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KINETICS AND MECHANISM OF THE RAPID OXIDATION OF HYDRAZINE BY IODINE IN WEAKLY ACIDIC SOLUTIONS

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In weakly acidic solutions the rate of oxidation of hydrazine by iodine is so fast that studies on the kinetics of the reaction have not been reported in literature. In the present work, the kinetics of the reaction has been studied by the continuous flow technique from measurement of diffusion current due to iodine at a platinum microelectrode. The reaction is of the second order and at 25 °C and at *p*H 5.2, the specific reaction rate is $5.02 \times 10^3 M^{-1} s^{-1}$. The energy of activation, entropy of activation and frequency factor are 71.2 KJ $mole^{-1}$, 56.6J K^{-1} $mole^{-1}$ and 1.53×10^{16} M^{-1} s^{-1} respectively. The reaction rate increases sharply with *p*H and a plot of log k_2 *vs.* *p*H is a straight line with a slope slightly more than unity. In contrast, the specific reaction rate is unchanged due to variation in ionic strength and base concentration, but varies inversely with iodide ion concentration. Based on these observations, the most likely mechanism of the reaction has been proposed.

Key Words : Kinetics of Hydrazine – Iodine Reaction; Mechanism of Hydrazine – Iodine Reaction

INTRODUCTION

WHILE the oxidation of hydrazine by iodine has been known since long,[1,2] the kinetics of the reaction has been studied only in strongly acidic solutions where the reaction is quite slow and that too over a limited scope.[3-5] Indeed the reaction becomes very fast in weakly acidic or neutral solutions and under such conditions the kinetics of the reaction has not been reported. The reason for such large increase in the reaction rate with *p*H of the solution, and also the mechanism of the reaction have not been clearly established. In this background, it is proposed to carry out detailed kinetic studies in weakly acidic solutions to gain insight into the above mentioned aspects. Since in weakly acidic or neutral solutions the reaction is too rapid to be studied by conventional techniques, in the present work, it has been studied by the continuous flow technique[6] with a voltammetric probe.

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MATERIALS AND METHOD

The continuous flow technique with voltammetric probe consisting of platinum microelectrode and saturated calomel electrode has been described in full in earlier papers.[7,8]

Analytical grade (BDH/E.Merck) chemicals were used to prepare the following stock solutions : 0.5 M hydrazine sulphate, 0.042M iodine in 0.80M potassium iodide, 2.0M potassium chloride, 2.0M sodium acetate, 0.5M acetic acid and 0.80M potassium iodide. Iodine was standardised with sodium arsenite and thereafter, hydrazine sulphate was standardised with iodine.[9]

The required volumes of the stock solutions were diluted to obtain 2.0×10^{-4}M hydrazine in acetic acid-acetate buffer of the chosen *p*H in one of the reservoirs of the continuous flow assembly and 4.0×10^{-4}M iodine in 7.6×10^{-3}M potassium iodide and buffer of the same *p*H in the other reservoir of the assembly. The ionic strength of both the solutions was maintained at 0.10M by the addition of the required volumes of potassium chloride solution. Both the reservoirs were maintained at constant temperature in a thermostat to an accuracy of ± 0.1°.

In the kinetic experiment, the reactant solutions were driven through the mixing chamber and the observation tube of the continuous flow assembly by compressed air. Immediately on mixing, the initial concentrations of hydrazine and iodine were 1.0×10^{-4}M and 2.0×10^{-4}M respectively. The diffusion current at the voltammetric probe was measured at various distances of the probe from the mixing chamber with a moving coil mirror galvanometer. The linear flow veloctiy of the solution along the observation tube was evaluated and hence, the duration of the reaction was calculated for each observation point. By calibrating the diffusion current with known concentration of iodine under identical experimental conditions, the concentrations of iodine remaining unreacted at various instants during the course of the reaction were calculated. From these results the specific reaction rate* was determined as shown in Table I.

Each kinetic experiment was repeated several times to check the reproducibility of the results. The kinetics was similarly studied at various temperatures in the range of 20-40°C at *p*H 5.20 and the activation parameters were evaluated.

The kinetics was also studied to see the effects of ionic strength, base concentration, *p*H and iodide ion concentration on the specific rate of the reaction and hence to gain an insight into the mechanism of the reaction.

