

The Effect of Polarizability on Rate and Reaction Mechanism: Reactions of S-Aryl Substituted Thiobenzoates with HO^- and Aryloxide Ions

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Second-order rate constants have been determined spectrophotometrically for reactions of S-p-nitrophenyl substituted thiobenzoates with various phenoxide ions and S-aryl substituted thiobenzoates with HO^- ion. Thiol esters have been found to be more reactive than the corresponding oxygen esters toward phenoxide ions. The high reactivity of thiol esters relative to oxygen esters becomes insignificant as the basicity of the nucleophile increases. Furthermore, the highly basic HO^- ion is less reactive toward thiol esters than oxygen esters. The significant dependence of the reactivity of thiol esters on the basicity of nucleophiles has been attributed to the nature of the HSAB principle. The present kinetic study has also revealed that the reactivity of thiol esters compared to oxygen esters is not so pronounced as expected based on the enhanced nucleofugicity of thiol esters. However, the effects of substituents in the nucleophile and in the acyl moiety of the substrate on rate appear to be significant. These kinetic results have led to a conclusion that the present reactions proceed *via* a rate-determining formation of a tetrahedral intermediate followed by a fast breakdown of it. The magnitude of the β values shows no tendency either to increase or to decrease with the intrinsic reactivity of the reagents. The constancy of β values in the present system is suggestive that the RSP should have limited applicability.

Introduction

Kinetic and spectroscopic studies of thiol esters have been accelerated since the acylated coenzyme A, an intermediate in many biological reactions, was known to be a thiol ester.^{1,2} Intensive spectroscopic investigations have revealed that the replacement of oxygen atom in the ether-like oxygen in carboxylic esters by sulfur increases significantly the polarizability of the reaction center, and consequently causes great differences in reactivity.^{1,2} The unusual high reactivity of thiol esters toward polarizable nucleophiles such as sulfur and nitrogen centered nucleophiles³ has often been attributed to the hard and soft acids and bases (HSAB) principle.⁴ However, systematic studies concerning the HSAB principle have been lacking. Particularly, correlations of unusual reactivities with reaction mechanisms have not been studied systematically.

Thus we have chosen the following system to investigate systematically the effect of polarizability on rate as well as on reaction mechanism. The effect of polarizability on rate would be analyzed by comparing the reactivity of thiol esters with the one of corresponding oxygen esters whose kinetic data have recently been reported.⁵ A quantitative investigation of substituent effect on rate would be expected to eluci-

date reaction mechanism which has been a subject of controversy (one step concerted and stepwise mechanisms, as shown in equation 1) over the years.^{6,7}

Experimental

Materials. The S-aryl substituted thiobenzoates in the present study were prepared essentially by the method of Vogel⁸ using benzoyl chlorides prepared from the corresponding acids with thionyl chloride. Their purity was checked by means of their melting point and spectral data such as IR and $^1\text{H-NMR}$ characteristics. The chemicals used for the present study were of the highest quality available (Aldrich) and were generally recrystallized before use. Doubly glass distilled water was further boiled and cooled under a nitrogen atmosphere just before use. All the solutions were prepared and kept under a nitrogen atmosphere. Transfers of solutions were done by means of Hamilton Gas-tight syringes. Only freshly prepared solutions were used in the kinetic study.

Kinetics. Kinetic data were obtained spectrophotometrically by using 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 $25.0 \pm 0.1^\circ\text{C}$. The reactions were followed by monitoring the appearance of leaving thiophenoxides at a fixed wavelength corresponding to the maximum absorption (λ_{max}) of $\text{Y-C}_6\text{H}_4\text{S}^-$. All the reactions were carried out under pseudo-first-order conditions in which the concentration of nucleophile was generally 20 times, but at least 10 times greater than the substrate concentration. The stock solutions of the nucleophilic aryloxides were made up with NaOH solution and 2 equivalent corresponding phenol to suppress formation of hydroxide by solvolysis as described previously.^{7a}

