Kinetic Study on Reactions of O-*Y*-substituted Phenyl Thionobenzoates with Quinuclidine: Factors Governing Reactivity and Reaction Mechanism

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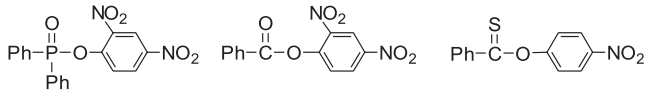
Second-order rate constants (k_{quin}) for the reactions of O-*Y*-substituted phenyl thionobenzoates (**3a–3i**) with quinuclidine have been measured spectrophotometrically. Comparison of k_{quin} with the rate constants reported previously for the corresponding reactions with benzylamine (k_{BzNH2}) has revealed that quinuclidine is less reactive than benzylamine toward **3a–3i** although the former is 2.1 pK_a units more basic than the latter. Steric hindrance exerted by quinuclidine has been suggested to be responsible for the decreased reactivity of the tertiary amine. The Brønsted-type plot for the reactions of **3a–3i** with quinuclidine is linear with $\beta_{lg} = -0.37$. The Hammett plot correlated with σ_Y^o constants exhibits many scattered points ($R^2 = 0.982$). In contrast, the Yukawa-Tsuno plot results in an excellent linear correlation ($R^2 = 0.9992$) with $\rho_Y = 0.96$ and $r = 0.51$, indicating that a negative charge develops partially on the O atom of the leaving group. Thus, the reactions of **3a–3i** with quinuclidine have been concluded to proceed through a concerted mechanism in which expulsion of the leaving group is advanced only a little in the rate-determining transition state.

Keywords: Quinuclidinolysis, O-Aryl thionobenzoates, Rate-determining step, Concerted mechanism, Steric hindrance

Introduction

Nucleophilic substitution reactions of esters with amines have intensively been investigated due to their importance in biological processes as well as in synthetic applications.[1–10] Aminolysis of esters has been reported to proceed through a concerted mechanism or via a stepwise pathway depending on reaction conditions (*e.g.*, nature of the electrophilic center, amines, and reaction medium).[2–10] Reactions of 2,4-dinitrophenyl diphenylphosphinate (**1**) with primary and secondary amines have been reported to proceed through a concerted mechanism on the basis of a linear Brønsted-type plot with $\beta_{nuc} = -0.4 \pm 0.1$.[6] The reactions of 2,4-dinitrophenyl benzoate (**2**) with a series of cyclic secondary amines in MeCN have also been suggested to proceed through a concerted mechanism on the basis of a linear Brønsted-type plot with $\beta_{nuc} = 0.40$.[7a] In contrast, the corresponding reactions of **2** in 80 mol% H_2O/20 mol% dimethyl sulfoxide (DMSO) have been reported to proceed through a stepwise mechanism with a change in the rate-determining step (RDS) on the basis of a curved Brønsted-type plot (*e.g.*, the slope decreases from 0.74 to 0.34 as the attacking amine becomes more basic than the leaving group by *ca.* 4.5 pK_a units).[7b]



1 **2** **3b**

Aminolysis of thione esters have been reported to proceed through a stepwise mechanism with one or two intermediates (*e.g.*, a zwitterionic tetrahedral intermediate $T^{\pm}$ and its deprotonated form T^-).[8] We have reported that reactions of O-4-nitrophenyl thionobenzoate (**3b**) with primary amines proceed through a stepwise mechanism with a change in the RDS on the basis of a curved Brønsted-type plot.[8a] In contrast, the corresponding reactions with secondary amines have been proposed to proceed through a stepwise mechanism with two intermediates (*i.e.*, $T^{\pm}$ and T^-) as plots of k_{obsd} vs. [amine] curved upward.[8b,c]

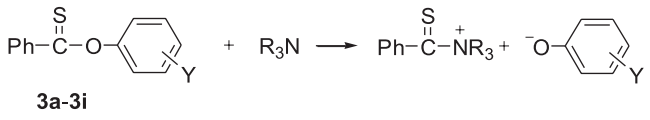
This study has now been extended to reactions of a series of O-*Y*-substituted phenyl thionobenzoates (**3a–3i**) with quinuclidine (a tertiary amine) to obtain further information on the reaction mechanism (Scheme 1). The kinetic data in this study have been compared with those reported previously[8b,9] for the reactions of **3a–3i** with benzylamine, N_3^-, and OH^- to investigate factors governing reactivity and reaction mechanism.

