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Kinetic Studies on the Addition of Thiophenol to α , N-Diphenylnitron

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The rate constants for the nucleophilic addition of thiophenol to α , N-diphenylnitron and its derivatives (*p*-OCH₃, *p*-Cl, *p*-NO₂) were determined from pH 3.0 to 13.0 by UV spectrophotometry and rate equations which can be applied over a wide pH range were obtained. On the basis of rate equation, general base and substituent effect a plausible addition mechanism of thiophenol to α , N-diphenylnitron was proposed: At high pH, the addition of sulfide ion to carbon-nitrogen double bond was rate controlling, however, in acidic solution, reaction was proceeded by the addition of thiophenol molecule to carbon-nitrogen double bond after protonation at oxygen of α , N-diphenylnitron.

Introduction

The nucleophilic addition of activated carbon-carbon and carbon-nitrogen double bond has been an important elementary process in organic chemistry.¹⁻⁴

Nitron, having carbon-nitrogen double bond and oxygen attached to nitrogen atom is very reactive and a nucleophile such as Grignard reagent,⁵ thiol^{6,7} and HCN⁸⁻¹¹ easily react with nitron and used as intermediate in organic synthesis.¹²

In previous paper,¹³ we described the hydrolysis mechanism of α , N-diphenylnitron over a wide pH range. In the present paper, we discuss the kinetic behavior of thiophenol to nitron.

Experimental

α , N-Diphenylnitron and its derivatives were prepared by condensation of N-phenylhydroxyamine and benzaldehyde.¹⁴ All of the synthetic reagent used commercial grade without purification and the ionic strength of buffer solution was constant 0.1 M by adding sodium chloride. The absorbance of nitron and its derivatives were determined by Pye Unicam SP 500 UV spectrophotometer.

Kinetic runs were made in water at 25°C. Each nitron and thiophenol were introduced as 1 ml of 2.0×10^{-3} M methanolic solution in 100 ml aqueous buffer solution, which

was then analyzed spectrophotometrically at the absorption maxima of nitron.

Results

The observed rate of reaction with excess thiophenol concentration were always of the pseudo-first order. Plots of the first-order rate constants against thiophenol concentration were also in all cases linear, showing the reaction are of the first order in nitron and thiophenol. Thus, the second-order rate constants simply can be calculated from the slope of the equal initial concentration (2.0×10^{-7} M) of nitron and thiophenol against time (Figure 1). The second-order rate constants (k_2) calculated from the slope at various pH are given Table 1 and Figure 2.

The relationship between acetate ion concentration and rate constant given by the point in Figure 3, was not catalyzed by general base.

As shown in Figure 4, the effect of substituent on the rate of addition was found to conform to the Hammett σ -constant with ρ is 0.77 at pH 4.0 and 1.25 at pH 10.0.

Discussion

As shown in Figure 2, the rate of addition of thiophenol to α , N-diphenylnitron is given by an expression of the

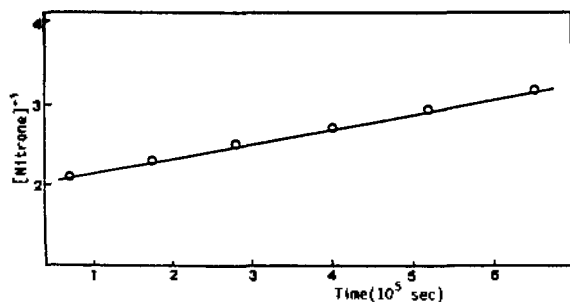


Figure 1. Reaction of thiophenol and α , N-diphenylnitron as second-order with equal initial concentration at pH 7.0 and 25°C.

