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The α-Effect in S_NAr Reaction of Y-Substituted-Phenoxy-2,4-Dinitrobenzenes with Amines: Reaction Mechanism and Origin of the α-Effect

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Second-order rate constants (k_N) have been measured spectrophotometrically for S_NAr reactions of Y-substituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) with hydrazine and glycylglycine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. Hydrazine is 14.6-23.4 times more reactive than glycylglycine. The magnitude of the α-effect increases linearly as the substituent Y becomes a stronger electron-withdrawing group (EWG). The Brønsted-type plots for the reactions with hydrazine and glycylglycine are linear with β_{lg} = –0.21 and –0.14, respectively, which is typical for reactions reported previously to proceed through a stepwise mechanism with expulsion of the leaving group occurring after rate-determining step (RDS). The Hammett plots correlated with σ^o constants result in much better linear correlations than σ^- constants, indicating that expulsion of the leaving group is not advanced in the transition state (TS). The reaction of **1a-1g** with hydrazine has been proposed to proceed through a five-membered cyclic intermediate (T_{III}), which is structurally not possible for the reaction with glycylglycine. Stabilization of the intermediate T_{III} through intramolecular H-bonding interaction has been suggested as an origin of the α-effect exhibited by hydrazine.

Key Words : The α-effect, S_NAr reaction, Hydrazine, 1-Aryloxy-2,4-dinitrobenzenes, Hammett plot

Introduction

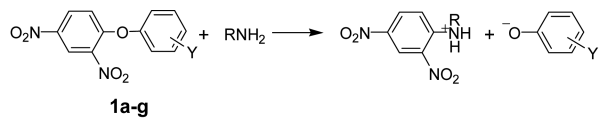
It is firmly understood that basicity of nucleophiles is one of the most common tools to predict nucleophilicity.[1] However, a certain group of nucleophiles has been reported to exhibit abnormally enhanced nucleophilic reactivity than would be expected from their basicity.[2] A common feature of these nucleophiles is possession of one or more non-bonding electron pairs on the atom α to the reaction site (*e.g.*, NH_2NH_2, NH_2OH, $R_1R_2C{=}NO^-$, $RC(O)NHO^-$).[2] Thus, the term α-effect was given to the enhanced nucleophilic reactivity exhibited by these nucleophiles.[2]

Some important theories suggested as the origin of the α-effect are: (1) Destabilization of the ground-state (GS) due to the electronic repulsion between the nonbonding electron pairs, (2) Stabilization of the transition-state (TS), (3) Thermodynamic stability of products, (4) Solvent effect.[3-8] However, the α-effect phenomenon has not been completely understood. Particularly, solvent effect on the α-effect is controversial for the α-effect exhibited by anionic α-effect nucleophiles (*e.g.*, hydrogen peroxide, oximates, hydroxamates).[4-8]

Although numerous studies on acyl-group transfer reactions have been carried out to investigate the origin of the α-effect, S_NAr reactions of activated aromatic or heteroaromatic compounds with α-nucleophiles have much less been investigated.[9] Moutiers *et al*. have reported that weakly basic oximates (*e.g.*, $pK_a < 7.5$) exhibit large α-effects in the S_NAr reaction of 1-fluoro-2,4-dinitrobenzene (DNFB), but the α-effect decreases rapidly as the basicity of oximates increases.[9] Partial desolvation of the strongly basic oximates before nucleophilic attack has been suggested to be responsible for the decreasing α-effect behaviour.[9]

