

mmHg. $^1\text{H-NMR}$ (CDCl_3) δ 5.36-5.48 (q, 1H), 5.83-5.97 (q, 1H), 6.73-6.83 (q, 1H), 7.45-7.94 (m, 4H), 9.97-10.03 (d, 1H); IR (neat) 1698 (C=O), 1627, 1600 (C=C) cm^{-1} . Anal. Calcd for $\text{C}_9\text{H}_8\text{O}$: C, 81.82; H, 6.06. Found: C, 81.75; H, 6.03.

Synthesis of 1, 1, 2, 2-Tetracyanocyclopropylstyrene (1). A solution of 3.5 g (0.021 mole) of potassium iodide in 10 ml of water was added slowly to the solution of vinyl benzaldehyde (1.32 g, 0.01 mole) and bromomalononitrile (1.45 g, 0.01 mole) in 10 ml of ethanol at room temperature. After stirring for 1 hr at room temperature, the product was filtered and rinsed with 20 ml of cold ethanol. The obtained white crystals were recrystallized from 95% ethanol to give 0.73 g (63% yield) of **1** (*m-p*-: 70/30, mole/mole). Mp 157-160°C (dec.). $^1\text{H-NMR}$ (acetone- d_6) δ 4.98-5.02 (d, 1H), 5.32-5.40 (m, 1H), 5.88-6.01 (M, 1H), 6.77-6.89 (q, 1H), 7.50-8.08 (m, 4H); IR (KBr) 2259 (CN), 1631, 1600 (C=C) cm^{-1} ; $^{13}\text{C-NMR}$ (acetone- d_6) δ 23.5 (s, $(\text{CN})_2\text{C}<$), 43.0 (s, $>\text{CH}<$), 109.5 (s, *cis*-CN), 111.2 (s, *trans*-CN), 115.6-116.2 (d, $\text{CH}_2=$), 127.3-130.4 (m, aromatic), 136.4 (s, $=\text{CH}<$), 139.5 (s, $-\text{C}<$). Anal. Calcd for $\text{C}_{15}\text{H}_8\text{N}_4$: C, 73.77; H, 3.28; N, 22.95. Found: C, 73.84; H, 3.23; N, 22.87.

Polymerization of Electron-Donor Monomers by 1, 1, 2, 2-Tetracyanocyclopropylstyrene (1). A representative polymerization procedure was as follows: A dichloromethane (10 ml) solution of N-vinylcarbazole (0.97 g, 5 mmole) and 1,1,2,2-tetracyanocyclopropylstyrene (0.012 g, 0.5 mmole) in 10 ml of dichloromethane were placed separately into a Y-shaped polymerization tube. The system was degassed by a freeze-thaw process under vacuum, and the vessel is filled with nitrogen gas. The two olefin solutions were combined, and the resulting solution was stirred for 8 hr at room temperature. Thus obtained viscous product was poured into

a 400 ml of diethyl ether. The precipitated polymer was collected and reprecipitated from chloroform into diethyl ether. **5**: 0.67 g (69% yield). The homopolymer of N-vinylcarbazole was identified by $^1\text{H-NMR}$, IR, and elemental analysis.

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Kinetics and Mechanism of the Hydrolysis of α , N-Diphenylnitron

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The rate constants of hydrolysis of α , N-diphenylnitron and its derivatives have been determined by UV spectrophotometry from pH 2.0 to 13.5, and a rate equation which can be applied over a wide pH range was obtained.

On the basis of rate equation, hydrolysis product, and general base and substituent effects, a plausible mechanism of hydrolysis has been proposed: Below pH 5, the hydrolysis was initiated by the protonation and followed by the addition of water to α -carbon. However, above pH 11, the hydrolysis was proceeded by the addition of hydroxide ion to α -carbon. In the range of pH 5-11, the addition of water to nitron is rate controlling step.

Introduction

The nucleophilic addition of activated carbon-carbon double bond and carbon-nitrogen double bond has been subjected to extensive mechanistic and synthetic studies.¹⁻⁴

Scott⁵ suggested $\text{S}_{\text{N}}1$ mechanism for the hydrolysis of N-arylbenzhydrazidic bromide in acidic solution. Kim and Lee⁶

pointed out that the hydrolysis of imidoyl chloride proceeds through $\text{S}_{\text{N}}1$ mechanism below pH 7, however, above pH 7.5, the reaction initiated by the attack of hydroxide ion.