Results and Discussion

The kinetic study was carried out spectrophotometrically under pseudo-first-order conditions in which the concentration of quinuclidine was kept at least 20 times in excess of the substrate concentration. All 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. quinuclidine concentration were linear. Accordingly, the second-order rate constants for the quinuclidinolysis of **3a–3i** (k_{quin}) were calculated from the slope of the linear plots. The k_{quin} values calculated in this way are summarized in Table 1 together with those reported previously[8b,9] for the corresponding reactions with benzylamine ($BzNH_2$), N_3^-, and OH^- for comparison. The uncertainty in the k_{quin} values is estimated to be less than ±3% based on the replicate runs.

Factors Influencing Reactivity of Thione Esters. As shown in Table 1, the reactivity of substrates **3a–3i** decreases as the basicity of the leaving group increases, *e.g.*, the k_N value for the reactions of **3a–3i** with quinuclidine decreases from 3.01 to 0.301 and 0.0465 M^{-1} s^{-1} as the pK_a of conjugate acid of the leaving aryloxide increases from 5.42 to 8.05 and 10.19, in turn. Similar results are demonstrated for the corresponding reactions with benzylamine ($BzNH_2$), N_3^-, and OH^-. However, the reactivity of these nucleophiles toward substrates **3a–3i** is independent of their basicity, *e.g.,* quinuclidine is less reactive than $BzNH_2$ and N_3^-, although it is 2.1 and 6.7 pK_a units more basic than $BzNH_2$ and N_3^-, respectively. Furthermore, N_3^- is more reactive than OH^- toward substrates possessing an electron-withdrawing group in the leaving group (*e.g.*, **3a–3d**), although the former is 11 pK_a units less basic than the latter. The fact that quinuclidine is less reactive than less basic benzylamine is quite an unexpected result. Because quinuclidines have been reported to be more reactive than isobasic cyclic secondary amines toward methyl chloroformate and diaryl carbonates.[10] Furthermore, cyclic secondary amines have been reported to be even more reactive than isobasic primary amines.



3a-3i

Y = 3,4-$(NO_2)_2$(**3a**), 4-NO_2(**3b**), 4-CHO(**3c**), 4-COMe(**3d**), 3-NO_2(**3e**), 3-COMe(**3f**), H(**3g**), 4-Me(**3h**), 4-MeO(**3i**).

R_3N = 

Scheme 1. Quinuclidinolysis of **3a–3i**.

Steric hindrance exerted by quinuclidine would not be so significant for the reactions of phenyl *Y*-substituted phenyl carbonates, although quinuclidine (a tertiary amine) is bulkier than piperidine (a secondary cyclic amine) and benzylamine (a primary amine). However, one might expect that steric hindrance is an important factor that influences reactivity of quinuclidine in the current reactions of thione esters **3a–3i**. Because the C=S bond in **3a–3i** is much larger than the C=O bond in phenyl *Y*-substituted phenyl carbonates. Furthermore, steric hindrance exerted by the Ph group in **3a–3i** would be more significant than that shown by the PhO group in the diaryl carbonates on the basis of their E_s values (*i.e.*, E_s = −2.55 for Ph and the E_s value for PhO is not available but would be similar to E_s = −0.38 for $PhCH_2$).[13] Thus, one might suggest that steric hindrance is responsible for the kinetic result that quinuclidine is less reactive than the less basic benzylamine toward the C=S centered esters **3a–3i**.

