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## KINETICS AND MECHANISM OF ACID HYDROLYSIS OF NITROBENZALDEHYDE 2, 4-DINITROPHENYLHYDRAZONES

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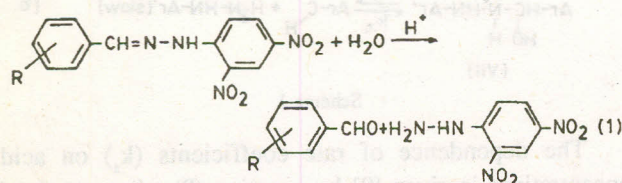
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Kinetics and activation parameters for the acid catalysed hydrolysis of 2-, 3- and 4-nitrobenzaldehyde 2,4-dinitrophenyl- hydrazones were investigated in 50% (v/v) aqueous acetone. The observed hydrolysis rates were first order with respect to substrate. The first order rate coefficients increase with the increase in acid concentrations in a non-linear fashion. The substituents on the aldehyde moiety decelerate the rate of hydrolysis reactions. A high negative value of Hammett reaction constant ( $\rho = -1.1 \pm 0.1$ ) was found for the series. A mechanism compatible with the observed results is proposed.

**Key words :** Kinetics, Hydrolysis, Hydrazines.

### Introduction

Hydrazones are special organic compounds of great chemical and physiological importance [1-5]. They belong to a general class referred to as azomethines ( $>C=N-$ ) which also include oximes, semicarbazones and Schiff's bases. Though kinetics and mechanism of hydrolysis of the other azomethines have been extensively investigated over the whole range of pH by various workers [6], only a few such studies are reported on hydrazones because of associated experimental difficulties. The mechanism of the hydrolysis reactions varied widely with the prevailing experimental conditions, and therefore, identifying the operational mechanism is of special interest to the chemists. We have studied the kinetics of hydrolysis of hydrazones derived from 2-, 3- and 4-nitrobenzaldehyde and 2,4- dinitrophenylhydrazine (II, III and IV respectively) in 50% (v/v) aqueous acetone containing various concentrations of hydrochloric acid. The overall hydrolysis reaction is represented by equation 1. We propose a mechanism which is consistent with the observed results.



R = H (I), 2-NO<sub>2</sub> (II), 3-NO<sub>2</sub> (III), 4-NO<sub>2</sub> (IV)

### Experimental

All chemicals were of analytical grade. Distilled acetone and doubly distilled deionized water were used for preparation of solvent mixtures and acid solutions. The hydrazones were prepared by condensing 2,4-dinitrophenylhydrazine with appropriate aldehyde. Their purity was checked by comparing melting points with available literature values. A Beckman

Model 35 spectrophotometer fitted with constant temperature-circulating bath and cell holders was employed to measure absorbance at  $\lambda_{\text{max}}$  (375-395 nm) of the hydrazones to follow the time course of the reactions. The temperature of the reaction cell was directly measured with Phywe NiCr-Ni digital thermometer. One of the products (amine) also absorb slightly at the  $\lambda_{\text{max}}$  of the hydrazones. An analytical equation for measuring rate coefficients at these wave lengths ( $\lambda_{\text{max}}$ ) can be deduced with the help of the following relations.

$$[\text{HY}]_t = [\text{HY}]_i + [\text{AM}]_t = [\text{AM}]_f \quad (2a)$$

$$A_t = \epsilon_H [\text{HY}]_t \quad (2b)$$

$$A_f = \epsilon_A [\text{AM}]_f = \epsilon_A [\text{HY}]_i \quad (2c)$$

$$A_{\text{obs}} = \epsilon_H [\text{HY}]_t + \epsilon_A [\text{AM}]_t = \epsilon_H [\text{HY}]_t + \epsilon_A \{ [\text{HY}]_i - [\text{HY}]_t \} \\ = (\epsilon_H - \epsilon_A) [\text{HY}]_t + \epsilon_A [\text{HY}]_i \quad (2d)$$