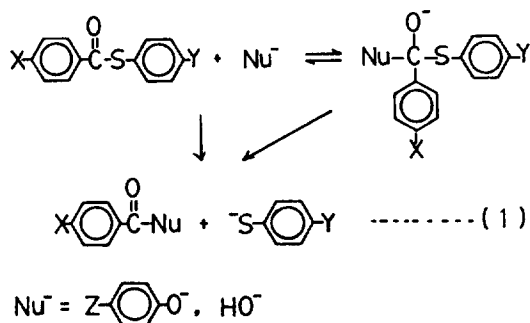


Table 1. Summary of Second-Order Rate Constant k ($M^{-1}s^{-1}$) for Reactions of S-p-Nitrophenyl Substituted Thiobenzoates (4-X-C₆H₄C(O)SC₆H₄-NO₂) with Substituted Phenoxides (4-Z-C₆H₄O⁻) in 20 mole % DMSO-H₂O Mixture at 25°C

X	Z	10×k, M ⁻¹ s ⁻¹					
		CHO	CN	CH ₃ CO	Cl	H	OCH ₃
CN		8.78	17.1 (1.21) ^a	20.0	358 (59.2)	638 (189)	—
Cl		—	2.32 (0.135)	—	49.3 (6.04)	94.7 (20.5)	262 (55.8)
H		0.385 (0.0249)	0.717 (0.0510)	0.930 (0.0785)	14.9 (1.85)	22.5 (4.52)	62.6 (12.7)
^t Bu		—	0.288 (0.0247)	—	6.17 (0.726)	11.3 (1.84)	26.6 (5.40)
OCH ₃		0.0909	0.112 (0.0133)	0.169	3.69 (0.344)	5.71 (0.889)	17.7 (2.68)

^aFigures in parentheses are the second-order rate constant for oxygen esters obtained from ref. 5.

Table 2. Summary of Second-Order Rate Constant k ($M^{-1}s^{-1}$) for Reaction of S-p-Nitrophenyl Substituted Thiobenzoates (4-X-C₆H₄C(O)SC₆H₄-4-NO₂) with HO⁻ in 20 mole % DMSO-H₂O Mixture at 25°C

X	Cl	H	^t Bu	OCH ₃
pK_a (X-PhCO ₂ H) ^a	3.99	4.20	4.40	4.47
k , M ⁻¹ s ⁻¹	28.5 (36.0) ^b	9.99 (13.4)	4.76 (6.14)	3.76 (3.98)

^a pK_a values are taken from ref. 11. ^bFigures in parentheses are the second-order rate constants for the corresponding oxygen esters.

Results

Pseudo-first-order rate constants (k_{obs}) were obtained from the plots of $\ln(A_{\infty}-A_t)$ vs. t , which were linear over ca. 90% reaction. Second-order rate constants were obtained from the slopes of the linear plots of k_{obs} vs. the concentration of nucleophile.^{7d} Oxidation of the leaving thiophenoxide to form a disulfide was not observed in the present reaction condition.

In Table 1 are presented second-order rate constants for the reactions of S-p-nitrophenyl X-substituted thiobenzoates with Z-substituted phenoxide ions at 25°C in water containing 20 mole % dimethyl sulfoxide (DMSO) to eliminate a solubility problem. The corresponding data for the reactions of HO⁻ ion with S-Y-substituted phenyl thiobenzoates and with S-p-nitrophenyl X-substituted thiobenzoates are given in Tables 2 and 3, respectively. The kinetic data are shown graphically in Figures 1-5. The results of the Bronsted correlations are summarized in Tables 4 and 5 for the reactions of S-p-nitrophenyl X-substituted thiobenzoates with Z-substituted phenoxide ions.

Discussion

Table 3. Summary of Second-Order Rate Constant k ($M^{-1}s^{-1}$) for Reactions of S-p-Substituted Phenyl Thiobenzoates (C₆H₅C(O)SC₆H₄-4-Y) with HO⁻ in 20 mole % DMSO-H₂O Mixture at 25°C

Y	NO ₂	Br	H	OCH ₃
pK_a (Y-C ₆ H ₄ SH) ^a	4.72	6.02	6.62	6.78
k , M ⁻¹ s ⁻¹	9.99	1.47	0.711	0.457

^a pK_a values are taken from F. G. Bordwell and D.L. Hughes, *J. Org. Chem.*, **47**, 3324 (1982)

Table 4. Summary of Bronsted Correlations (β_{acyl}) for Reactions of S-p-Nitrophenyl Substituted Thiobenzoates (4-X-C₆H₄C(O)-SC₆H₄-4-NO₂) with Substituted Phenoxides (4-Z-C₆H₄O⁻) in 20 mole % DMSO-H₂O Mixture at 25°C

Z	CHO	CN	CH ₃ CO	Cl	H	OCH ₃
pK_a (Z-PhOH) ^a	7.66	7.73	8.05	9.35	9.95	10.2
β_{acyl}	-2.14	-2.27	-2.22	-2.13	-2.19	-2.38
r	0.999	0.992	0.998	0.999	0.995	0.994

^a pK_a values are taken from ref. 11.

