

The Effect of Solvation and Polarizability on the α -Effect: Nucleophilic Substitution Reactions of *p*-Nitrophenyl Benzoate with Various Anionic Nucleophiles

Ik-Hwan Um

Department of Chemistry, Ewha Womans University, Seoul 120-750. Received April 27, 1992

Second-order rate constants have been determined spectrophotometrically for nucleophilic substitution reactions of *p*-nitrophenyl benzoate with various anionic nucleophiles including 6 α -effect nucleophiles. The logarithmic second-order rate constants for the aryloxides give a good Brønsted correlation with the respective basicity while the ones for *p*-chlorothiophenoxide and hydroxide exhibit significantly positive and negative deviations, respectively, from the Brønsted linear line. The deviations are attributed to a solvation effect rather than a change in the reaction mechanism. The α -effect nucleophiles except highly basic ones demonstrate significantly higher nucleophilicity (the α -effect) than would be predicted from the respective basicity. The effect of solvation and polarizability appears to be important for the α -effect as well as for the reaction rate.

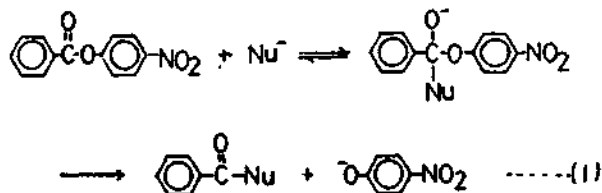
Introduction

The rationalization of nucleophilic reactivity has been one of the major goal in physical organic chemistry. Numerous equations have been proposed in order to correlate nucleophilicity with one or more properties of nucleophiles.¹⁻³ Among them the Brønsted equation⁴ has been and is still applied most successfully to a variety of nucleophilic reactions.

However, a group of nucleophiles containing a hetero atom with one or more nonbonding electron pairs adjacent to the reaction center (the α -position) has often exhibited abnormally higher reactivity than would be predicted from their respective basicity. Thus this type of bases was termed the α -nucleophile and the enhanced nucleophilic reactivity shown by the α -nucleophiles has been called the α -effect.⁵

The magnitude of the α -effect has been suggested to be significantly dependent on solvents,⁶ Brønsted β values⁷ and structural factors such as hybridization of the reaction center.⁸ Besides, many theories have also been proposed to explain the origin of the α -effect,⁹ including (a) destabilization of the ground state due to repulsion between the nonbonding electron pairs,¹⁰ (b) stabilization of the transition state by overlap of the orbitals of the nonbonding pair of electrons in the α -position,¹¹ (c) product stability,¹² (d) intramolecular general acid catalysts,¹³ (e) polarizability,¹⁴ (f) solvation effect.^{6,15,16}

However, the α -effect has not been completely understood. Particularly, factors (e) and (f) have been the subject of controversy, and lack of systematic study is considered to be responsible for the controversy. Thus, for a systematic investigation of the α -effect, we have chosen the following reaction system.



Nu⁻ = various types of anionic nucleophiles as listed in Tables 1 and 2

Table 1. Summary of second-order rate constants (k_2) for the reactions of *p*-nitrophenyl benzoate with various types of anionic nucleophiles in 10 mole% DMSO-H₂O at 25°C

Nu ²	pK_a (NuH) ^a	k_2 , M ⁻¹ s ⁻¹
1. <i>p</i> -CHOPhO ⁻	7.66	0.00180
2. <i>p</i> -CNPhO ⁻	7.73	0.00375
3. <i>p</i> -CH ₃ COPhO ⁻	8.05	0.00466
4. <i>p</i> -ClPhO ⁻	9.35	0.136
5. <i>p</i> -PhO ⁻	9.95	0.273
6. <i>p</i> -CH ₃ PhO ⁻	10.07	0.567
7. <i>p</i> -CH ₃ OPhO ⁻	10.20	0.813
8. CF ₃ CH ₂ O ⁻	12.37	22.9
9. OH ⁻	15.75	5.83
10. <i>p</i> -ClPhS ⁻	7.50	0.594

^a pK_a data were taken from ref. 30.