As shown in Table 1, N_3^- is more reactive than OH^- toward substrates **3a–3d**, although the former is 11 pK_a units less basic than the latter. This is in contrast to the report that N_3^- is 383-fold less reactive than OH^- toward **2**.[14] It is well known that a C=S bond is significantly more polarizable than a C=O bond because the overlap between 2p and 3p orbitals in a C=S bond is not as strong as that between 2p and 2p orbitals in a C=O bond. Besides, N_3^- was reported to be a highly polarizable base while OH^- is a nonpolarizable one.[14] Thus, the high polarizability of N_3^- could be responsible for the enhanced reactivity of N_3^- toward the highly polarizable C=S esters at least in part.

Another factor that might affect reactivity of **3a–3i** is nature of the reaction mechanism. Nucleophilic substitution reactions of esters have been reported to proceed through a

Table 1. Summary of the kinetic data for the reactions of O-*Y*-substituted phenyl thionobenzoates (**3a–3i**) with quinuclidine, benzylamine, N_3^-, and OH^- in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C.

	Y	pK_a[a]	k_{quin}/M^{-1} s^{-1}	[b]k_{BzNH2}/M^{-1} s^{-1}	[c]k_{N3}–/M^{-1} s^{-1}	[d]k_{OH}–/M^{-1} s^{-1}
3a	3,4-$(NO_2)_2$	5.42	3.01	12.7	183	10.5
3b	4-NO_2	7.14	0.735	3.71	11.0	1.87
3c	4-CHO	7.66	0.360	—	2.50	0.846
3d	4-COMe	8.05	0.301	2.14	1.39	0.650
3e	3-NO_2	8.35	—	—	—	1.46
3f	3-COMe	9.19	0.165	1.87	—	0.489
3g	H	9.95	0.0645	0.915	0.0122	0.210
3h	4-Me	10.19	0.0465	0.871	0.00509	0.161
3i	4-MeO	10.20	0.0442	—	0.00544	0.172

[a] pK_a data taken from Ref. 11.
[b] Kinetic data taken from Ref. 8b.
[c] Kinetic data taken from Ref. 9.
[d] Kinetic data taken from Ref. 12.

concerted mechanism or via a stepwise pathway depending on reaction conditions.[2–10] Reactions of **3a–3i** with benzylamine have been reported to proceed through a stepwise mechanism with one or two intermediates (*e.g.*, $T^{\pm}$ and T^{-} when the substituent *Y* in the leaving group is an electron-donating group such as 4-Me but the deprotonation process is absent when *Y* is an electron-withdrawing group).[8b] Reactions of **3a–3i** with N_3^- and OH^- have also been reported to proceed through a stepwise mechanism, in which the RDS is dependent on the nucleophiles (*e.g.*, the RDS for the reactions with N_3^- changes from formation of an addition intermediate to its breakdown as the leaving group becomes 1.6 pK_a units more basic than N_3^-, while the RDS for the reactions with OH^- is formation of an intermediate regardless of the leaving-group basicity).[9,12]

Deduction of Reaction Mechanism. To investigate the reaction mechanism, Brønsted-type plots for the reactions with quinuclidine and N_3^- have been constructed. As shown in Figure 1, the Brønsted-type plot for the reactions of **3a–3i** with quinuclidine is linear with $\beta_{lg} = -0.37$. This is in contrast to the curved Brønsted-type plot for the corresponding reactions with N_3^-. The reactions of **3a–3i** with N_3^- have previously been reported to proceed through a stepwise mechanism with a change in the RDS on the basis of the curved Brønsted-type plot, *i.e.*, from formation of an addition intermediate to its breakdown as the leaving group becomes 1.6 pK_a units more basic than N_3^-.[9] The linear Brønsted-type plot for the quinuclidinolysis of **3a–3i** indicates that the reaction proceeds without changing the reaction mechanism including the RDS.