Table 5. Summary of Bronsted Correlations (β_{nuc}) for Reactions of S-p-Nitrophenyl Substituted Thiobenzoates (4-X-C₆H₄C(O)SC₆H₄-4-NO₂) with Substituted Phenoxides (4-Z-C₆H₄O⁻) in 20 mole % DMSO-H₂O Mixture at 25°C

X	CN	Cl	H	^t Bu	OCH ₃
pK_a (X-PhCO ₂ H) ^a	3.55	3.99	4.20	4.40	4.47
β_{nuc}	0.81	0.79	0.80	0.77	0.87
r	0.990	0.993	0.991	0.995	0.991

^a pK_a values are taken from ref. 11.

Effect of The Replaced Sulfur on Reactivity. Thiol esters have often been reported to be more reactive than the corresponding oxygen esters toward nitrogen and sulfur centered nucleophiles.^{18,3} However, oxygen centered nucleophiles such as H₂O and HO⁻ ion in acid and base catalyzed hydrolysis have been demonstrated to be much less reactive toward thiol esters than oxygen esters.^{3,9} The significant dependence of the reactivity of thiol esters on the nature of nucleophilic center would be understood in terms of the so-called hard and soft acids and bases (HSAB) principle, since nitrogen and sulfur nucleophiles are considered to be soft bases and accordingly to show high reactivity toward the soft acid of thiol esters.

In Table 1 is demonstrated that thiol esters are generally more reactive than the corresponding oxygen esters toward substituted phenoxide ions. On the other hand, a hard base HO⁻ ion is less reactive toward thiol esters than the corresponding oxygen esters as shown in Table 2. Since the negative charge on the oxygen atom in substituted phenoxide ions would be delocalized on the aromatic ring, the hardness of the nucleophilic center would be significantly reduced.

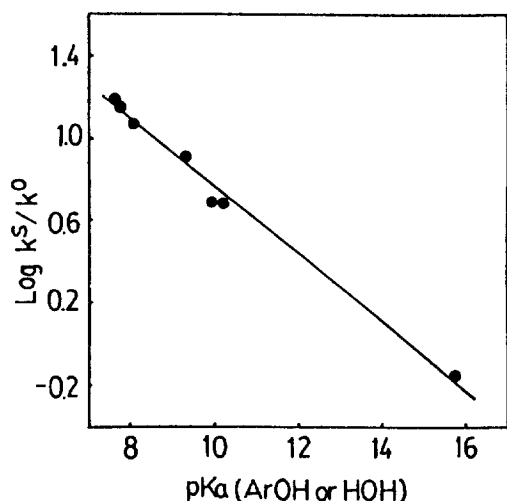


Figure 1. Plot showing the correlation of logarithmic relative rate constant (k^s/k^o) with basicity of nucleophile. k^s and k^o represent second order rate constants for the nucleophilic substitution reactions of S-p-nitrophenyl thiobenzoate and p-nitrophenyl benzoate with aryloxides and hydroxide ions, respectively.^a

^aThe rate data are taken from Table 1 and 2.

Therefore, phenoxide ions are considered to exhibit higher reactivity toward the soft thiol esters compared to the hard oxygen esters in accord with the HSAB principle. However, such a charge delocalization would be diminished with increasing the base strengthening ability of the substituent in phenoxide, which consequently decreases the softness of phenoxide ions. Therefore, if HSAB principle is responsible for the present rate data, the effect of polarizability on rate would become insignificant as the basicity of the nucleophilic phenoxide increases. This has nicely been demonstrated in Figure 1, *i.e.*, the logarithmic relative rate constant ($\log k^s/k^o$) decreases gradually with increasing the basicity of the nucleophilic phenoxide and finally it becomes negative for the highly basic and nonpolarizable HO^- .