Table 2. Summary of second-order rate constants (k_2) for the reactions of *p*-nitrophenyl benzoate with various α -effect nucleophiles in 10 mol% DMSO-H₂O at 25°C

Nu ²	pK_a (NuH) ^a	k_2 , M ⁻¹ s ⁻¹
11. N ₃ ⁻	4.0	0.00290
12. SO ₃ ²⁻	7.21	0.246
13. BzH ⁻ (benzohydroxamate)	8.88	7.64
14. Ox ⁻ (butane-2,3-dione monoximate)	9.44	18.1
15. APOx ⁻ (acetophenonoximate)	11.4	20.2
16. AOx ⁻ (acetonoximate)	12.42	19.0

^a pK_a data were taken from ref. 30.

The nucleophiles employed in the present study are in a wide pK_a range and the nucleophilic center atom varies from oxygen to nitrogen and sulfur. Such a wide pK_a range and changes in the nucleophilic atom would cause significant differences in solvation as well as in polarizability. Furthermore, the reaction mechanism of the acyl-transfer reaction has been extensively studied.¹⁷ Therefore the present system

would be considered to be proper for a systematic investigation of the α -effect.

Experimental

Materials. *p*-Nitrophenyl benzoate, benzohydroxamic acid, acetophenoxime and acetoxime were easily prepared by known procedures¹⁸ and their purity was checked by means of their melting point and spectral data such as IR and NMR spectra. Other chemicals used in the present study were of the highest quality available (Aldrich) and were generally recrystallized before use. Dimethyl sulfoxide was distilled over calcium hydride under a reduced pressure (64–66°C at 6–7 mmHg). Doubly glass distilled water was boiled and cooled under a nitrogen atmosphere just before use. Only freshly prepared solutions were used in the kinetic study, and transfers of solutions were performed by means of Hamilton gas-tight syringes.

Kinetics. Kinetic data were obtained spectrophotometrically by using a Hitachi U-2000 Model UV-VIS Spectrophotometer. A Neslab RTE-110 Model constant temperature circulating bath was used to keep the reaction temperature at $25.0 \pm 0.1^\circ\text{C}$.

The reaction was monitored by measuring the appearance of the leaving *p*-nitrophenoxide at 410 nm. All the reactions were carried out under pseudo-first-order conditions in which the concentration of nucleophile was generally 20 to 100 times greater than the one for the substrate (2.4×10^{-5} M).

The stock solution of nucleophile was made up with NaOH solution and 2 equivalent respective conjugate acid of the nucleophile, except N_3^- and HO^- ions, to suppress formation of hydroxide ion by solvolysis as described previously.¹⁸ The stock solution of N_3^- was made up with 0.05 M borate buffer solution, and 0.1 M NaOH solution was used as the stock solution of HO^- ion.

Results

Pseudo-first-order rate constant (k_{obs}) were calculated from the Guggenheim plots, $\ln(A_\infty - A_t) = k_{\text{obs}}t + c$, which were linear over 90% reaction for all the nucleophiles. Second-order rate constants were obtained from the slopes of the linear plots of k_{obs} versus the concentrations of nucleophiles. More than 5 different concentrations of nucleophile were generally used to obtain second-order rate constants.

Second-order rate constants obtained in this way are presented in Table 1 for the reactions of *p*-nitrophenyl benzoate (PNPB) with 7 aryloxides, *p*-ClPhS⁻, CF₃CH₂O⁻ and HO⁻ ions at 25°C in H₂O containing 10 mole % dimethyl sulfoxide (DMSO) to eliminate a solubility problem. The kinetic data are shown graphically in Figure 1 for the aryloxides system (Hammett plot) and in Figure 2 for all the nucleophiles (Brønsted plot). In Table 2 are summarized second-order rate constants for the reactions of PNPB with various types of α -effect nucleophiles at 25°C in H₂O containing 10 mole % DMSO. The kinetic data are plotted in Figure 3 for the reactions of PNPB with all the nucleophiles listed in Tables 1 and 2.