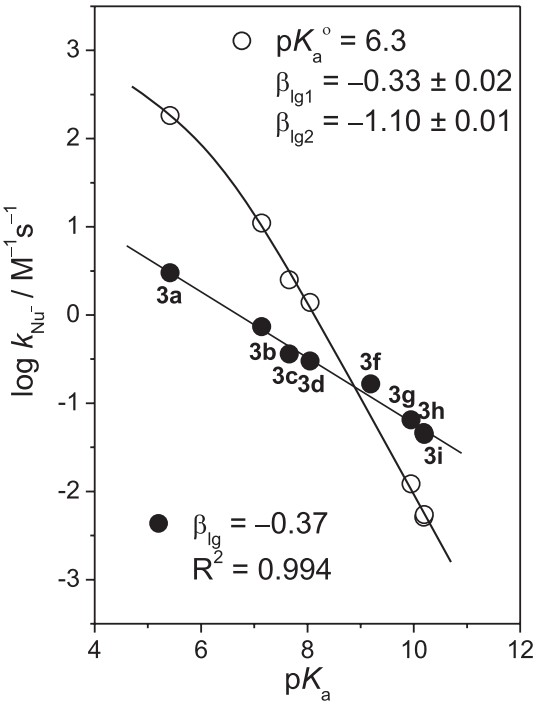


Figure 1. Brønsted-type plots for the reactions of O-*Y*-substituted phenyl thionobenzoates (**3a–3i**) with quinuclidine (●) and N_3^- (○) in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

A linear Brønsted-type plot with $\beta_{lg} = -0.37$ is typical for reactions reported previously to proceed through a stepwise mechanism with formation of an intermediate being the RDS.[2–10] Thus, one might suggest that the quinuclidinolysis of **3a–3i** proceeds through a stepwise mechanism in which expulsion of the leaving group occurs after the RDS.

It is well known that Hammett plots correlated with σ^- and σ^o constants give useful information on reaction mechanism particularly on the RDS. If the quinuclidinolysis of **3a–3i** proceeds through a stepwise mechanism, in which expulsion of the leaving group occurs after the RDS, no negative charge would develop on the O atom of the leaving group in the rate-determining TS. In this case, σ^o constants should result in a better Hammett correlation than σ^- constants. In contrast, if the reactions of **3a–3i** with quinuclidine proceed either through a concerted mechanism or via a stepwise pathway with expulsion of the leaving group being the RDS, a negative charge would develop partially on the O atom of the leaving group. As such a negative charge can be delocalized to the substituent *Y* in the leaving group through resonance interactions, one might expect that σ^- constants should result in a better Hammett correlation than σ^o constants. In fact, Figures S1 and S2 in the Supporting Information demonstrate that σ^o constants result in a much better correlation than σ^- constants for the reactions of **3a–3i** with benzylamine and hydroxide ion, respectively.

Thus, Hammett plots for the reactions of **3a–3i** with quinuclidine have been constructed using σ_Y^o and σ_Y^- constants to investigate the nature of the RDS. As shown in Figure 2, the Hammett plot correlated with σ_Y^o constants results in a poor correlation ($R^2 = 0.982$). The one correlated with σ_Y^- constants results in a slightly better correlation but with many scattered points ($R^2 = 0.991$). Accordingly, one cannot obtain conclusive information on the RDS from these Hammett plots.

To obtain more conclusive information on the RDS of the current reactions, the Yukawa-Tsuno equation has been employed, which was originally derived to account for the kinetic results obtained from solvolysis of benzylic systems.[15] However, we have shown that Eq. (1) is highly effective to clarify ambiguities in reaction mechanisms for nucleophilic substitution reactions of esters with various nucleophiles (*e.g.*, neutral amines as well as anionic nucleophiles such as OH^-, N_3^-, and CN^-).[5,9,12]

$$\log k^Y/k^H = \rho_Y\left[\sigma_Y^o + r\left(\sigma_Y^- - \sigma_Y^o\right)\right] \quad (1)$$