The charge polarization of the carbonyl group in thiol esters would be expected to be significantly increased on the basis of the following spectral data. (1) The ^{13}C -NMR spectra have been demonstrated to be *ca.* 20-30 ppm down field shift for the carbonyl carbon when the ether-like oxygen atom is replaced by S in carboxylic esters.^{1a-e} (2) The carbonyl stretching vibrations in thiol esters shift *ca.* 50-70 cm^{-1} to the lower frequency compared to the ones in oxygen esters.^{1a-e} (3) The greater hydrogen-bonding for thiol esters than oxygen esters has been observed from a ^{13}C -NMR study performed by changing solvent with progressively stronger hydrogen-bonding solvent such as from CDCl_3 to $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3\text{CO}_2\text{H}$.^{2d} Such spectral data would give more credence to the conclusion that **2** makes significant contribution to the structure of a thiol ester relative to an oxygen ester.^{1e} Therefore, a thiol ester would have been expected to have significantly increased electrophilicity which would lend it higher reactivity than the corresponding oxygen ester. However, it appears that the enhanced electrophilicity would not be fully reflected in the reactivity of thiol esters, since rate enhancements for the present system are not so significant as expected. Thus, the nature of the HSAB principle would

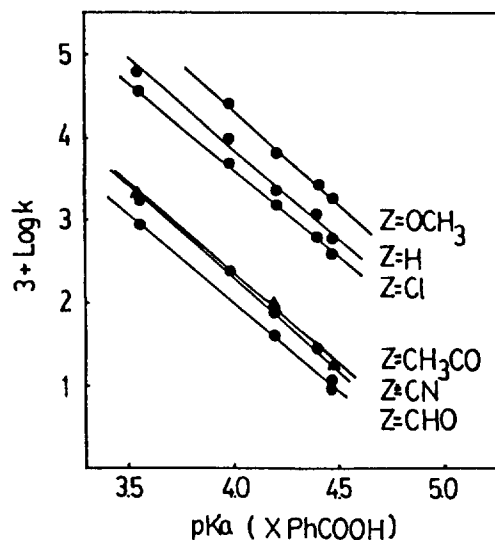
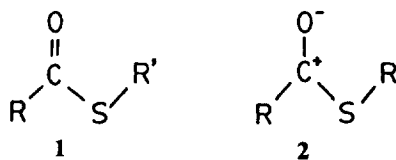


Figure 2. Bronsted type plots for reactions of S-p-nitrophenyl substituted thiobenzoates ($4\text{-X-C}_6\text{H}_4\text{C(O)SC}_6\text{H}_4\text{-4-NO}_2$) with substituted phenoxide ($4\text{-Z-C}_6\text{H}_4\text{O}^-$) in 20 mole % DMSO- H_2O mixture at 25°C . The particular substituted phenoxide is fixed for each line as indicated.

be considered to be responsible for the absence of the enhanced electrophilicity effect on rate.



The reactivity of a substrate toward a given nucleophile would also be influenced by nucleofugicity (leaving group ability).^{9,10} The nucleofugicity of thiol esters has been expected to be significantly higher than the one of the corresponding oxygen esters based on the facts that the leaving thiophenoxide is *ca.* 4 pK_a unit less basic than the corresponding phenoxide¹¹ and the bond dissociation energy of the C-O bond is over 19 kcal/mole greater than the C-S bond.¹² Thus, thiol esters would have been expected to exhibit a remarkably enhanced reactivity. However, they show only slightly higher reactivities than oxygen esters toward phenoxide ions. Moreover, thiol esters are less reactive than oxygen esters toward HO^- as shown in Table 2. Therefore, it appears highly unlikely that the HSAB principle would be fully responsible for the present rate data. The nature of the rate-determining step would also be considered to be responsible for the absence of the nucleofugicity effect on rate, since the enhanced nucleofugicity would not be reflected in reactivity of thiol esters if the leaving group departure is not involved in the rate-determining step.

Reaction Mechanism. In Tables 1-3 are shown the effects of substituent on second-order rate constants for the present reaction system. It is clearly demonstrated that the reactivity increases with increasing electron withdrawing ability of the substituent in the acyl and aryl moiety of the substrate, and with increasing electron donating ability of the substituent in the nucleophilic phenoxide. In Figure 2