We have recently reported that S_NAr reaction of DNFB with a series of secondary amines in MeCN proceeds through a stepwise mechanism with two intermediates (*e.g.*, a zwitterionic Meisenheimer complex $MC^{\pm}$ and it deprotonated form MC^-) on the basis of the kinetic results that plots of k_{obsd} *vs.* [amine] curve upward.[10] In contrast, the corresponding reactions with primary amines including hydrazine have been reported to proceed through a stepwise mechanism, in which expulsion of the leaving group occurs after RDS (*i.e.*, absence of the deprotonation process to form MC^- from $MC^{\pm}$) on the basis of a linear Brønsted-type plot with β_{nuc} = 0.46.[11] Besides, hydrazine has been found to be *ca*. 10 times more reactive than similarly basic glycylglycine.[11] The α-effect found for the S_NAr reaction is much smaller than that reported for acyl-group transfer reactions which proceed through a stepwise mechanism with expulsion of the leaving group being the RDS.[12] Thus, it has been proposed that destabilization of the GS of hydrazine (*e.g.*, electronic repulsions between the nonbonding electron pairs) is mainly responsible for the small α-effect found in the S_NAr reaction of DNFB.[11]

Our study has now been extended to reactions of Y-sub-



1a-g

Y = 4-NO_2 (**1a**), 4-CN (**1b**), 4-COMe (**1c**), 3-Cl (**1d**), 4-Cl (**1e**), H (**1f**), 4-CH_3 (**1g**).
RNH_2 = hydrazine, glycylglycine.

Scheme 1

stituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) with hydrazine and glycylglycine as an α-nucleophile and a reference normal-nucleophile, respectively to obtained further information on the origin of the α-effect in the S_NAr reaction (Scheme 1). The reaction mechanism including a plausible intermediate has also been discussed through analysis of Brønsted-type and Hammett correlations.

Results and Discussion

The kinetic study was performed under pseudo-first-order conditions in which the amine concentration (*i.e.*, hydrazine and glycylglycine) was kept in excess over the substrate concentration. All of the reactions in this study obeyed first-order kinetics, and pseudo-first-order rate constants (k_{obsd}) were calculated from the equation, $\ln (A_\infty - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} *vs*. [amine] were linear and passed through the origin, indicating that general-base catalysis by a second amine molecule is absent and contribution of H_2O and/or OH^- to the k_{obsd} value is negligible. Thus, the second-order rate constants (k_N) were calculated from the slope of the linear plots. Based on replicate runs, it is estimated that the uncertainty in the k_N values is less than ± 3%. The k_N values calculated in this way are summarized in Table 1 for the S_NAr reactions of **1a-1g** with hydrazine and glycylglycine together with the magnitude of the α-effect (*i.e.*, the $k_N^{hydrazine}/k_N^{glycylglycine}$ ratio).

Reaction Mechanism. As shown in Table 1, the k_N value decreases as the leaving-group basicity increases, *e.g.*, it decreases from 18.6×10^{-3} $M^{-1}s^{-1}$ to 9.86×10^{-3} and 4.18×10^{-3} $M^{-1}s^{-1}$ for the reaction with hydrazine as the pK_a of Y-substituted-phenol increases from 7.14 to 9.02 and 10.19, in turn. A similar result is demonstrated for the corresponding reactions with glycylglycine, although dependence of k_N on the leaving-group basicity is not significant. It is also notable that hydrazine is more reactive than glycylglycine regardless of the leaving-group basicity, indicating that the α-effect is operative in the current reaction system.

The effect of leaving-group basicity on reactivity of substrates **1a-1g** is illustrated in Figure 1. The Brønsted-type plots for the reactions with hydrazine and glycylglycine are

Table 1. Summary of Kinetic Data for the Reactions of Y-Substituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) with Hydrazine and Glycylglycine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C[a]

	Y	p$K_a^{Y\text{-}PhOH}$	$10^4k_N/M^{-1}s^{-1}$		α-effect
			hydrazine	glygly	
1a	4-NO_2	7.14	186	7.96	23.4
1b	4-CN	7.95	146	7.23	20.2
1c	4-COMe	8.05	121	6.13	19.7
1d	3-Cl	9.02	98.6	5.47	18.0
1e	4-Cl	9.38	76.7	4.67	16.4
1f	H	9.95	50.4	3.36	15.0
1g	4-CH_3	10.19	41.8	2.87	14.6

[a]The pK_a data were taken from ref. 13.