Azomethine N-oxides (commonly known as nitrones) have a carbon-nitrogen dipolar double bond and the structure is conveniently viewed as a resonance hybrid of following three canonical forms.

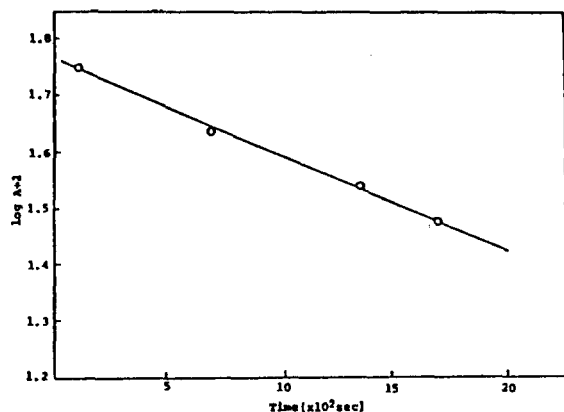
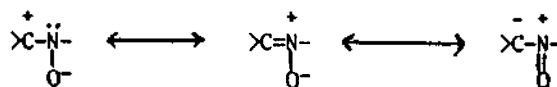


Figure 1. The plot of log absorbance vs time for the hydrolysis of α , N-diphenylnitron at pH 3.52 and 25 °C.



It follows that nitrones should be subject to electrophilic attack at oxygen and nucleophilic attack at carbon⁷⁻¹⁴ and this is borne out in many organic synthesis.

In spite of many uses of nitron as dye, medicament, sensitizer and intermediates in organic synthesis^{15,16}, nitron has been the subject of only a few kinetic studies. The mechanism of formation of aliphatic nitrones in aqueous buffer solution of pH 1.5-9.4 was proposed by Masui¹⁷ and Jencks reported that the reaction of oxime and nitron formation proceeds by a similar mechanism¹⁸. However, there has been no report on kinetic studies of hydrolysis of nitrones.

Experimental

NMR spectra were obtained with a Varian V-4391 (100 MHz) and a Varian EM 360 (60 MHz) spectrometer in DMSO- d_6 or $CDCl_3$. IR spectra were recorded with a Perkin Elmer 735 B spectrophotometer and gas chromatogram was recorded by Varian 204-IC Chromatography. UV spectra were obtained with a Varian Cary 14 and Beckman DU 2 spectrophotometer.

α , N-Diphenylnitron and its derivatives were prepared by the condensation of N-phenylhydroxylamine and benzaldehyde¹⁹ and were identified by the m.p. and spectral data. All of the synthetic reagents were of commercial grade without purification. All of the buffer solutions were prepared from reagent grade chemicals and the ionic strength was kept constant to 0.1 M by adding sodium chloride.

Kinetic runs were made in water at 25.0°C. The nitron was introduced as 1 ml of 3×10^{-3} M methanolic solution in 100 ml of final aqueous solution, which was then analyzed spectrophotometrically at the absorption maxima. The product of hydrolysis, benzaldehyde was identified by the gas chromatography and the formation of 2, 4-dinitrophenyl hydrozone (m.p. 234°C).

Results

Figure shows a typical logarithmic plots of absorbance (A) of α , N-diphenylnitron recorded at 315 nm during the

Table 1. Rate Constants for the Hydrolysis of α , N-diphenylnitron at various pH and 25 °C

pH	Buffer solution	$k_t \times 10^6$ (s ⁻¹)	
		$k_{obs} \times 10^6$ (s ⁻¹)	$k_{calc} \times 10^6$ (s ⁻¹)
2.0	HCl	4600	7270
2.5		1850	2290
3.0		714	727
3.5		140	229
4.0	HAc+NaAc	59.5	73.0
5.0		2.9	7.57
6.0		0.38	1.03
7.0	KH ₂ PO ₄ +K ₂ HPO ₄	0.25	0.37
8.0		0.20	0.34
9.0	H ₃ BO ₃ +NaOH	0.46	0.65
10.0		0.60	3.77
11.0		1.56	34.7
12.0	NaOH	77.0	347
12.5		1200	1090
13.0		3200	3470
13.5		3400	10900