Table 1. Rate Constants for the Addition Reaction of Thiophenol to α , N-diphenylnitron at Various pH and 25°C

| pH | Buffer solution | k_t ($M^{-1} \cdot sec^{-1}$) | |
|------|-----------------------|-----------------------------------|-----------------------|
| | | k_{obs} | k_{cal} |
| 3.00 | HCl | 230 | 230 |
| 4.00 | HOAc+NaOAc | 19.6 | 23.0 |
| 5.00 | " | 2.50 | 2.30 |
| 6.00 | " | 28.0×10^{-2} | 23.6×10^{-2} |
| 7.00 | $KH_2PO_4 + K_2HPO_4$ | 34.7×10^{-3} | 23.7×10^{-3} |
| 7.50 | " | | 8.95×10^{-3} |
| 8.00 | $H_3BO_3 + NaOH$ | 20.1×10^{-3} | 7.36×10^{-3} |
| 8.50 | " | | 17.9×10^{-3} |
| 9.00 | " | 59.1×10^{-3} | 54.2×10^{-3} |
| 10.0 | " | 73.0×10^{-2} | 49.1×10^{-2} |
| 11.0 | NaOH | 5.10 | 4.91 |
| 12.0 | " | 49.1 | 49.1 |
| 13.0 | " | 491 | 491 |

form;

$$\begin{aligned}
 \text{Rate} &= k_t [S] [ArSH] \\
 &= \{k_H [H_3O^+] + k_{OH} [OH^-]\} [S] [ArSH] \\
 &= k_H [H_3O^+] [S] [ArSH]_e + k_{OH} [OH^-] \\
 &\quad \left(1 + \frac{[H_3O^+]}{K_a}\right) [S] [ArS^-] \quad (1)
 \end{aligned}$$

where, $[ArSH]_e$ is the concentration at equilibria, k_H and k_{OH} are the hydronium and hydroxide ion dependent rate constant and K_a is the acid ionization constant of thiophenol.

Therefore,

$$k_t = k_H [H_3O^+] + k_{OH} [OH^-] \cdot \left(1 + \frac{[H_3O^+]}{K_a}\right) \quad (2)$$

Substituting the $K_a = 3.16 \times 10^{-7}$ and obtained values of the k_H and k_{OH} from experimental data to equation (2),

$$\begin{aligned}
 k_t &= 2.30 \times 10^5 [H_3O^+] + 4.91 \times 10^5 [OH^-] \\
 &\quad \left(1 + \frac{[H_3O^+]}{3.16 \times 10^{-7}}\right) \quad (13)
 \end{aligned}$$

Table 1 and Figure 2 show that the over all rate constant (k_t) calculated by equation (3) were good a agreement with the observed. The curve A and B in Figure 2 represent

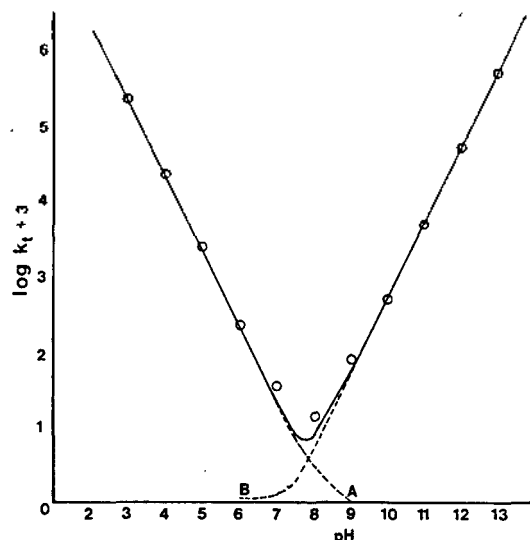


Figure 2. pH-Rate profile for the addition of thiophenol to α ,N-diphenylnitron at 25°C. Solid line: Calculated from equation (3). Dashed line: Represent the acid and base catalyzed rate constant.

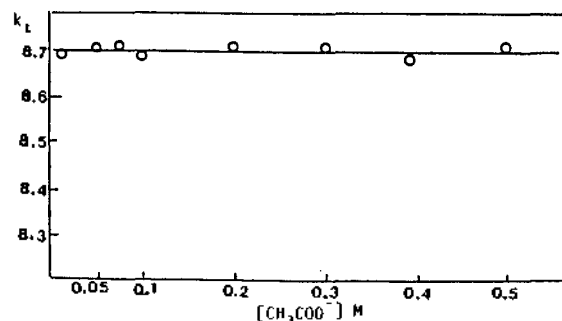


Figure 3. Plot rate constant vs concentration of acetate ion at pH 4.78 and 25°C.