RESULTS AND DISCUSSION

Determination of Specific Rate

The stoichiometry of the reaction under study was well known, as given by the equation

$$N_2H_4 + 2\ I_2 \rightarrow 4\ HI + N_2$$

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*specific rate, in brief.

The plot of the reciprocal of the concentration of hydrazine remaining unreacted *vs.* time gave a good straight line indicating that the reaction was of second order. Half of the slope of this line was the specific rate, k_2 (Table I).

The order of the reaction was confirmed by carrying out the kinetic measurements in several cases with non-stoichiometric concentrations of hydrazine (b) and iodine ($2a$) where $2a > b$ and plotting $\log \frac{a-x}{b-2}$ *vs.* time. In these cases also the same specific rate was obtained as with stoichiometric concentrations, within limits of experimental error.

Limits of Error

The kinetic measurements under every set of experiments were repeated several times to check the consistency of the specific rates. In the typical case of *p*H 5.20

TABLE I

Kinetics of the oxidation of hydrazine by iodine in aqueous solution at pH = 5.20 and 25 °C

Initial concentration of hydrazine sulphate (a) = 1.0×10^{-4}M
Initial concentration of iodine ($2a$) = 2.0×10^{-4}M
Ionic strength of reaction solution = 0.10M
Calibration of galvanometer deflection = 13.0 cm/10^{-4}M
Linear flow velocity = 122 cm/s

Distance of voltammetric probe from mixing chamber d/cm	Time/s	Galvanometer deflection/cm	Concentration of unreacted iodine $(2a-2x)/10^{-4}$M	Concentration of unreacted hydrazine $(a-x)/10^{-4}$M	$\frac{1}{(a-x)}$, 10^4M^{-1}
0	0	26.0	2.00	1.00	1.10
7	0.057	24.5	1.88	0.940	1.06
17	0.139	22.7	1.74	0.870	1.14
27	0.221	21.5	1.65	0.825	1.21
37	0.303	20.2	1.55	0.775	1.29
47	0.385	18.9	1.45	0.725	1.38
57	0.467	17.5	1.34	0.670	1.49
67	0.549	16.9	1.30	0.650	1.54
77	0.631	16.0	1.23	0.615	1.63
87	0.713	15.3	1.18	0.590	1.69
97	0.795	14.7	1.13	0.565	1.77

Slop of $1/(a - x)$ *vs.* time plot = 10.04×10^3 M^{-1} s^{-1} Specific reaction rate = 5.02×10^3 M^{-1} s^{-1}

and 25.0 °C, several repeated trials gave specific rates with a mean value of 5.02×10^3 M^{-1} s^{-1}, mean deviation of 0.140×10^3 M^{-1} s^{-1} and standard deviation of 0.155×10^3 M^{-1} s^{-1}. Thus the experimental errors were within limits of ± 3%.

Energy of Activation

The temperature dependence of specific rate is shown in Table II. The energy of activation, the entropy of activation and the frequency factor were found to be 71.2 kJ mole ^{1}, 56.6 JK^{-1} $mole^{-1}$ and 1.53×10^{16} M^{-1} s^{-1} respectively.

TABLE II

Temperature dependence of the specific reaction rate for the oxidation of hydrazine by iodine in aqueous solution at pH = 5.20

Temperature $t/°C$	$T/°K$	$\frac{1}{T}$ $/10^{-3}$ K^{-1}	$k_2/10^3$ M^{-1} s^{-1}	$\log k_2$
20.0	293	3.41	3.17	3.501
25.0	298	3.36	5.02	3.701
30.0	303	3.30	8.00	3.903
35.0	308	3.25	12.6	4.100
40.0	313	3.19	20.6	4.314

Slope of the plot of $\log k_2$ *vs.* $1/T$ = $-3.72 \times 10^3 K$ ∴ Energy of activation = 71.2 kJ $mole^{-1}$ Entropy of activation = 56.6 JK^{-1} $mole^{-1}$ Frequency factor = 1.53×10^{16} M^{-1} s^{-1}

Effects of Ionic Strength and Base Concentration

The kinetic studies at various ionic strengths showed that the specific rate was independent of them. Hence, from the consideration of primary salt effect, the rate-determining step must involve at least one uncharged species. Further, the specific rate was also found to be independent of the concentration of base, i.e., sodium acetate (at constant ionic strength and *p*H) and hence the reaction was not base catalysed.