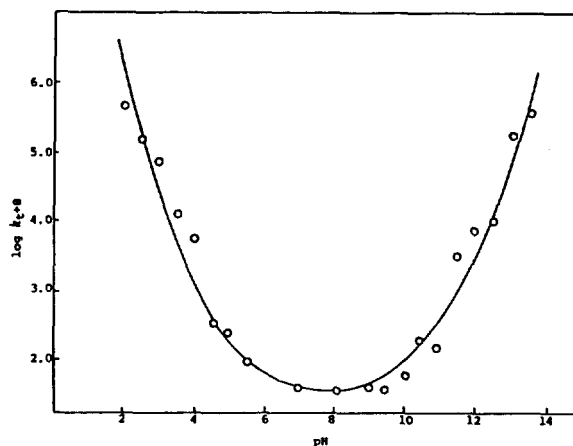


Figure 2. pH Dependence of the first order rate constant for the hydrolysis of α , N-diphenylnitron at 25°C; points are experimental, the solid line represents calculated values from the equation (2).

hydrolysis at pH 3.52 vs time.

As shown in Figure 1, the observed rate of hydrolysis of α , N-diphenylnitron was always of the first order. The first order rate constants (k_{obs}) calculated from the slope at various pH are given in Table 1 and Figure 2 shows pH-rate profile of this reaction. First order rate constants of the α , N-diphenylnitron derivatives were also determined by the same way.

As shown in Figure 3 the effect of substituent on the hydrolysis rate was found to conform to the Hammett σ -constant with ρ is 1.00, 1.11 and 1.36 at pH 3.0, 7.0 and 12.0 respectively.

The relationship between monochloroacetate ion concentration and rate constant given by the points in Figure 4, indicated that this reaction is not catalyzed by general base.

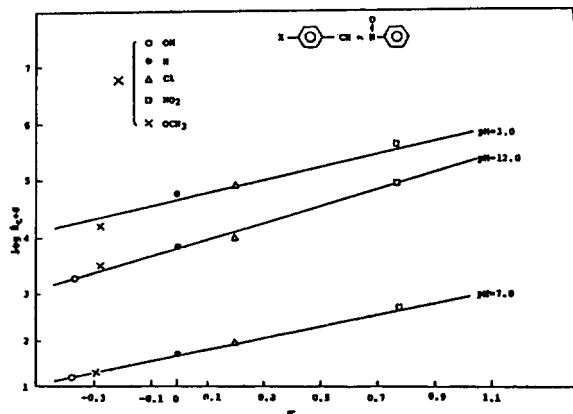


Figure 3. Hammett plots for the hydrolysis of α , N-diphenylnitron.

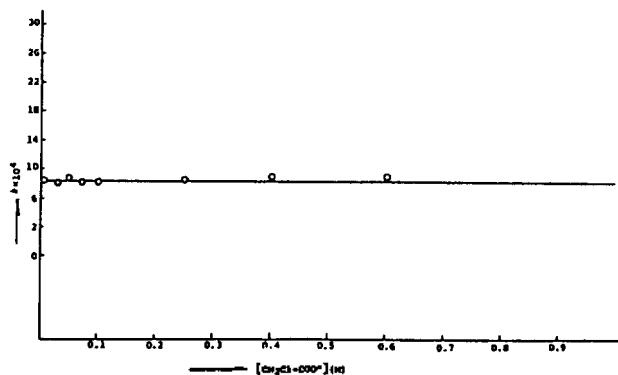


Figure 4. Effect of general base concentration on the rate of hydrolysis of α -(*p*-chlorophenyl)-N-phenylnitron at pH 2.85 and 25 °C.

Discussion

As shown in Figure 1, the hydrolysis rate of α , N-diphenylnitron is given by an expression of the form:

$$\text{Rate} = k_t[\text{Nitron}] \\ = \{k_0 + k_H[\text{H}_3\text{O}^+] + k_{\text{OH}}[\text{OH}^-]\} [\text{Nitron}] \quad (1)$$

Where k_0 is the pH independent and k_H and k_{OH} are hydronium and hydroxide ion dependent part, respectively.

