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Aminolysis of *S*-4-Nitrophenyl X-Substituted Thiobenzoates: Effect of Nonleaving-Group Substituents on Reactivity and Mechanism

Li-Ra Im, Sang-Eun Jeon,[a] and Ik-Hwan Um*

*Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea. *E-mail: ihum@ewha.ac.kr*
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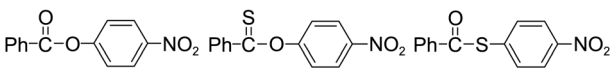
A kinetic study is reported for aminolysis of *S*-4-nitrophenyl X-substituted thiobenzoates **3a-g** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. Thiol esters **3a-g** are 7.8-47.6 fold more reactive than the corresponding oxygen esters (i.e., 4-nitrophenyl X-substituted benzoates **1a-g**). Such reactivity order appears to be in accordance with the expectation that 4-nitrothiophenoxide in **3a-g** is a better nucleofuge than 4-nitrophenoxide in **1a-g** since the former is 2.64 pK_a units less basic than the latter. Hammett plot for the reactions of **3a-g** exhibit poor correlation coefficients (R^2 = 0.977-0.986) with negative deviation by substrates possessing an electron-donating group (EDG), while the Yukawa-Tsuno plots result in excellent linear correlation (R^2 = 0.995-0.997) with ρ = 0.93-1.23 and r = 0.57-0.67, indicating that the negative deviation shown by substrates possessing an EDG is caused by ground-state stabilization through resonance interactions but not due to a change in rate-determining step upon changing the nonleaving-group substituent X. The ρ value increases as the incoming amine becomes more basic and more reactive, indicating that the RSP is not operative in the current reactions.

Key Words : Aminolysis, Electrophilicity, Nucleofugality, Polarizability, Thiol ester

Introduction

Aminolysis of carboxylic esters has generally been understood to proceed through a stepwise mechanism with a zwitterionic tetrahedral intermediate $T^{\pm}$.[1-12] It has been reported that nucleophilic substitution reactions of 4-nitrophenyl benzoate (**1**) with a series of alicyclic secondary amines proceed through $T^{\pm}$, in which expulsion of the leaving group from $T^{\pm}$ occurs in the rate-determining step (RDS).[5] In contrast, the corresponding reactions of *O*-4-nitrophenyl thionobenzoate (**2**), the thiono analogue of **1**, have been shown to proceed through two intermediates, i.e., $T^{\pm}$ and its deprotonated form T^{-}.[6a,b]



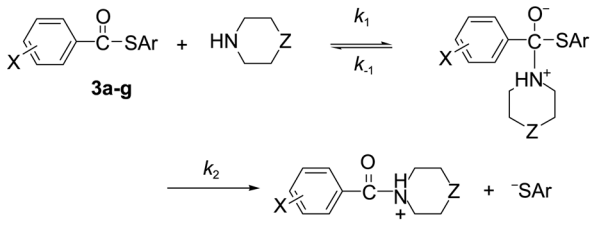
1 **2** **3**

Aminolysis of *S*-4-nitrophenyl thiobenzoate (**3**) has been reported to proceed through a stepwise mechanism with a change in rate-determining step (RDS) on the basis of a curved Brønsted-type plot.[7,8] The pK_a at the center of Brønsted curvature, defined as pK_a^o has been analyzed to be 10.0 for the reactions run in 44% aqueous ethanol[7] and 10.2 for those performed in 80 mol % H_2O/20 mol % DMSO,[8] indicating that pK_a^o is nearly independent of the nature of reaction media. However, the effect of nonleaving-group substituent on pK_a^o is controversial. Some studies have concluded that pK_a^o increases as the substituent in the nonleaving group changes from an electron-donating group (EDG) to an electron-withdrawing group (EWG),[9-11] other studies have proposed that pK_a^o is independent of the electronic nature of the substituent in the nonleaving group.[12]

We have now performed nucleophilic substitution reactions of *S*-4-nitrophenyl X-substituted thiobenzoates **3a-g** with three different alicyclic secondary amines as shown in Scheme 1 to investigate the effect of substituents X on reactivity and mechanism. The kinetic results for the reactions of **3a-g** have been compared with those reported previously for the corresponding reactions of 4-nitrophenyl X-substituted benzoates **1a-g**,[5] the oxygen analogues of **3a-g**, to investigate the effect of replacing the O atom by a polarizable S atom in the leaving group (i.e., **1a-g** → **3a-g**) on reactivity and mechanism.