As shown in Figure 3, the Yukawa-Tsuno plot for the quinuclidinolysis of **3a–3i** exhibits excellent linearity (R^2 = 0.9992) with $\rho_Y = 0.96$ and $r = 0.51$. The *r* value in Eq. (1) represents the resonance demand of the reaction center or the extent of resonance contribution, while the term $(\sigma_Y^- - \sigma_Y^o)$ is the resonance substituent constant that measures the capacity for π-delocalization of the π-electron acceptor substituent.[15,16] The *r* value of 0.51 observed for the quinuclidinolysis of **3a–3i** clearly indicates that a partial negative charge develops on the O atom of the leaving group, which

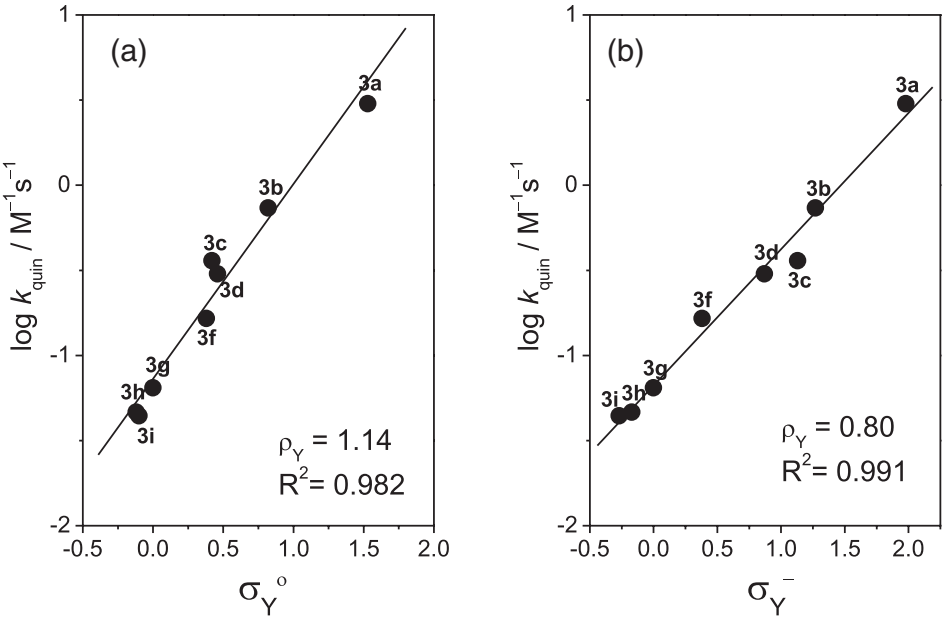


Figure 2. Hammett plots correlated with σ_Y^o (**a**) and σ_Y^- (**b**) for the reactions of O-*Y*-substituted phenyl thionobenzoates (**3a–3i**) with quinuclidine in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

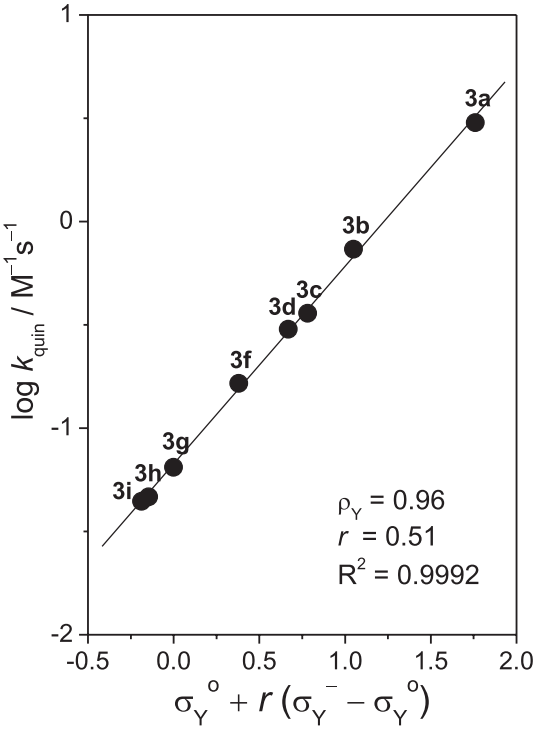


Figure 3. Yukawa-Tsuno plot for the reactions of O-*Y*-substituted phenyl thionobenzoates (**3a–3i**) with quinuclidine in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

can be delocalized to the substituent *Y* through resonance interactions. This case is possible for reactions that proceed either through a concerted mechanism or via a stepwise pathway with expulsion of the leaving group being the RDS. However, we propose that the current reactions of **3a–3i** with quinuclidine proceed through a concerted mechanism as a β_{lg} value of −0.37 is too small for a stepwise mechanism in which expulsion of the leaving group occurs in the RDS.

