtOH (ρ=2.58)[7] than in H_2O (ρ=2.113).[8] Therefore, direct comparison of the ρ value in EtOH with the one in H_2O would give no significant information on the TS structure, *i.e.* the magnitude of ρ values in different solvents for a given reaction system can be used only as a relative sensitivity or selectivity parameter but not as an absolute measure

Table 3. Summary of Second-order Rate Constants (k_2, $M^{-1}s^{-1}$) for the reaction of *p*-Nitrophenyl X-Substituted Benzoates with Phenoxide (PhO^-), Ethoxide (EtO^-) and Acetophenone oximate (Ox^-) in Absolute EtOH at 25.0 ℃

	X	σ^a	k_2, $M^{-1}s^{-1}$ PhO⁻	EtO⁻	Ox⁻
1	*p*-NO_2	0.78	29.5	2,290	2,400
2	*p*-CN	0.66	15.7	1,280	1,950
3	*p*-Cl	0.23	1.08	73.4	90.9
4	H	0	0.21	11.8	16.3
5	*p*-CH_3	−0.17	0.084	4.69	4.88
6	*p*-OCH_3	−0.27	0.030	1.87	1.50

[a]Data from reference 15.

of bond formation between the substrate and nucleophile at the TS of the RDS.

As shown in Table 1, the effect of substituent Z on acetophenone oximate (Ox^-) exerts very little influence to the reactivity of Ox^- toward PNPB, since the ρ^- value obtained is very small, $\rho^-=+0.09$. Strikingly, the sign of ρ^- in the present system is definitely positive, *i.e.* the reactivity increases with increasing electron withdrawing ability of substituent Z. Such a positive ρ value is surprising and quite unexpected.

Nonlinear Brönsted type plots have often been observed for nucleophilic substitution reactions with highly basic anionic nucleophiles (*e.g.* HO^- and alkoxides) in H_2O.[9] Jencks *et al.* have attributed the nonlinear Brönsted plot to strong solvation of highly basic anionic nucleophiles by H_2O for the reaction of *p*-nitrophenyl acetate (PNPA) with aryloxides, HO^- and alkoxides in H_2O.[9]

Ox^- is more basic than PhO^-,[10] and the former is considered to be more strongly solvated than the latter in protic solvents. Therefore, the degree of H-bonding would be more significant for the oximate containing a stronger electron donating substituent (*e.g.* MeO>Me>H>Cl>CN). In consequence, the energy required for desolvation would be proportional to the basicity of respective oximate, which would result in the decreasing rate trend in Figure 1 as the electron donating ability of the substituent increases.

It has generally been known that the effect of solvation (or desolvation) on reaction rates is significant.[11] As shown in Table 1, acetophenone oximates appear to be more reactive than aryloxides toward PNPB. However, Ox^- (Z=H) is only 32 times more reactive than $MeOPhO^-$, which is much smaller than would be predicted based on the basicity difference.[10] In addition, one would expect that the α-effect nucleophile (Ox^-) shows a significantly large α-effect,[12] but the α-effect shown by Ox^- in the present system is negligible. Absence of the α-effect has often been reported for highly basic α-effect nucleophiles,[13,14] and solvation effect is considered to be responsible for it. The small α-effect observed in the present system is consistent with the previous results reported by Hudson[13] and Terrier.[14] Therefore, Ox^- is considered to be more strongly solvated than PhO^- in EtOH, and one can attribute the positive ρ^- value obtained in the present system to solvation effect but not to any unusual reaction mechanism. In order to get solid information on the reaction mechanism, substituent effects in the leaving and acyl groups have been studied.