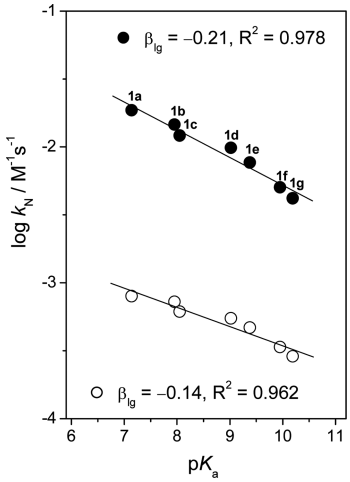


Figure 1. Brønsted-type plots for the S_NAr reactions of Y-substituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) with hydrazine (●) and glycylglycine (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

linear with $\beta_{lg} = -0.21$ and -0.14, respectively. These values are quite small but are consistent with the kinetic result that the k_N value decreases only 3 to 5 times upon increasing the leaving-group basicity over 3 pK_a units. The magnitude of β_{lg} value has been most commonly used to deduce the reaction mechanism.[14-16] A β_{lg} value of -0.5 ± 0.1 is typical for reactions reported to proceed through a concerted mechanism. In contrast, the β_{lg} value for a stepwise mechanism is known to be strongly dependent on the nature of RDS, *e.g.*, $\beta_{lg} = -0.3 \pm 0.1$ when expulsion of the leaving group occurs after RDS but $\beta_{lg} = -1.6 \pm 0.3$ when expulsion of the leaving group occurs in RDS.[14-16] Thus, one can suggest that the S_NAr reactions of **1a-1g** proceed through a stepwise mechanism in which expulsion of the leaving group occurs rapidly after RDS on the basis of the β_{lg} value of –0.21 or –0.14. This idea is consistent with the fact that expulsion of the leaving group from $MC^{\pm}$ regains the lost aromaticity of the aromatic ring.

More conclusive information on the nature of RDS can be obtained from Hammett plots correlated with σ^o and σ^- constants. If expulsion of the leaving group occurs in RDS, a partial negative charge would develop on the O atom of the leaving group (*i.e.*, Y-substituted-phenoxide ion) in the TS. Since such a negative charge could be delocalized to the substituent Y through resonance interactions, one might expect that σ^- constants should result in a better Hammett correlation than σ^o constants. In contrast, if expulsion of the leaving group occurs after RDS, no negative charge would develop on the O atom of the leaving group in the TS. In this case, σ^o constants should result in a better Hammett correlation than σ^- constants. Thus, Hammett plots have been constructed to investigate the nature of RDS. As shown in Figure 2, the Hammett plots correlated with σ^o constants result in much better linearity than σ^- constants with $\rho_Y = 0.69$ and 0.48 for the reactions with hydrazine and glycylglycine, respectively. The fact that σ^o constants result in much better linearity than σ^- constants clearly indicates that no

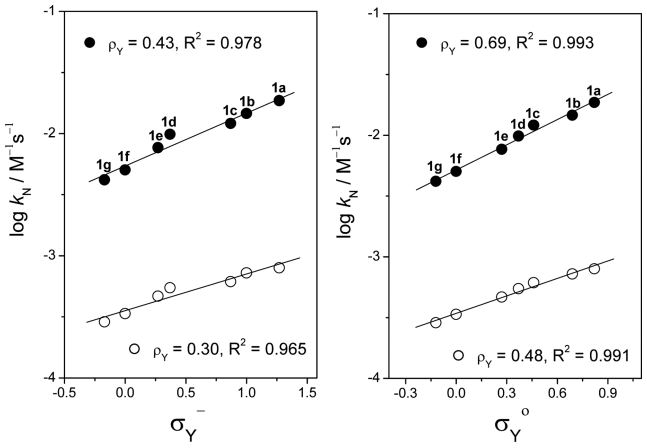


Figure 2. Hammett correlations of log k_N with σ_Y^- and σ_Y^o for the S_NAr reactions of Y-substituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) with hydrazine (●) and glycylglycine (○) in 80 mol % H_2O/ 20 mol % DMSO at 25.0 ± 0.1 °C.