Discussion

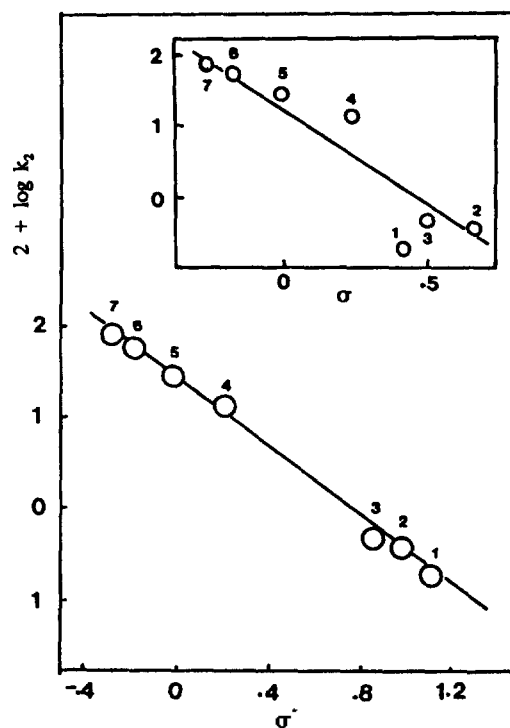


Figure 1. Hammett plots for the reactions of *p*-nitrophenyl benzoate with substituted phenoxides in 10 mole% DMSO at 25°C. The numbers refer to nucleophiles in Table 1.

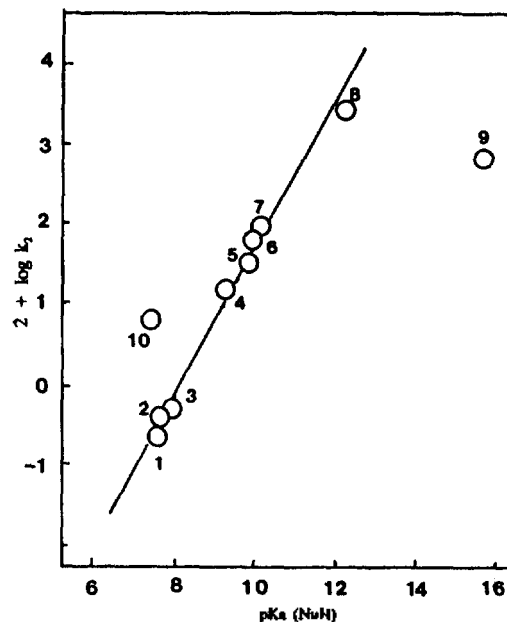


Figure 2. Brønsted plot for the reactions of *p*-nitrophenyl benzoate with various types of anionic nucleophiles in 10 mole% DMSO at 25°C. The numbers refer to nucleophiles in Table 1.

The Effect of Polarizability and Solvation on Rate.

In Figure 1 is graphically demonstrated a structure-reactivity relationship for the reaction of PNPB with 7 aryloxide. As shown in the Figure, the nucleophilicity of the aryloxides increases with increasing electron donating ability of the substituent on the phenoxide ring *i.e.*, the correlation of the logarithmic second-order rate constant ($\log k$) with the Ham-

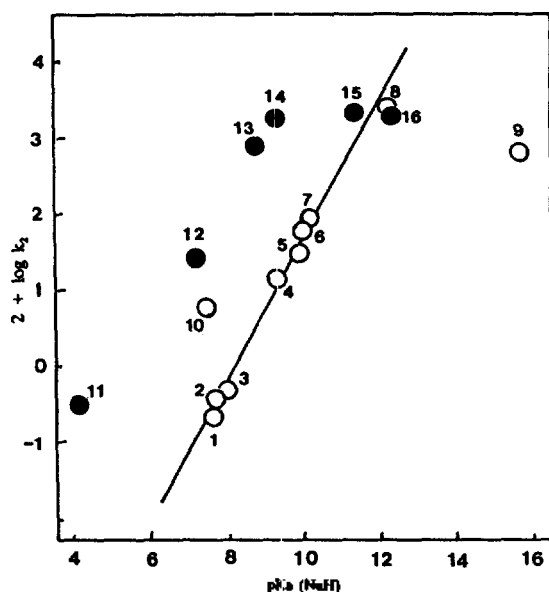


Figure 3. Brønsted plot for the reactions of *p*-nitrophenyl benzoate with various types of anionic nucleophiles including α -effect nucleophiles in 10 mole% DMSO at 25°C. The numbers refer to nucleophiles in Tables 1 and 2.