Effect of Steric Hindrance on Reaction Mechanism. As mentioned in the preceding section, the reactions of **3a–3i** with quinuclidine would experience significant steric hindrance. Steric hindrance would be more significant on going from the ground state (GS) to the zwitterionic tetrahedral intermediate ($T^{\pm}$). Because the dihedral angle of the reaction center decreases from 120° (an sp^2 hybridization in the GS) to *ca.* 109° (an sp^3 hybridization in the intermediate). Consequently, a plausible intermediate $T^{\pm}$ formed from the reactions of **3a–3i** with quinuclidine would be highly unstable due to the enhanced steric hindrance.

One might expect that expulsion of the leaving group from the plausible intermediate diminishes the steric hindrance significantly by increasing the dihedral angle from *ca.* 109° (an sp^3 hybridization in the intermediate) to 120° (an sp^2 hybridization in the product). Accordingly, we propose that the enhanced steric hindrance in the plausible intermediate $T^{\pm}$ forces the reactions to proceed through a concerted mechanism with a TS structure similar to a zwitterionic tetrahedral intermediate, in which expulsion of the leaving group is advanced only a little.

Conclusion

This study has led us to conclude the following:

1. Quinuclidine is less reactive than less basic benzylamine. Steric hindrance is responsible for the decreased reactivity of quinuclidine toward **3a–3i**.

2. The Brønsted-type plot for the reactions with quinuclidine is linear with $\beta_{lg} = -0.37$, which is in contrast to the curved plot for the corresponding reactions with N_3^-.
3. The Yukawa-Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 0.96$ and $r = 0.51$, indicating that a partial negative charge develops in the leaving group in the rate-determining TS.
4. The reactions of **3a–3i** with quinuclidine proceed through a concerted mechanism in which expulsion of the leaving group is advanced only a little.
5. Steric hindrance exerted by quinuclidine forces the current reactions to proceed through a concerted mechanism.
6. Reactivity of nucleophiles toward **3a–3i** is independent of their basicity. Steric hindrance, polarizability and nature of reaction mechanism affect their reactivity.

Experimental Section

Materials. Substrates **3a–3i** were readily prepared from the reaction of dithiobenzoic acid with *Y*-substituted phenol in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) in methylene chloride as reported previously.[17] The crude compounds were purified by recrystallization. The purity was confirmed by melting points and ^{1}H and ^{13}C NMR spectra. The stock solutions of quinuclidine was prepared by adding two equivalent of quinuclidine hydrochloride and one equivalent of standardized NaOH to make a self-buffered solution just before use. Doubly glass distilled H_2O was further boiled and cooled under N_2 gas. Due to low solubility of substrates **3a–3i** in pure water, 80 mol% H_2O/20 mol DMSO was used as the reaction medium.

Kinetics. The kinetic study was performed using a UV–Vis spectrophotometer equipped with a constant-temperature circulating bath. The reactions were followed by monitoring the appearance of the leaving *Y*-substituted-phenoxide ion. Reactions were followed generally for 9–10 half-lives and k_{obsd} values were calculated using the equation, $\ln(A_\infty - A_t) = -k_{obsd}t + C$. Typically, the reaction was initiated by adding 5 μL of a 0.02 M solution of the substrate **3a–3i** in CH_3CN by a 10 μL syringe to a 10-mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and aliquot of the quinuclidine stock solution.

Supporting Information. Additional supporting information is available in the online version of this article.

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