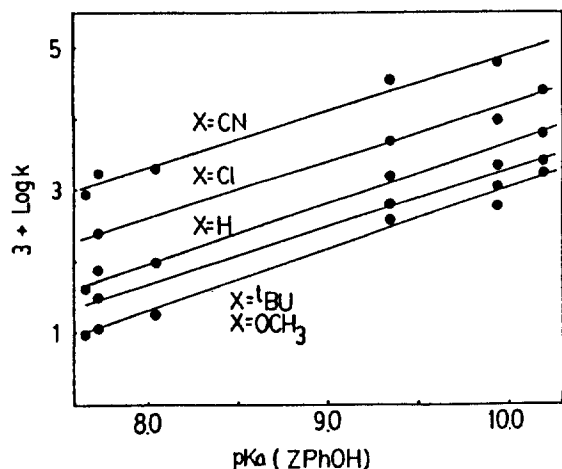


Figure 3. Bronsted type plots for reactions of S-p-nitrophenyl substituted thiobenzoates ($4\text{-X-C}_6\text{H}_4\text{C(O)SC}_6\text{H}_4\text{-4-NO}_2$) with substituted phenoxides ($4\text{-Z-C}_6\text{H}_4\text{O}^-$) in 20 mole % DMSO- H_2O mixture at 25°C . The particular substituted benzoic acid is fixed for each line as indicated.

have been constructed the Bronsted type plots to investigate quantitatively the effect of substituent in the acyl moiety on rate. Excellent Bronsted coefficient β_{acyl} values so obtained indicate that the reactivity of the present thiol esters is significantly sensitive to the electronic nature of the substituent X in the acyl moiety for all the nucleophilic aryloxides studied.

If the leaving group departure is involved in the rate-determining step, the nucleofugicity of the leaving thiophenoxide would be more decreased with increasing the acid strengthening ability of the substituent X in the acyl moiety of the substrate, and consequently the magnitude of Bronsted slope (β_{acyl}) would not be so large. On the other hand, positive β_{acyl} values would be expected if the leaving group departure is significantly more important than the nucleophilic attack. Thus the large negative β_{acyl} values for the present system clearly indicate that the leaving group departure would be little advanced at the transition state of the rate-determining step. This is consistent with the preceding argument that the leaving group departure is not involved in the rate-determining step based on the nature of nucleofugicity of thiol esters.

In Figure 3 has been demonstrated graphically the effect of substituent Z in the nucleophilic phenoxide on rate. As is shown in Figure 3, fairly large Bronsted coefficients (β_{nuc}) with good linearities have been obtained. This would imply that the nucleophilic attack by aryloxides is obviously involved in the rate-determining step. The present results, therefore, enable one to propose a stepwise mechanism, *i.e.*, a rate-determining nucleophilic attack to form a tetrahedral intermediate followed by a fast breakdown of it. This proposal could have obtained more credence by comparing β_{nuc} and β_{lg} values.

However, β_{lg} values for S-substituted phenyl thiobenzoates with aryloxides could not be obtained due to experimental difficulty.¹³ Alternatively, β_{acyl} and β_{lg} values for reaction of HO^- ion with S-p-nitrophenyl substituted thiobenzoates and with S-substituted phenyl thiobenzoates have been determi-

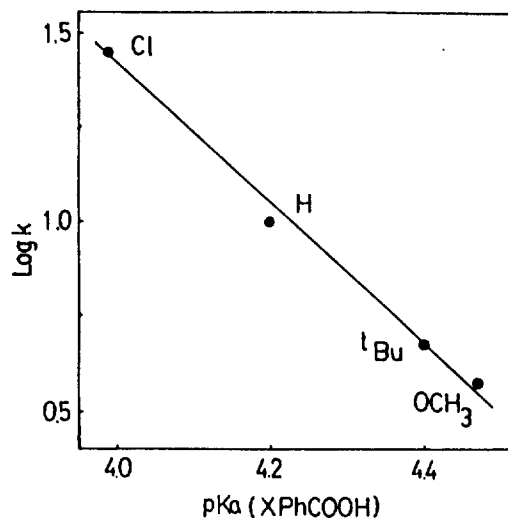


Figure 4. Bronsted type plot for reactions of S-p-nitrophenyl substituted thiobenzoates ($4\text{-X-C}_6\text{H}_4\text{C(O)SC}_6\text{H}_4\text{-4-NO}_2$) with HO^- in 20 mole % DMSO- H_2O mixture at 25°C . The slope of the plot is calculated to be -1.83 ($r=0.996$).