where HY and AM stand for the hydrazone and the amine respectively and their concentrations at the beginning, at any time t and after completion of the reaction being referred to with subscripts I, t and F respectively;  $A_{\text{obs}}$  denotes absorbance at any time t,  $A_i$  and  $A_f$  denote initial and final absorbances whereas  $\epsilon_H$  and  $\epsilon_A$  represent the molar extinction coefficients of the hydrazone and amine respectively. Using equations 2a-2d following relations are obtained

$$[\text{HY}]_t = (A_i - A_f) / (\epsilon_H - \epsilon_A) \text{ and } [\text{HY}]_t = (A_{\text{obs}} - A_f) / (\epsilon_H - \epsilon_A)$$

$$\text{Hence } [\text{HY}]_t / [\text{HY}]_i = (A_i - A_f) / (A_{\text{obs}} - A_f).$$

Therefore,

$$K_a = \frac{1}{t} \ln \frac{[\text{HY}]_i}{[\text{HY}]_t} = \frac{1}{t} \ln \frac{A_i - A_f}{A_{\text{obs}} - A_f} \quad (2e)$$

$$\text{or } -\ln (A_{\text{obs}} - A_f) = K_a t - \ln (A_i - A_f) \quad (2f)$$

The pseudo-first-order rate coefficients ( $k_a$ ) with acid concentrations in large excess were calculated from linear plots according to above equation (2f).

The initial concentrations of the hydrazones were in the range  $0.5 - 1.5 \times 10^{-5} \text{ mol dm}^{-3}$  and the acid concentrations varied from 2.98 to  $4.90 \text{ mol dm}^{-3}$ . The kinetic measurements were carried out at  $25^\circ$ ,  $30^\circ$  and  $35^\circ$ . Blank experiments involving 2,4-dinitrophenylhydrazine (one of the products) in  $3.92 \text{ mol dm}^{-3}$  acid at  $30^\circ$  showed no detectable reaction with the solvent (aqueous acetone) in the time range of our reactions. 50% (v/v) acetone-water was chosen as solvent in order to overcome solubility problems of the substrates in wholly aqueous medium.

Least square analysis were applied to calculate the values of the rate coefficients and activation parameters. The correlation coefficients for these plots were respectively in the range 0.995-1.000 and 0.995-0.998.

### Results and Discussion

The first order plots of  $-\ln(A_{\text{obs}} - A_p)$  against time yielded good straight lines. Therefore, the reactions were first order with respect to substrate. However, the rate of the overall reaction can be represented as:

$$-dc/dt = k[H^+]^n [\text{substrate}] = k_a [\text{substrate}]$$

where  $k$  is the rate coefficient for the overall hydrolysis reaction (equation 1) and  $n$  is the order of the reaction with respect to acid. The values of the rate coefficients ( $k_a$ ) at various acid concentrations are presented in Table 1.

TABLE 1. FIRST ORDER RATE COEFFICIENTS ( $k_a$ ) FOR THE HYDROLYSIS OF THE HYDRAZONES AT DIFFERENT ACID CONCENTRATIONS AT  $30^\circ$

[H <sup>+</sup> ]/mol dm <sup>-3</sup>	10 <sup>4</sup> k <sub>a</sub> /s <sup>-1</sup>			
	I(H)[13]	II(2-NO <sub>2</sub> )	III(3-NO <sub>2</sub> )	IV(4-NO <sub>2</sub> )
2.98	33.23	2.82	8.19	4.10
3.47	48.78	3.44	10.88	5.12
3.92	63.12	4.78	15.24	6.53
4.44	102.39	5.89	18.24	9.65
4.90	151.33	8.00	24.48	12.90

The rate coefficients ( $k_a$ ) increase as the acid concentrations increase in a non-linear fashion as shown in Fig. 1 for the hydrolysis of IV. As  $k_a = k[H^+]^n$ , a plot of  $\log k_a$  versus  $\log [H^+]$  was expected to be linear with the slope equal to the order of the reaction with respect to acid. However, such a plot produced a curve over the range of acid concentrations employed for hydrolysis studies. The slope at different points increased with increasing acid concentrations. Such behaviour can be explained in terms