The Effect of Substituent in the Leaving Group (Y). The mechanism of acyl-transfer reactions as in the present system has been a subject of controversy (*e.g.* concerted *vs.* stepwise mechanism).[1~5] Williams *et al.* have suggested that the acyl-transfer reactions of *p*-nitrophenyl acetate with aryloxides proceed *via* a concerted mechanism,[4,5] while others favor stepwise mechanisms.[2,3] In order to investigate the extent of leaving group departure at the TS of the RDS, the effect of substituent Y in the leaving phenoxide on reaction rates has been studied. As shown in Table 2, the reactivity of Y-substituted phenyl benzoates toward EtO^- increases with increasing electron withdrawing ability of the substituent Y in general. The presence of a strong electron withdrawing substituent in the leaving phenoxide decreases the basicity of the leaving group. Since leaving group ability (nucleofugality) is considered to be inversely proportional to the basicity of the leaving group, one might expect that the reactivity of the present aryl benzoates would be inversely proportional to the leaving group basicity. However, as shown in Figure 2, the plot of log k versus pK_a of the conjugated acid of the leaving group (Y-C_6H_4OH) gives poor correlation (c.c.=0.945). This result indicates that the leaving group departure is little involved in the RDS.

To obtain further information about the RDS, Hammett type plots have been constructed from the data in Table 2. As shown in Figure 3, the plot of log k *vs.* σ^- (Y) constant demonstrates very poor Hammett correlation (*eg.* c.c.=0.939, $\rho^-=1.33\pm0.20$). However, as shown in the inlet of Figure 3, the correlation with σ^o (Y) constant gives much better linearity (*eg.* c.c.=0.989, $\rho^o=2.42\pm0.14$).

If the leaving group departure is involved in the RDS, whether a concerted or stepwise mechanism, a partial negative charge would be developed at the oxygen atom of the leaving aryloxide. Since any negative charge developed on the oxygen atom can be delocalized onto the para substituents such as NO_2, $COCH_3$ and CHO by direct resonance, one should have observed good Hammett correlation when σ^- (Y) constant is used. The poor Hammett correlation with σ^- constants in the present system is contrary to what would have been expected if the leaving group departure were advanced in the RDS. Therefore, the leaving group departure is considered to occur after the RDS.

σ^o constant was devised from the ionization of substituted phenylacetic acid (X-$C_6H_4CH_2CO_2H$),[15] in which charge delocalization by direct resonance is entirely excluded by the presence of the methylene group between the phenyl and CO_2H moiety. Therefore, σ^o constant would fit best for an insulated reaction system (*e.g.* a resonance free system). As shown in Figure 3, σ^o constant gives much better correlation than σ^- constant. This result clearly supports that there develops no negative charge on the oxygen atom of the leaving phenoxide, and the leaving group departure proceeds after the RDS rapidly, as mentioned above. Therefore, one can eliminate both concerted mechanism and stepwise mechanism in which the RDS is the breakdown of the tetrahedral intermediate.

If the leaving group departure occurs after the RDS rapid-

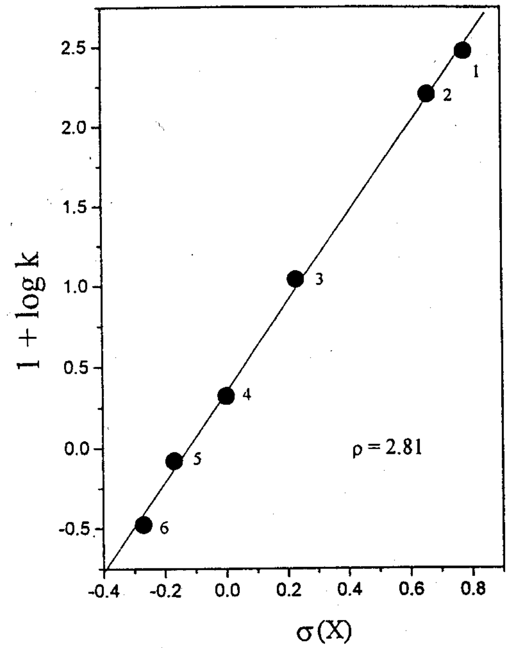


Figure 4. Hammett plot for the reaction of *p*-nitrophenyl X-substituted benzoates ($X\text{-}C_6H_4CO_2C_6H_4\text{-}4\text{-}NO_2$) with phenoxide in absolute EtOH at 25.0 ℃. The numbers refer to the substrate in Table 3.