mett substituent constant (σ^-) gives a good linearity ($r = 0.998$) with a large negative slope ($\rho^- = -1.92$). Such a large ρ^- value obtained in the present system implies that the attack of the nucleophiles is definitely involved in the rate determining step. This is further supported from the fact the correlation of $\log k$ with σ gives much poorer linearity than with σ^- as shown in the inset of Figure 1.

A Brønsted type plot has been constructed to correlate the nucleophilic reactivity with the basicity of all the nucleophiles listed in Table 1. As shown in Figure 2, the basicity of the aryloxides and trifluoroethoxide correlates nicely with nucleophilicity. However, *p*-ClPhS⁻ shows a significant positive deviation while HO⁻ deviates negatively from the linear line.

A linearity obtained from a Brønsted plot has generally been suggestive of a common reaction mechanism for a series of reactants.¹⁻³ On the contrary, a break in a Brønsted plot has been considered to indicate a change in the rate-determining step.¹⁻³ Thus a change in the reaction mechanism would be considered to be responsible for the significant deviation displayed by OH⁻ ion in Figure 2. However, such a deviation shown by HO⁻ in some Brønsted plots has often been observed and ascribed to differential solvation rather than a change in the reaction mechanism.¹⁹ Similarly, the structural difference between *p*-ClPhS⁻ and the oxygen nucleophiles would be more responsible than a change in the reaction mechanism for the large positive deviation of *p*-ClPhS⁻ in the present Brønsted plot. In fact, sulfur centered nucleophiles has frequently exhibited significant rate enhancements toward carbonyl carbon.^{3a,20} Furthermore, the rate enhancement by sulfur centered nucleophiles has been reported to be more pronounced as the carbonyl carbon becomes more polarizable.^{20a} Therefore, the significant positive deviation shown by *p*-ClPhS⁻ would be attributed to the fact that sulfur is much more polarizable than oxygen.

However, a solvation factor would be considered to be also responsible for the present deviations in Figure 2. It has well been known that sulfur does not form a strong H-bonding and consequently sulfur containing compound is much less soluble than the corresponding oxygen compound in H₂O. In fact, PhS⁻ has been reported to be less solvated than PhO⁻ in H₂O by 6 kcal/mole,²¹ which would account for the high nucleophilicity of the thiophenoxide compared with phenoxide of a similar basicity. Such a solvation effect on rate is reflected in the reactivity of HO⁻. As shown in Figure 2, HO⁻ is less reactive than CF₃CH₂O⁻ although the former is much more basic than the latter. The unusual low reactivity of HO⁻ is clearly attributable to the solvation effect, since the highly basic HO⁻ ion has been reported to be 22 and 32 kcal/mole more solvated than the less basic CF₃CH₂O⁻ and PhO⁻ in H₂O, respectively.²¹ Therefore, the deviations shown by *p*-ClPhS⁻ and HO⁻ ions in the present system would be attributed to the effect of polarizability and solvation but not to any change in the reaction mechanism.

The Effect of Solvent on the α -Effect. In Table 2 have been summarized second-order rate constants for the reaction of PNPB with various types of α -effect nucleophiles. The reactivity of these nucleophiles is generally increasing with increasing basicity. For a quantitative analysis of the α -effect, a Brønsted type plot has been constructed for all the nucleophiles including the ones listed in Table 1.