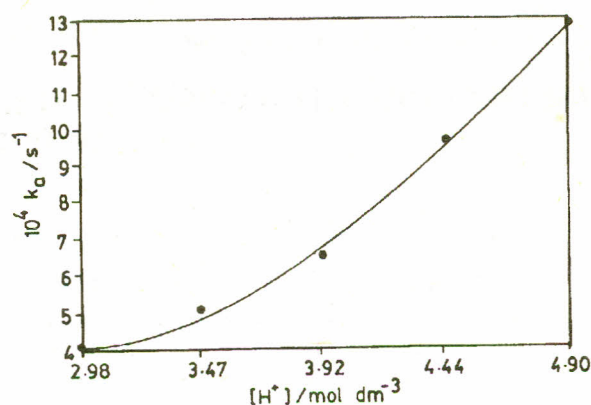
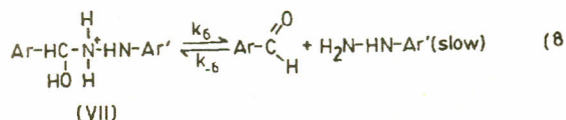
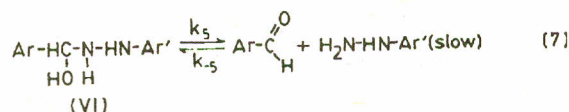
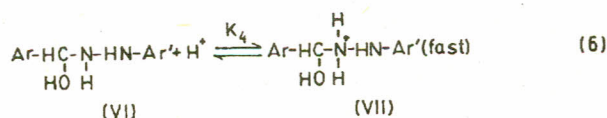
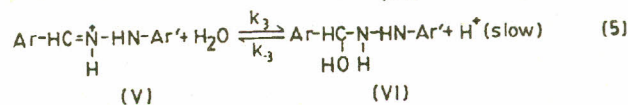
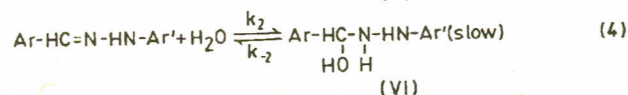
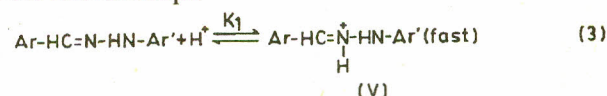


Fig. 1. Plot of  $k_a$  versus  $[H^+]$  for the hydrolysis of IV at  $30^\circ$  in 50% aqueous acetone.

of a mechanism [7,8] shown in Scheme 1 where  $k$ 's and  $K$ 's respectively refer to rate coefficients and equilibrium constants of the relevant steps.



Scheme 1

The dependence of rate coefficients ( $k_a$ ) on acid concentrations is given [9] by equation (9) when attack of water on the substrate and the protonated substrate (V) (equations 4 and 5) in conjunction with the cleavage of the intermediate carbinolamine (VI) and its conjugate acid (VII) (equations 7 and 8) contribute as rate-determining steps.

$$K_a = \frac{K_0 + K_1 [H^+] K_{II} [H^+]^2}{K_{III} + [H^+]} \quad (9)$$

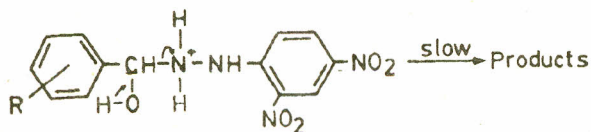
Where  $K_0 = K_2 K_5 / K_6 K_4$ ,  $K_1 = K_2 K_6 / (K_3 + K_6)$ ,  $K_{II} = K_3 K_6 K_1 / (K_3 + K_6)$  and  $k_{III} = k_{-2} / k_6 k_4$

A non-linear dependence of rate coefficients on acid concentrations, and hence variation of the order with respect to acid is predicted by equation (9). This is compatible with the observed behaviour of our systems. The nucleophilic attack of water on an unprotonated substrate (equation 4) has not yet been observed [10,11], and also considering the high acid concentration of the reaction medium, we may suggest that conjugate acids of the substrate (equation 5) and the carbinolamine (equation 8) are involved in the rate-determining steps.