ly, the nucleofugality of the leaving group would not affect reaction rates significantly, and one might expect small σ^o value. The ρ^o value in the present system has been obtained to be 2.42, which is fairly large. Therefore, one might raise a question about the RDS. However, substituent Y can also influence electrophilicity of the reaction site of the aryl benzoates in an inductive manner, *i.e.* the electrophilicity of the reaction center increases with increasing electron withdrawing ability of the substituent Y. Therefore, the large ρ^o value obtained in the present system suggests that the effect of the leaving group substituent Y appears to be more significant on the electrophilicity of the reaction center than on the nucleofugality of the leaving group.

The Effect of Substituent in the Acyl Group (X). As evident from Table 3, the effect of acyl substituent X on reactivity is significant, *i.e.* the reactivity of *p*-nitrophenyl X-substituted benzoates increases significantly with increasing electron withdrawing ability of the substituent X. For example, the rate enhancement upon the substituent change from X=MeO to X=NO_2 are 980, 1220 and 1600 for PhO^-, EtO^-, and Ox^- system, respectively. The Hammett plot exhibits good linear correlation for the reaction of the *p*-nitrophenyl X-substituted benzoates with PhO^-, as shown in Figure 4. The corresponding reactions with EtO^- and Ox^- have also resulted in good Hammett correlations with large values (Figures 5 and 6). The linear Hammett correlation obtained in the present system suggests that there is no mechanism change upon the acyl substituent change. Interestingly, the present result is quite different from our previous results, in which nonlinear Hammett plots were obtained for the reactions of *p*-nitrophenyl X-substituted benzoates with aryloxides in H_2O containing 20 mole % DMSO.[3b]

The ρ values in the present system have been calculated

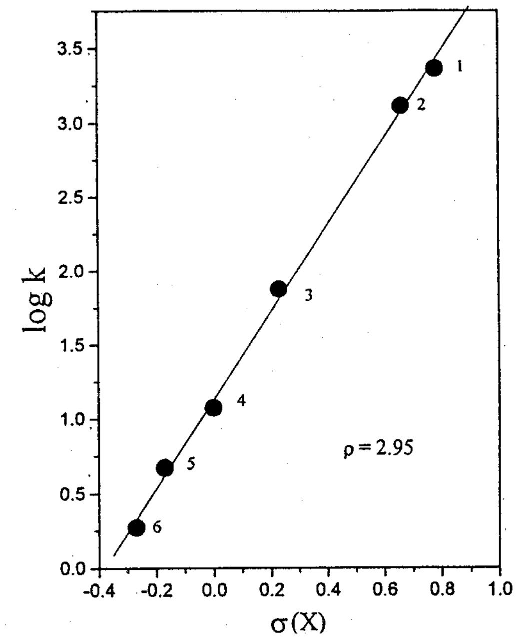


Figure 5. Hammett plot for the reaction of *p*-nitrophenyl X-substituted benzoates ($X\text{-}C_6H_4CO_2C_6H_4\text{-}4\text{-}NO_2$) with ethoxide in absolute EtOH at 25.0 ℃. The numbers refer to the substrate in Table 3.

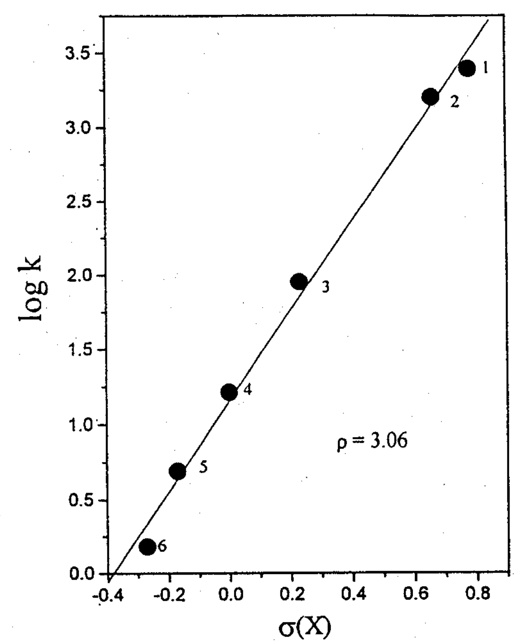


Figure 6. Hammett plot for the reaction of *p*-nitrophenyl X-substituted benzoates ($X\text{-}C_6H_4CO_2C_6H_4\text{-}4\text{-}NO_2$) with acetophenone oximate in absolute EtOH at 25.0 ℃. The numbers refer to the substrate in Table 3.