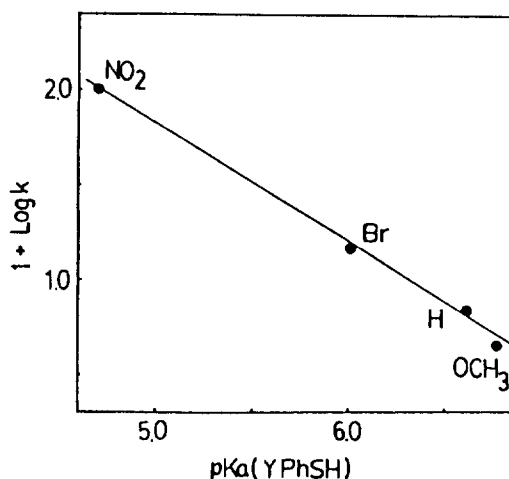


Figure 5. Bronsted type plot for reactions of S-p-substituted phenyl thiobenzoates ($\text{C}_6\text{H}_5\text{C(O)SC}_6\text{H}_4\text{-4-Y}$) with HO^- in 20 mole % DMSO- H_2O mixture at 25°C . The slope of the plot is calculated to be -0.63 ($r=0.998$).

ned. The kinetic results are summarized in Tables 2 and 3 and plotted in Figures 4 and 5, respectively. As shown in Figures 4 and 5, the Bronsted type plots for both system give good linearities, and the magnitude of β_{acyl} (1.83) is much larger than β_{lg} (0.63). Such a large β_{acyl} value compared to β_{lg} might be attributed to the proximity effect, *i.e.*, the reacting bond being one atom closer to the acyl substituent than it is to the leaving thiophenoxide.

However, as discussed in the previous paper,⁵ the nature of reaction mechanism would be more responsible than the proximity effect for the large difference between β_{acyl} and β_{lg} values. It is evident that the substituent in the leaving group would not influence the reactivity of the substrate as strongly as the one in the acyl moiety if the leaving group departure occurs after the rate-determining step. On the contrary, the effect of substituent in the leaving group would

be more significant than the one in the acyl moiety if the leaving group departure is involved in the rate-determining step. In fact, aminolysis of esters has generally been known to proceed *via* a rate-determining leaving group departure, and β_{lg} values have often been reported to be much larger than β_{acyl} values¹⁴ although the former would have been expected to be smaller than the latter if the proximity effect is important. Thus, the large β_{acyl} values obtained in the present system would be considered to originate not from the proximity effect rather from the nature of rate-determining step.

The Reactivity Selectivity Principle (RSP). The RSP has been a guiding principle of chemical behavior, and numerous types of chemical reactions have successfully been explained in terms of the RSP.¹⁵ However, the validity of the RSP is currently under critical discussion.^{15,16}

In Tables 4 and 5 are summarized the Bronsted β values for the present system to investigate the reactivity-selectivity correlation, since the magnitude of Bronsted β together with Hammett ρ has most commonly been used as a selectivity parameter. Interestingly, the Bronsted β_{acyl} values are demonstrated to be almost constant, *i.e.*, the magnitude of β_{acyl} is in the range of -2.2 ± 0.1 . Furthermore, it shows no tendency either to increase or to decrease as the intrinsic reactivity of the nucleophilic phenoxide varies. This is quite an unexpected result on the basis of the RSP, since one would have expected that the magnitude of β_{acyl} would decrease as the reactivity of nucleophile increases. A similar result can be seen for the β_{nuc} values. As shown in Table 5, the magnitude of β_{nuc} is practically constant (0.80 ± 0.05) and gives no correlation with the reactivity of the substrate, indicating that the RSP is definitely invalid in the present system.

Failures of the RSP have often been reported. In the alkaline hydrolysis of aryl substituted benzoates, a constant selectivity has been found.¹⁷ Furthermore, the selectivity parameters (β_{acyl} and β_{nuc}) for acyl transfer reactions of aryl substituted benzoates with aryloxides have recently been reported to show an increasing trend with increasing the reactivity of the reactants.⁵

Many explanations have also been suggested for non RSP behaviors. These have focused mainly on solvent and steric effects, changes in mechanism, anti Hammond effects, inconsistent intrinsic barriers of a series of reactions.¹⁵ The origin for the present failure of the RSP is not clear at this moment, however, it is evident that the RSP should have limited applicability.

Conclusions

The present studies have allowed us to conclude the followings. (1) The effect of polarizability of reactants is significant on reaction rates. (2) The present acyl-transfer reaction is considered to proceed *via* a stepwise mechanism in which the formation of tetrahedral intermediate is rate determining. (3) The RSP is not operative in the present system.

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