The values of the rate coefficients for the hydrolysis of hydrazones, II-IV, in 3.92 mol dm<sup>-3</sup> acid and at 30°C were found lower than I (Table 1) and follow the order :



Electron-withdrawing inductive effect, and simultaneous resonance effect of nitro group (effective electron withdrawal only for I and IV) on the benzene ring of aldehyde moiety are operating in the rate-determining steps (equations 5 and 8). Due to overall electron withdrawal by nitro groups, the rate of formation of carbinolamine (equation 5), via nucleophilic attack of water on the azomethine carbon, will be enhanced. In contrast, electron-withdrawing effect will reduce the rate of decomposition of the carbinolamine (Scheme 2), and therefore the rate of reaction. In the cases of II and IV both types of electron-withdrawing effects are operating. Since the observed rate coefficients for the hydrazones, II-IV are lower compared to I, we may suggest that, of the two competing rate-determining steps, decomposition of carbinolamine plays more dominant role.



Scheme 2.

It is well known that the electron-withdrawing effects are more when the NO<sub>2</sub> group is present at 2-position as compared to its presence at 3- and 4-positions. Therefore, lowering of rate coefficient for I(2-NO<sub>2</sub>) by inductive effect is most pronounced (Table 1). However, the substituent in 3-position (3-NO<sub>2</sub>) has no effective electron-withdrawing resonance effect on the reaction centre. Consequently lowering of rate coefficients for I(3-NO<sub>2</sub>) is least among the three substrates. The rate coefficients increase in the order I>III>IV but the values of the Hammett [12] substituent constant (ρ) increase in the reverse order. This yields a negative value of the reaction constant (ρ = -1.1 to 0.1). A negative ρ-value is generally associated with a positively charged intermediate [12]. The proposed mechanism involving a positively charged intermediate (Scheme 2), therefore, explains the order of the

rate coefficients with respect to ρ-values, and also a negative ρ-value.

It is expected that lower is the energy of activation (E<sub>a</sub>) higher is the value of rate coefficients. This expectation does not hold good for the series (Table 2). However, the apparent inconsistency can be explained by Arrhenius equation (10).

$$K_a = A e^{-E_a/RT} \dots \dots \dots (10)$$

Since the rate coefficient (k<sub>a</sub>) is the product of frequency factor (A) and an exponential term we should expect a higher value of k<sub>a</sub> if the values of E<sub>a</sub> and A are also correspondingly higher. Therefore, we may explain the relative values of the rate coefficients (Table 1) in terms of both energy of activation and frequency factor. The values of enthalpy of activation (ΔH) follow the same trend as energy of activation (Table 2).

The values of the rate coefficients increase in the reverse order compared to the free energies (ΔG) of activation which is consistent with the predictions of theory of absolute reaction rates, equation (11).

$$K_a = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \dots \dots \dots (11)$$

where k and h are respectively Planck's and Boltzmann constants.

The values of entropy of activation (ΔS<sup>‡</sup>) for the hydrolysis of hydrazones are negative (Table 2). In a polar solvent as aqueous acetone, this is indicative of formation of a relatively polar activated complex [14] which binds the solvent molecules much more strongly than the reactants.

TABLE 2. THERMODYNAMIC PARAMETERS OF ACTIVATION OF THE HYDROLYSIS OF THE HYDRAZONES.

Compound	E <sub>a</sub> KJ mol <sup>-1</sup>	ΔH <sup>‡</sup> KJmol <sup>-1</sup>	-ΔS <sup>‡</sup> JK <sup>-1</sup> mol <sup>-1</sup>	ΔG <sup>‡</sup> KJmol <sup>-1</sup>	10 <sup>8</sup> .A/s. <sup>-1</sup>
I(H)[13]	77.20	74.76	39.73	86.81	1399.30
I(2-NO <sub>2</sub> )	73.19	70.67	75.92	93.69	18.58
I(3-NO <sub>2</sub> )	66.48	63.89	88.74	90.79	4.10
I(4-NO <sub>2</sub> )	81.50	78.99	45.01	92.63	764.28

High negative value of the Hammett reaction constant and dependence of rate coefficients on acid concentrations suggest that formation of carbinolamine via conjugate acids of the hydrazones, and decomposition of the conjugate acid of the carbinolamine are rate-determining steps. Furthermore, the observed inductive and resonance effects on the rates lead us to conclude that the latter contributes predominantly to the rate-determining processes.

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