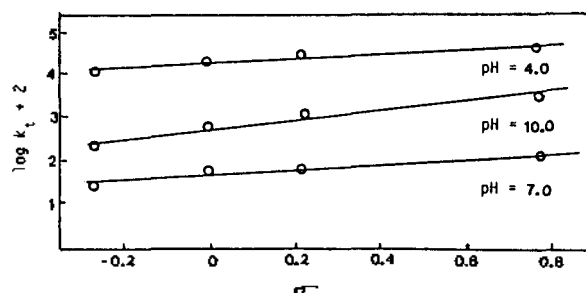


Figure 4. Hammett plots for the addition reaction of thiophenol to α ,N-diphenylnitron at various pH.

the acid and base catalyzed rate constant in equation (3).

Similarly, the rate equation obtained for the addition of thiophenol to α , N-diphenylnitron derivatives are;

$$p\text{-OCH}_3: k_t = 1.09 \times 10^5 [H_3O^+] +$$

$$1.31 \times 10^3 [OH^-] \left(1 + \frac{[H_3O^+]}{3.16 \times 10^{-7}}\right)$$

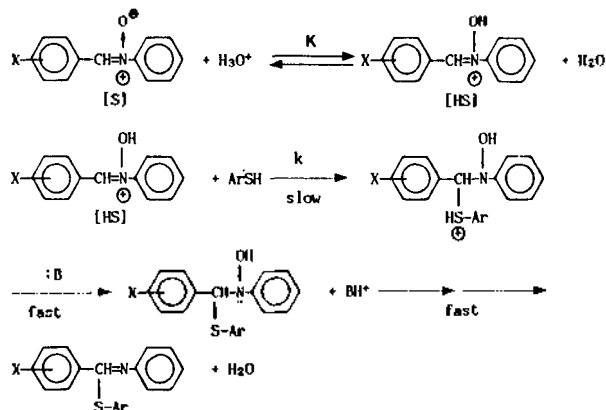
$$p\text{-Cl}: k_t = 3.00 \times 10^5 [H_3O^+] +$$

$$+ 1.20 \times 10^4 [\text{OH}^-] \left(1 + \frac{[\text{H}_3\text{O}^+]}{3.16 \times 10^{-7}}\right)$$

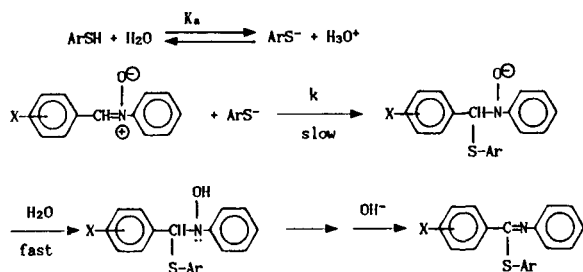
$$p\text{-NO}_2: k_1 = 3.80 \times 10^5 [\text{H}_3\text{O}^+]$$

$$+ 2.61 \times 10^4 [\text{OH}^-] \left(1 + \frac{[\text{H}_3\text{O}^+]}{3.16 \times 10^{-7}}\right)$$

In acidic media, we explain the substituent, general base effect and rate equation in term of the mechanism shows in the accompanying diagram:



Where B is a general base and α -thiophenoxybenzylidene-aniline was isolated as a product.



In the basic solution, the following addition reaction mechanism was proposed:

In alkaline pH's, rate limiting step is the attack of thiophe-

nolate anion, we expect electron withdrawing substituents increase the rate of reaction ($\rho = 1.25$ at $\text{pH} = 10.0$). However, in acidic solution, the rate controlling step is the addition of thiophenol to protonated nitron (HS), and $k_1 = K_1$. Under this condition, the concentration of HS is increased by the electron donating groups, but k is enhanced by electron withdrawing substituents. Since the two effect are in opposition, the rate constant k_1 should be insensitive to change in σ ($\rho = 0.48$ at $\text{pH} = 4.0$).

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