Results and Discussion

The kinetic study was performed spectrophotometrically under pseudo-first-order conditions in which the amine concentration was kept in excess over the substrate concentration. The reactions obeyed first-order kinetics and pseudo-



3a-g

X = 4-CN(**3a**), 3-Cl(**3b**), 4-Cl(**3c**), H(**3d**), 4-Me(**3e**), *t*-Bu(**3f**), 4-MeO(**3g**).

⁻SAr = ⁻S–NO2; HN Z ; Z = CH_2, NH, O.

Scheme 1

[a]Present address: Environmental Research Complex, Incheon 404-708, Korea

Table 1. Summary of Second-order Rate Constants for Reactions of *S*-4-Nitrophenyl X-Substituted Thiobenzoates (**3a-g**) and 4-Nitrophenyl X-Substituted Benzoates (**1a-g**, in parenthesis) in H_2O Containing 20 mol % DMSO at 25.0 ± 0.1 °C[a]

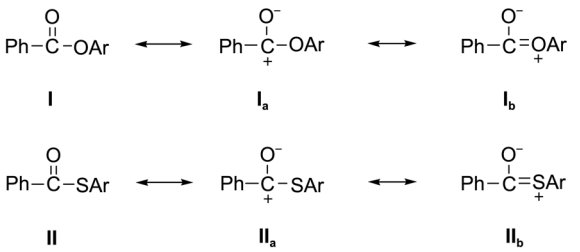
	X	k_N /$M^{-1}s^{-1}$		
		Piperidine	Piperazine	Morpholine
a	4-CN	364 (18.7)	79.1 (2.06)	8.52 (0.179)
b	3-Cl	205 (12.8)	46.5 (1.67)	5.78 (0.15)
c	4-Cl	109 (8.14)	26.9 (1.14)	3.08 (0.111)
d	H	61.4 (5.94)	17.3 (0.851)	2.14 (0.0876)
e	4-Me	31.6 (3.68)	9.54 (0.629)	1.39 (0.0659)
f	4-*t*-Bu	30.6 (-)	9.10 (-)	1.26 (-)
g	4-MeO	15.3 (1.95)	5.20 (0.344)	0.687 (0.0365)

[a]The data in parenthesis for the reactions of **1a-g** were taken from ref. 5.

first-order rate constants (k_{obsd}) were determined from the equation, $\ln (A_\infty - A_t) = -k_{obsd}t + C$. Plots of k_{obsd} *vs.* [amine] were linear and passed through the origin, indicating that the contribution of water and/or OH^- from hydrolysis of amine to k_{obsd} is negligible. The second-order rate constants (k_N) were determined 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 determined in this way are summarized in Table 1 together with the k_N values reported previously for the corresponding reactions of 4-nitrophenyl X-substituted benzoates (**1a-g**) for comparison.

Effect of Replacing O by S in the Leaving Group on Reactivity. As shown in Table 1, thiol esters **3a-g** are more reactive than oxygen esters **1a-g**, e.g., **3a** is 19.5, 38.4 and 47.6 times more reactive than **1a** toward piperidine, piperazine and morpholine, in turn. Such reactivity order appears to be in accordance with the expectation that 4-nitrothiophenoxide in **3a-g** is a better nucleofuge than 4-nitrophenoxide in **1a-g** since the former is 2.64 pK_a units less basic than the latter (i.e., pK_a = 4.50 and 7.14 for 4-nitrothiophenol and 4-nitrophenol, respectively).[13]