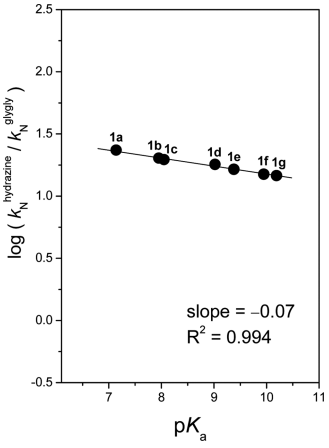
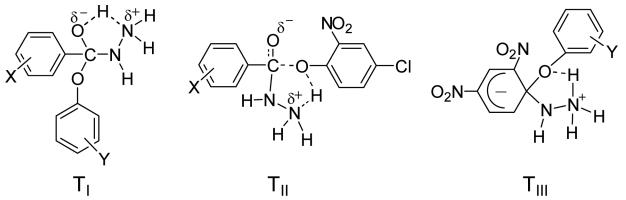


Figure 3. Plot showing dependence of the α-effect on the leaving-group basicity for the reactions of Y-substituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) with hydrazine and glycylglycine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

negative charge is developing on the O atom of the leaving group in the TS. Thus, one can conclude that the S_NAr reactions of **1a-1g** proceed through a stepwise mechanism in which expulsion of the leaving group occurs after RDS.

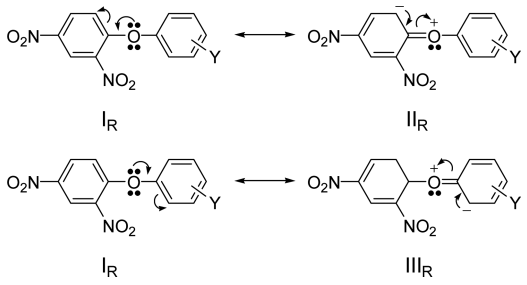
Origin of the α-Effect. It is generally understood that oxyanions are strongly solvated in H_2O due to strong H-bonding interactions with H_2O molecules. However, HOO^- ion has been reported to be 12 kcal/mol less strongly solvated than OH^- ion in H_2O.[17] Our calorimetric study has also revealed that butane-2,3-dione monoximate ion is 5.7 kcal/mol less solvated than 4-chlorophenoxide ion (*i.e.*, a reference normal-nucleophile).[18] Thus, solvent effect has been suggested as an important origin for the α-effect exhibited by anionic α-nucleophiles (*e.g.*, HOO^- and oximate anions).[3a,3b,18] In contrast, neutral amines are much less strongly solvated than oxyanions in H_2O. Accordingly, one might expect that solvent effect is not responsible for the α-effect shown by hydrazine. In fact, stabilization of the intermediates (or TSs) as modeled by T_I and T_{II} has been suggested as an origin of the α-effect exhibited by hydrazine.[19] Because such a cyclic intermediate (or TS), which is stabilized through the H-bonding interaction, is structurally not possible for the reactions with glycylglycine.



A similarly stabilized intermediate would be possible for the reactions of **1a-1g** with hydrazine (*e.g.*, T_{III}). Scrutiny of the intermediate T_{III} reveals that the H-bonding interaction could facilitate expulsion of the leaving group. It is apparent that the enhanced nucleofugality through the H-bonding interaction would be highly effective in increasing the overall reaction rate, if expulsion of the leaving group is involved in RDS. However, it would be ineffective for the reactions of **1a-1g** with hydrazine, since expulsion of the leaving group in this study occurs after RDS. Thus, one can suggest that stabilization of the cyclic intermediate T_{III} through the H-bonding interaction (but not by increasing nucleofugality) is an origin of the α-effect exhibited by hydrazine.