Substituting the numerical values obtained from the fit of experimental data to equation (1), the k_t is given by equation (2)

$$k_t = 3.0 \times 10^{-7} + 7.27 \times 10^{-1}[\text{H}_3\text{O}^+] + 3.47 \times 10^{-2}[\text{OH}^-] \quad (2)$$

Table 1 and Figure 2 show that the overall rate constant, k_t , calculated by equation (2) are in good agreement with the observed values.

The rate equations obtained for the hydrolysis of α , N-diphenylnitron derivatives obtained in the same way are;

$$\alpha\text{-}(p\text{-Chlorophenyl})\text{-N-phenylnitron} \\ k_t = 6.24 \times 10^{-7} + 3.18 \times 10^{-1}[\text{H}_3\text{O}^+] + 7.47 \times 10^{-2}[\text{OH}^-]$$

$$\alpha\text{-}(p\text{-Nitrophenyl})\text{-N-phenylnitron} \\ k_t = 3.10 \times 10^{-6} + 2.96 \times 10^{-1}[\text{H}_3\text{O}^+] + 6.24 \times 10^{-2}[\text{OH}^-]$$

$$\alpha\text{-}(p\text{-Nitrophenyl})\text{-N-phenylnitron} \\ k_t = 3.10 \times 10^{-6} + 2.96 \times 10^{-1}[\text{H}_3\text{O}^+] + 6.24 \times 10^{-2}[\text{OH}^-]$$

$$\alpha\text{-}(p\text{-Hydroxyphenyl})\text{-N-phenylnitron} \\ k_t = 2.04 \times 10^{-5} + 2.82 \times 10^{-1}[\text{H}_3\text{O}^+] + 3.48 \times 10^{-2}[\text{OH}^-]$$

$$\alpha\text{-}(p\text{-Methoxyphenyl})\text{-N-phenylnitron} \\ k_t = 1.17 \times 10^{-6} + 2.01 \times 10^{-1}[\text{H}_3\text{O}^+] + 5.12 \times 10^{-3}[\text{OH}^-]$$

$$\alpha\text{-Phenyl-N-}p\text{-chlorophenylnitron} \\ k_t = 8.00 \times 10^{-7} + 6.29 \times 10^{-1}[\text{H}_3\text{O}^+] + 5.98 \times 10^{-3}[\text{OH}^-]$$

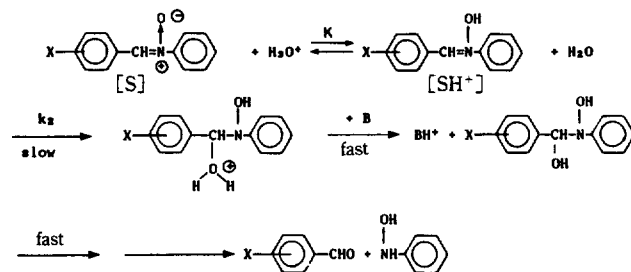
$$\alpha\text{-}(p\text{-Chlorophenyl})\text{-N-}p\text{-chlorophenylnitron} \\ k_t = 4.00 \times 10^{-6} + 6.32 \times 10^{-1}[\text{H}_3\text{O}^+] + 9.09 \times 10^{-2}[\text{OH}^-]$$

$$\alpha\text{-}(p\text{-Nitrophenyl})\text{-N-}p\text{-chlorophenylnitron} \\ k_t = 3.20 \times 10^{-6} + 3.08 \times 10^{-1}[\text{H}_3\text{O}^+] + 9.30 \times 10^{-2}[\text{OH}^-]$$

$$\alpha\text{-}(p\text{-Hydroxyphenyl})\text{-N-}p\text{-chlorophenylnitron} \\ k_t = 6.40 \times 10^{-6} + 7.36 \times 10^{-2}[\text{H}_3\text{O}^+] + 5.80 \times 10^{-4}[\text{OH}^-]$$

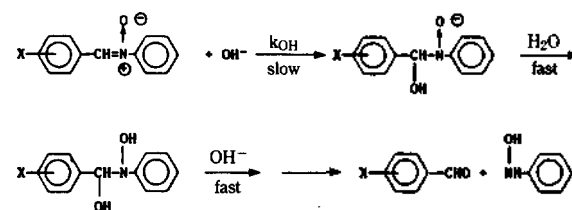
$$\alpha\text{-}(p\text{-Methoxyphenyl})\text{-N-}p\text{-chlorophenylnitron} \\ k_t = 7.20 \times 10^{-7} + 1.77 \times 10^{-1}[\text{H}_3\text{O}^+] + 3.08 \times 10^{-3}[\text{OH}^-]$$