In Figure 3 is demonstrated that the low basic α -effect nucleophiles (e.g., N₃⁻, SO₃²⁻, BxH⁻ and Ox⁻) show significant positive deviations from the linear line. Interestingly, when the basicity of the α -effect nucleophile becomes greater than that of phenoxide, the α -effect is getting smaller and finally no α -effect is observed for the highly basic α -effect nucleophile (AOx⁻). Hudson and his coworkers have observed a similar result in the reaction of *p*-nitrophenyl acetate and attempted to explain the disappearance of the α -effect for the highly basic α -effect nucleophile in terms of molecular orbital theory.²² However, the argument concerning HOMO energies of α -effect nucleophiles has been a subject of controversy.^{10,23}

It has been well known that the effect of solvation on reactivity is significant for the reactions of present type. Furthermore, it is evident that the degree of solvation of anionic species in H₂O would increase with increasing basicity as discussed in the preceding section. Thus solvation of the highly basic α -effect nucleophile (AOx⁻) would be expected to be highly solvated, which in consequence would be responsible, at least in part, for the absence of the α -effect.

As shown in Figure 3, Ox⁻ shows a large α -effect in the present system. This is consistent with the recent study that the α -effect nucleophile (Ox⁻) is more reactive than the corresponding normal nucleophile (*p*-ClPhO⁻) toward *p*-nitrophenyl acetate in H₂O.^{6a} It has been also reported that the α -effect becomes more significant upon additions of a cationic surfactant in the reaction medium.²⁴ Therefore, the large α -effect shown by Ox⁻ was attributed to a solvation factor, since the fact that Ox⁻ shows much higher rate enhancement than *p*-ClPhO⁻ in the cationic micellar solution could lead a conclusion that the former is less solvated than the latter in H₂O.²⁴ This was further supported by a calorimetric study which has revealed that Ox⁻ is less solvated than *p*-ClPhO⁻ by 4 kcal/mole in H₂O.²⁵

Unlike Ox^- , BzH^- has been reported to be highly solvated. Therefore, one would not expect a large α -effect for BzH^- if the solvation effect is an important factor for the α -effect. In fact, BzH^- has been reported to show no α -effect in the presence of a cationic surfactant.²⁶ However, interestingly, BzH^- exhibits a large α -effect in the absence of a cationic surfactant as shown in Figure 3. Therefore, the solvation effect does not appear to be solely responsible for the α -effect, at least for the BzH^- system.

The Effect of Polarizability on the α -Effect. As shown in Figure 3, N_3^- ion exhibits a large positive deviation from the Brønsted line. The origin for the deviation would be attributed to a difference in the reaction mechanism. It has generally been believed that the reactions of aryl benzoates with anionic nucleophiles such as HO^- and aryloxides proceed *via* a rate-determining formation of the tetrahedral intermediate,^{3,17} while the break-down of the intermediate has been considered to be the rate-determining step (RDS) for the reactions of the esters with neutral amines.²⁷ However, although N_3^- is an anionic nucleophile, it would proceed in a different manner from other anionic nucleophiles such as HO^- and aryloxides. It is because N_3^- is much less basic than the leaving *p*-nitrophenoxide, and consequently it would exert higher nucleofugicity than the leaving *p*-nitrophenoxide ion. In fact, the reaction of aryl benzoates with N_3^- in CH_3CN has been reported to proceed *via* a rate-determining break-down of the tetrahedral intermediate.²⁷ However, the nature of the RDS for N_3^- in H_2O is not clearly understood and remains still in controversy.^{3a}

On the other hand, it has been reported that N_3^- has molar refraction of 12.27 which would exert unusually high polarizability.²⁸ Furthermore, N_3^- has often exhibited abnormally higher reactivity compared with amines of comparable basicity toward a variety of polarizable carbon electrophiles.²⁸ Therefore, it is clear that basicity alone does not determine nucleophilicity, particularly for the reaction of different families of reactants as discussed in the preceding section for the *p*-ClPhS⁻ system. This has been demonstrated successfully for many simple displacement reactions by the Edward's two-parameter correlation of nucleophilicity with polarizability and basicity.²⁹ Therefore, the present deviation shown by N_3^- would be attributed to the high polarizability of N_3^- . The importance of polarizability effect on the α -effect is nicely demonstrated for the reaction of polarizable SO_3^{2-} . Like *p*-ClPhS⁻, SO_3^{2-} has been considered to be highly polarizable since the nucleophilic atom of SO_3^{2-} is the polarizable sulfur but not oxygen when the electrophilic atom is a polarizable carbonyl carbon. Therefore, the abnormally high reactivity of SO_3^{2-} in the present system is evidently associated with its high polarizability and credence would be given to the argument that high polarizability of N_3^- is responsible for its large α -effect.