The ^{13}C NMR chemical shifts of the C=O bond in thiol esters have been reported to exhibit 20-30 ppm downfield shifts relative to the oxygen esters.[14] Besides, the C=O stretching vibration of thiol esters has been reported to shift to 40-60 cm^{-1} lower frequencies than that of the corresponding oxygen esters.[15] These spectral data imply that the carbonyl carbon atom of thiol esters has a more partial positive charge and weaker double bond character than that of the corresponding oxygen esters. It is also well known that the overlap between 2p and 3p orbitals is weaker than that between 2p orbitals.[16] Thus, it has been suggested that the contribution of resonance structures I_b and II_a is more significant than I_a and II_b, respectively.[14-16]



One might expect that the C=O bond in thiol esters is significantly more electrophilic than that in oxygen esters on the basis of the idea that II_a is more important resonance structure than I_a. Furthermore, **3a-g** possess a better nucleofuge than **1a-g** since 4-nitrothiophenoxide is 2.64 pK_a units less basic than 4-nitrophenoxide. Accordingly, one might expect that **3a-g** are significantly more reactive than **1a-g**. However, as shown in Table 1, **3g** is only 7.8-18.5 times more reactive than **1g**, indicating that the enhanced electrophilicity and nucleofugality are not fully reflected in reactivity toward the amine nucleophiles. Thus, one might suggest that the nature of nucleophiles also influences the reactivity of polarizable substrates **3a-g**.

The above argument is consistent with the report that the reactivity of thiol esters is strongly dependent on the nature of nucleophiles.[17] For example, 4-chlorothiophenoxide, a polarizable nucleophile has been reported to be *ca.* 300-fold more reactive toward *S*-4-nitrophenyl thioacetate than toward its oxygen analogue 4-nitrophenyl acetate, while OH^- ion, a nonpolarizable hard nucleophile is *ca.* 2-fold less reactive toward the former than toward the latter.[17] Since amines have been classified to be nonpolarizable hard bases,[18] one can suggest that the hard nature of amines is responsible for the unexpectedly small rate enhancement toward polarizable substrates **3a-g**.

Effect of Nonleaving-group Substituent X on Mechanism. As shown in Table 1, the reactivity of **3a-g** decreases as the substituent X in the benzoyl moiety changes from an EWG to an EDG, e.g., the k_N for the reaction with piperidine decreases from 364 $M^{-1}s^{-1}$ to 61.4 and 15.3 $M^{-1}s^{-1}$ as X changes from 4-CN to H and 4-MeO, respectively. Similar results are shown for the reactions with piperazine and morpholine, although they are less reactive than piperidine. The effect of substituent X on reactivity is illustrated in Figure 1. The Hammett plots are linear but exhibit many

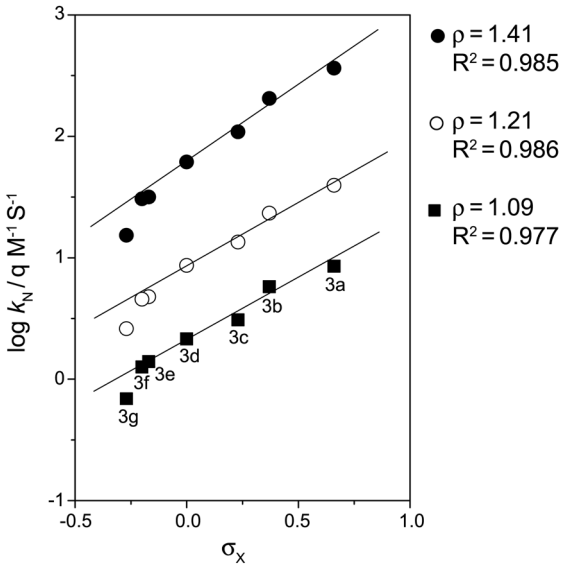


Figure 1. Hammett plots for reactions of *S*-4-nitrophenyl X-substituted thiobenzoates **3a-g** with piperidine (●), piperazine (○) and morpholine (■) in H_2O containing 20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

scattered points. Especially, **3g** (X = 4-MeO) deviates significantly from the linearity.