to be 2.81, 2.95 and 3.06 for the PhO^-, EtO^-, and Ox^- system, respectively. Since the magnitude ρ value has long been used as a measure of selectivity parameter, the relative selectivity for the present system is considered to be in the order $Ox^- > EtO^- > PhO^-$ system. Therefore, the reactivity selectivity principle (RSP) is not applicable to the present system, since the more reactive system exhibits the larger selectivity. Such a failure of the RSP has often been observed for the reaction where anti-Hammond effect is dominent.[16] Therefore, the more reactive nucleophile is considered to form tighter bond formation with the substrate at the TS of the RDS.

As mentioned in the preceding section, the effects of substituent on rates and equilibria are more significant in less polar solvents. Therefore, one needs to normalize ρ (rate) with ρ (equilibrium) in order to eliminate solvent effect and to get useful information about the TS structure at the RDS. The ρ value for dissociation of $X\text{-}C_6H_4CO_2H$ in EtOH has been reported to be 1.957.[8] Division of the ρ value in the present system by 1.957 gives normalized ρ values of 1.44. 1.51 and 1.56 for PhO^-, EtO^-, and Ox^- system, respectively. The normalized ρ values in the present system are still large. One might attribute the large value to a proximity effect, since the acyl substituents (X) are closely located from the reaction center. However, the nature of reaction mechanism is considered to be more responsible for the large ρ values. The attack of the anionic nucleophiles to the carbonyl carbon would be significantly faciliated by an electron withdrawing substituent (EWS) in the acyl moiety, since EWS can increase the electrophilicity of the electrophilic center, the carbonyl carbon, and stabilize the negatively charged TS at the RDS. In this case, a large positive ρ value would be expected for the attacking process of anionic nucleophile to the carbonyl carbon. However, the negative charge in the TS would be diminished upon the departure of the anionic leaving group (*p*-nitrophenoxide). In this case, electron donating substituents would accelerate leaving group departure, and the sign of the ρ value for the leaving group departing process would be negative.

Therefore, if the leaving group departure is involved in the RDS, the ρ value would be small due to compensation by the opposite substituent effect. In fact small ρ values have often been reported for the reactions in which leaving group departure is known to be the RDS.[17] However, if the leaving group departure occurs after the RDS rapidly, the electronic nature of the acyl substituent X would affect only the nucleophilic attack process but not the leaving group departing process. In this case, one would expect large positive value, as mentioned above. Therefore, the large positive ρ values obtained in the present system clearly suggest that the leaving group departure occurs after the RDS. This is consistent with the preceeding argument based on the result that σ^o (Y) constant gives better Hammett correlation than σ^- (Y) constant.

Summary

The present study has allowed us to summarize the following. (1) The reactivity of Z-substituted phenoxides toward PNPB increases with increasing electron donating ability of the substituent Z, and results in a large negative ρ^- value, while that of acetophenone oximate exhibits an opposite behaviour (*e.g.* small but positive ρ^- value). The positive ρ^- value for the Ox^- system is attributed to solvation effect but not to any unusual reaction mechanism. (2) The leaving group departure is not considered to be involved in the RDS for the reaction of Y-substituted phenyl benzoates with EtO^-, based on the fact that σ^- (Y) gives poor Hammett correlation while σ^o (Y) gives much better correlation. (3) The large ρ value obtained for the reaction of *p*-nitrophenyl X-substituted benzoates with PhO^-, EtO^-, Ox^- suggests that this reaction proceeds *via* a stepwise mechanism in which formation of a tetrahedral intermediate is the RDS.

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