At low pH, hydrolysis of nitron is no subject to general base catalysis and the rate of hydrolysis of nitron is proportional to the hydronium ion concentration (Eq. 2). Thus pH dependence must be caused by very rapid equilibrium of nitron, S, with its conjugate acid, SH⁺ which undergoes rate controlling through the attack of water. It follows that $k_H = k_2K = 7.27 \times 10^{-1} \text{sec}^{-1}$. Although no intermediate could be shown experimentally, Jencks suggest that the diol is the intermediate¹⁸ of nitron formation. These results may be explained in term of the mechanism in following reaction scheme.



In the acidic solution, the concentration of SH⁺ is increased by the electron donating group, but k_2 is enhanced by electron withdrawing substituents. Since the two effects are in opposition, the rate constant k_H should be insensitive to change in σ .

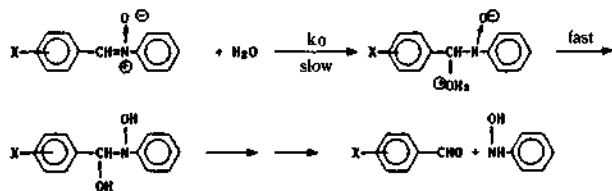
At high pH, since the rate constant is directly proportional to hydroxide ion concentration, the following reaction mechanism is proposed.



In alkaline pH's, where the rate limiting step is the direct attacking of hydroxide ion at carbon atom, we expect that

the rate constant, k_{OH} should be more sensitive to change in σ than k_H ($\rho=1.00$ at pH 3.0, $\rho=1.36$ at pH 12.0).

On the other hand, at medium pH, the hydrolysis rate of nitron is almost independent of pH change, therefore, it seems most reasonable to conclude that the addition of water to carbon atom is the rate controlling step.



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Electrochemical Behaviors of Sparteine-Copper (II) Dihalide

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Electrochemical behaviors of optically active sparteine-Cu(II) dihalide complexes were investigated by polarography and cyclic voltammetry (CV). These Cu(II) complexes are rather easier to be reduced to Cu(I) states when comparison is made with other nonplanar copper complexes. We have assigned the CV peaks and polarographic waves related to the redox processes for these complexes. We could also observe the exchange reaction of Cu(II) ion in the complex with mercury metal in the cell having mercury pool. The redox mechanism of these complexes is as follows; The 1st wave appeared at +0.47 V/+0.65 V corresponds to the reaction of $SpCuX_2 + e \rightleftharpoons SpCuX_2^-$ and the 2nd one at +0.26 V/+0.21 V does the reaction of $SpCuX_2^- + e \rightleftharpoons SpCuX_2^{2-}$. The 3rd one at -0.35 V/-0.27 V is due to the reduction of mercury complex formed via exchange reaction. Where, X is chloride ion.

Introduction

The copper (II) ion ($3d^9$) has one unpaired electron in the 3d shell, and a four-coordinated copper (II) complex usually maintains a planar structure to be attributed to the Jahn-Teller effect with the exception of a few compounds, which have pseudo-tetrahedral structure.¹⁻⁴ The tetrahalo-cuprate (II) ions have been found to possess a variety of geometries, e.g., (a) pseudo-tetrahedral D_{2d} symmetry in Cs_2CuCl_4 ^{5,6}

(b) planar and pseudo-tetrahedral geometry in $\{(CH_3)_2CHNH_3\}CuCl_4$ ⁷ (c) six coordinated tetragonal octahedral geometry (or 4+2 coordination) in $(C_6H_5NH_3)_2CuCl_4$ ⁸ and (d) complexes associated to yield five-coordination in the dimeric anion, $Cu_2Cl_6^{4-}$ which can be isolated as the tris (ethylenediamine) cobalt (III) salt.⁹ It has been considered that, based on the potential values reported for Cu(II)/Cu(I) redox couples, nonplanar bis-chelate complexes are easier to be reduced than their planar analogs, rigid planar four-coordinated com-