The reactions of 4-nitrophenyl benzoate **1** with a series of alicyclic secondary amines have been reported to proceed through a zwitterionic tetrahedral intermediate $T^{\pm}$.[5] The RDS has been suggested to be expulsion of the leaving group from $T^{\pm}$ on the basis of a linear Brønsted-type plot with β_{nuc} = 0.76 regardless of the basicity of the incoming amines.[5] In contrast, the corresponding reactions of *S*-4-nitrophenyl thiobenzoate **3d** have been reported to proceed through a stepwise mechanism with a change in RDS, e.g., from breakdown of $T^{\pm}$ to its formation as the basicity of the incoming amine increases.[7,8] The evidence provided for a change in RDS was a curved Brønsted-type plot, i.e., β_1 = 0.34 when $pK_a > 10.2$ while β_2 = 0.93 when $pK_a < 10.2$.[8]

One might suggest that the negative deviation shown by **3g** (X = 4-MeO) in Figure 1 is due to a change in RDS. This idea appears to be consistent with the reports that RDS is influenced by the electronic nature of the substituent in the nonleaving group for quinuclidinolysis of diary carbonates,[9] pyridinolysis of 2,4-dinitrophenyl X-substituted benzoates and aminolysis of *S*-2,4-dinitrophenyl X-substituted thiobenzoates.[10] However, we propose that the negative deviation shown by **3g** in Figure 1 is not due to a change in RDS but is caused by stabilization of the ground state (GS) of the substrate through resonance interactions as illustrated in resonance structures **3g** and **3g$_a$**. This is because such resonance interactions would stabilize the GS of the substrate and cause a decrease in reactivity. This argument is consistent with the fact that the substrates possessing a π-electron donating substituent (e.g., **3c**, **3e** and **3f**) deviate also negatively from the Hammett plots although the degree of deviation is not significant.

3g **3g$_a$**

To examine the above argument, the Yukawa-Tsuno equation (1) has been employed. Eq. (1) was derived to account for kinetic results obtained from solvolysis of benzylic systems in which a partial positive charge is developing in the transition state.[19] The *r* value in eq. (1) represents the resonance demand of the reaction center or the extent of resonance contribution between the reaction site and substituent X.[19,20] We have shown that eq. (1) is highly effective to clarify ambiguities in reaction mechanisms for various nucleophilic substitution reactions including aminolysis of esters.[5a,12,21-23]

$$\log k_N^X/k_N^H = \rho\,(\sigma_X^o + r\,(\sigma_X^+ - \sigma_X^o)) \quad (1)$$

Accordingly, Yukawa-Tsuno plots have been constructed in Figure 2. One can see that the plots exhibit excellent linear correlation (e.g., $R^2 > 0.995$) with ρ = 0.93-1.23 and *r* = 0.57-0.67. Such linear Yukawa-Tsuno plots with *r* values of 0.57-0.67 clearly indicate that the negative deviation is due to stabilization of the ground state of substrates through resonance interactions (e.g., **3g** ↔ **3g$_a$**) but not due to a change in RDS.

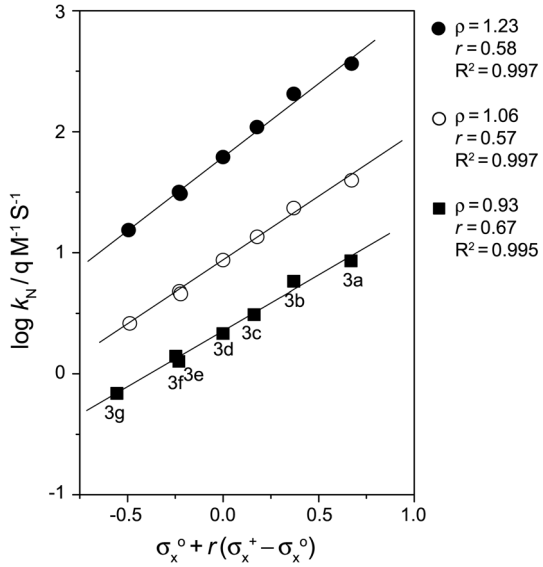


Figure 2. Yukawa-Tsuno plots for reactions of *S*-4-nitrophenyl X-substituted thiobenzoates **3a-g** with piperidine (●), piperazine (○) and morpholine (■) in H_2O containing 20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