Conclusion

The effect of solvation and polarizability appears to be important for the α -effect as well as for the reaction rate.

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Preferential Solvation and Statistical Analysis for Solvent Polarity Parameters in MeOH Binary Mixtures

Yeol Sakong*, Seoung-Kyo Yoo, and Ikchoon Lee†

Department of Chemistry, Hanyang University, Seoul 133-791

†Department of Chemistry, Inha University, Incheon 402-751. Received June 4, 1992

Preferential solvation (PS) phenomena of solutes based on solvent polarity, E_T and AN , were studied by UV/vis. and NMR spectra in MeOH binary mixtures. According to the extent of solvent-solvent interaction, different solvation phenomena were found. PS concept was applied to explain the reactivity of *tert*-butyl halides solvolysis. The findings of solvation phenomena have been related to the rate of solvolysis and PS suggested as a reason for the solvent dependence of the rates of reaction. Moreover, we found that the results of principal components analysis using six parameters are in good accordance with the results of PS phenomena in mixed methanol systems.

Introduction

Although the effect of solvent on the rate and the position of equilibrium of chemical reactions has been known for over a hundred year,¹ there are still no reliable and exact methods for a quantitative description and prediction of such solvent effects. But one of the most important selection criteria in this connection is a property of solvents generally known as 'solvent polarity'. Various empirical solvent polarity parameters have been often used effectively to describe the influence of solvents on physicochemical solute properties of different kinds^{2,3} and there have been several attempts to correlate with the solvation phenomena of empirical or experimental parameters of solvent polarity and kinetic data in mixed binary solvents.⁴⁻⁷

In this work, we have studied solvation phenomena of solvent polarity (E_T ⁸ and AN ⁹) in eight methanol mixtures since mixed binary solvents are extremely versatile and useful solvent systems, particularly in kinetic and spectroscopic studies. However, there have often been abnormal problems in kinetic and spectroscopic studies in mixed solvent systems. One of those involves the possibility of PS. This implies that the difference in the specificities of interaction of solute with the component solvents, the composition of the solvents in the immediate vicinity of the solute may be different from that in the bulk. It is obvious that PS may be of paramount importance in the interpretation of spectroscopic

and kinetic data obtained in binary systems.¹⁰⁻¹⁴ In this reason, the reactivity of *tert*-butyl halides solvolysis has been discussed by comparing PS phenomena of polar solutes based on solvent polarity in methanol mixtures.

And that the classification of mixed binary solvents is proposed by treating a basis set of six solvent parameters (the Reichardt's E_T , solvatochromic parameters (π^* , α , β)^{15,16} of Kamlet-Taft and Gutmann's AN , DN ^{17,18}) by the principal components analysis.^{19,20} This classification is based on the representation of 41 mixed methanol solvents as points in a two-dimensional space, solvent similarity being measured from the distance between two points within this space.

Experimental

Materials. The solvents used were methanol (MeOH), dimethylsulfoxide (DMSO), pyridine (PY), dimethylformamide (DMF), methylcyanide (MeCN), dioxane, acetone (AC), 1,2-dichloroethane (DCE), 1,1,2,2-tetrachloroethane (TCE), *n*-hexane and carbon tetrachloride. All of the solvents were spectrophotometric grade of Aldrich Chemicals and each solvent was dried over molecular sieve 4 Å. Binary solvent mixture use were MeOH-DMSO, MeOH-PY, MeOH-DMF, MeOH-MeCN, MeOH-dioxane, MeOH-AC, MeOH-DCE and MeOH-TCE and prepared by weight at nominally round mole fraction with intervals of 0.1.

AN indicator, triethylphosphine oxide (Et_3PO) was pur-