Effect of Substituent Y on Magnitude of the α-Effect. As shown in Table 1, the α-effect increases as the leaving-group substituent Y becomes a stronger EWG (or as the leaving-group basicity decreases), *e.g.*, it increases from 14.6 to 18.0 and 23.4 as the pK_a of the Y-substituted-phenol decreases from 10.19 to 9.02 and 7.96, in turn. The effect of leaving-group basicity on the magnitude of the α-effect is illustrated in Figure 3. The plot exhibits an excellent linear correlation with a slope of –0.07. This is consistent with the kinetic result that the reactions with hydrazine result in larger β_{lg} and ρ_Y values than those with glycylglycine.

Substrates **1a-1g** can be represented by three different resonance structures as illustrated in the resonance structures I_R, II_R and III_R. It is evident that the resonance structure II_R would be more favorable than III_R regardless of the electronic nature of the substituent Y, since the negative charge can be delocalized to the two NO_2 groups. However, the contribution of the resonance structure II_R would decrease as the substituent Y becomes a stronger EWG.



One might expect that the positively charged O atom in II_R would inhibit formation of the cyclic intermediate T_{III}. However, such inhibition would be less significant as the

substituent Y becomes a stronger EWG. Because the contribution of the resonance structure II_R would decrease as the substituent Y becomes a stronger EWG. Thus, the rate enhancement through the cyclic intermediate T_{III} would increase as the substituent Y changes from 4-Me to a strong electron withdrawing 4-NO_2. This idea can be further supported by the kinetic result that the α-effect increases linearly as the substituent Y becomes a stronger EWG.

Conclusion

The current study has allowed us to conclude the following: (1) The linear Brønsted-type plots for the reactions of **1a-1g** with a small β_{lg} value indicate that the reactions proceed through a stepwise mechanism, in which expulsion of the leaving group occurs after RDS. (2) The kinetic result that σ^o constants result in much better linear Hammett correlations than σ^- constants is consistent with the proposed reaction mechanism. (3) A five-membered cyclic intermediate T_{III}, which is stabilized through H-bonding interaction, is proposed to account for the α-effect exhibited by hydrazine. (4) The H-bonding interaction would facilitate expulsion of the leaving group. However, the enhanced nucleofugality through the H-bonding interaction is not the origin of the α-effect exhibited by hydrazine in this study. (5) Decreasing contribution of resonance structure II_R is responsible for the increasing α-effect as the substituent Y becomes a stronger EWG.

Experimental Section

Materials. Y-Substituted-phenoxy-2,4-dinitrobenzenes (**1a-1g**) were readily prepared from the reaction of the respective Y-substituted-phenol with 1-fluoro-2,4-dinitrobenzene in anhydrous ethanol under the presence of sodium ethoxide. The crude products were purified by column chromatography and the purity was checked by their melting points and spectral data such as ^{1}H and ^{13}C NMR spectra. Other chemicals were of the highest quality available. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic study was performed using a UV-Vis spectrophotometer equipped with a constant temperature circulating bath to maintain the reaction mixture at 25.0 ± 0.1 °C. The reactions were followed by monitoring the appearance of *N*-(2,4-nitrophenyl)amines. All of the reactions in this study were carried out under pseudo-first-order conditions, in which the concentration of hydrazine or glycylglycine was kept in excess over that of the substrate.

Typically, the reaction was initiated by adding 5 μL of a 0.02 M solution of the substrate in acetonitrile to a 10-mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and aliquot of the amine stock solution, which was prepared by adding 2 equiv. of amine-hydrochloride and 1 equiv. of standardized NaOH solution to make a self-buffered solution. All solutions were transferred by gas-tight syringes. The plots of ln $(A_\infty - A_t)$ *vs.* time were linear over 90% of the total reaction. Usually, five different amine concentrations were employed to obtain the second-order rate constants (k_N) from the slope of linear plots of k_{obsd} *vs*. amine concentrations.

Products Analysis. *N*-(2,4-Dinitrophenyl)hydrazine was liberated quantitatively and identified as one of the products for the reactions with hydrazine by comparison of the UV-Vis spectrum after completion of the reaction with that of authentic sample under the same reaction condition.

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