It is noted that the ρ value for the reactions of **3a-g** increases as the incoming amine becomes more basic and more reactive, i.e., the ρ value increases from 0.93 to 1.06 and 1.23 as the pK_a of the conjugated acid of the incoming amine increases from 8.65 (morpholine) to 9.85 (piperazine) and 11.02 (piperidine), in turn.[24] The effect of amine basicity on ρ is illustrated in Figure 3. The plot exhibits excellent linear correlation although the slope is small. Since the magnitude of ρ represents a relative degree of charge transfer from the amine nucleophile to the electrophile, one can

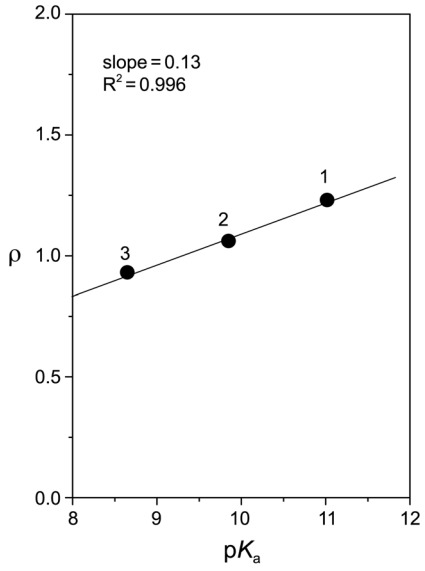


Figure 3. Plot showing dependence of ρ on pK_a of the conjugate acid of the amines for reactions of *S*-4-nitrophenyl X-substituted thiobenzoates **3a-g** with piperidine (1), piperazine (2) and morpholine (3) in H_2O containing 20 mol % DMSO at 25.0 ± 0.1 °C.

suggest that the degree of charge transfer becomes greater as the amine basicity increases. This is consistent with the definition that bases are electron-pair donors. However, the fact that the ρ value increases as the incoming amine becomes more basic is against the reactivity-selectivity principle (RSP).[25] This is because the ρ value represents also a sensitivity parameter and the more reactive amine results in a larger ρ value.

Conclusions

The current study has allowed us to conclude the following: (1) Thiol esters **3a-g** are 7.8-47.6 times more reactive than the corresponding oxygen esters **1a-g**. However, the rate enhancement is much smaller than would be expected from the fact that **3a-g** possess a less basic nucleofuge and a more electrophilic center than **1a-g**. (2) The Hammett plots for the reactions of **3a-g** result in poor correlation coefficients, while the Yukawa-Tsuno plots exhibit excellent linear correlation with $\rho = 0.93$-1.23 and $r = 0.57$-0.67, indicating that the electronic nature of the nonleaving-group substituent X does not influence reaction mechanism. (3) The ρ value increases as the incoming amine becomes more basic and more reactive, indicating that the RSP is not operative in the current reactions.

Experimental Section

Materials. Substrates **3a-g** were readily prepared from the reaction of X-substituted benzoyl chloride with 4-nitrothiophenol in the presence of triethylamine in anhydrous ether. Their purity was confirmed from the melting point and spectral data such as ^{1}H NMR. Secondary amines and 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 for slow reactions ($t_{1/2} \geq 10$ s) or a stopped-flow spectrophotometer for fast reactions ($t_{1/2} < 10$ s) equipped with a constant temperature circulating bath to keep the reaction temperature at 25.0 ± 0.1°C. All the reactions were carried out under pseudo-first-order conditions in which the amine concentration was at least 20 times greater than the substrate concentration. Due to low solubility of substrates **3a-g** in pure water, reactions were carried out in 80 mol % H_2O/20 mol % DMSO. Typically, the reaction was initiated by adding 5 μL of a 0.01 M of substrate stock solution in MeCN by a 10 μL syringe to a 10 mm UV cell containing 2.50 mL of the reaction medium and amine. The reactions were followed by monitoring the leaving 4-nitrothiophenoxide at 410 nm.

Product Analysis. 4-Nitrothiophenoxide was liberated and identified as one of the reaction products by comparison of the UV-vis spectra after completing the reactions with those of authentic samples under the same kinetic conditions. It was also observed that oxidation of 4-nitrothiophenoxide occurs for slow reactions.

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