Effect of pH

An important feature of the reaction was that the specific rate was very sensitive to *p*H. An increase in *p*H even by one unit caused many fold increase in the specific rate (Table III). Therefore, in the present study, the specific rates were determined in the limited *p*H range of 5.0 to 6.0.

The increase in the specific rate with *p*H was most likely due to the increased concentration of N_2H_4, the base form of hydrazine. In the *p*H range of 5.0 to 6.0, the hydrazine was essentially monohydrogen hydrazinium ion $N_2H_5^+$ which ionized as a weak acid according to the equation

$$N_2H_{5aq}^+ \rightleftharpoons N_2H_4 + H_{aq}^+ \qquad K_a = \frac{[H_{aq}^+]\,[N_2H_4]}{[N_2H_5^+]}$$

TABLE III

pH dependence of specific reaction rate for the oxidation of hydrazine by iodine in aqueous solution at 25.0°C

*p*H	Specific reaction rate $k_2/10^3$ M^{-1} s^{-1}	log k_2
5.00	2.80	3.447
5.20	5.02	3.701
5.40	8.00	3.903
5.60	16.2	4.209
5.82	34.1	4.532
6.00	56.6	4.753

The pK_a value of $N_2H_5^+$ was 8.48 while the pK_b value[10] of the conjugate base N_2H_4 was 5.52. Evidently, if the *p*H was increased, the relative concentration of N_2H_4 increased largely and the specific rate also increased similarly. Indeed, when log k_2 was ploted *vs.* *p*H, one obtained a straight line. This indicated that the base form of hydrazine was the reactive species and the acid form was unreactive.[11]

Effect of Iodide Ion Concentration

The kinetic studies at various concentrations of the iodide ion showed that the specific rate decreased with increased iodide ion concentration. In fact, the specific rate varied linearly with the reciprocal of iodide ion concentration (Fig. 1).

Since the present kinetic study was in aqueous solution, potassium iodide was necessary to keep the iodine in solution. It is well known that in the presence of iodide ion, iodine exists mostly as the triiodide ion according to the equilibrium[12]

$$I_2 + I^- \rightleftharpoons I_3^-, \quad K = \frac{[I_3^-]}{[I_2]\,[I^-]}$$

which is rapidly established.[13,14] Because of this equilibrium, at higher concentrations of the iodide ion, the concentration of I_3^- would be more while that of I_2 would be less. Since it was observed that the specific rate varied linearly with the reciprocal of the iodide ion concentration, it was logical to infer that I_2, rather than I_3 was the active oxidant.

If, in order to support the inference that molecular iodine was the active oxidant, the kinetics of the reaction was studied in any solvent other than water, it would significantly change the dielectric constant of the medium and the solvation of the ions. Therefore, it would seriously affect the several equilibria in the reaction medium such as the acetic acid-sodium acetate buffer, the ionization of the monohydrogen

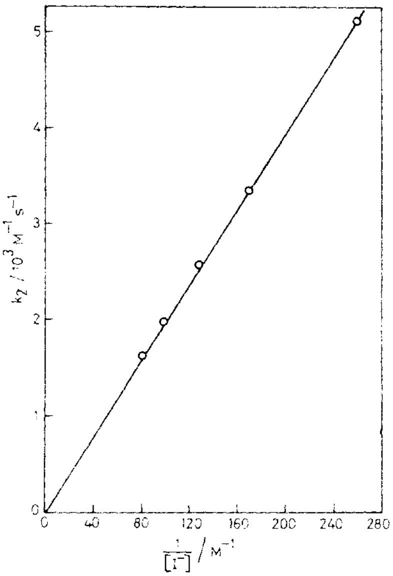

FIG 1 Dependence of specific reaction rate of the oxidation of hydrazine by iodine on iodide ion concentration in aqueous solution at $pH = 5.20$ and 25.0°C

hydrazinium ion, the formation of the triiodide complex and the formation of the activated complex. Hence, the kinetic measurements in such a solvent could hardly be compared with those in water.

Although it is known that halogens in aqueous solution undergo hydrolysis according to the equation

$$X_{2(aq)} \rightleftharpoons H^+ + X^- + HOX,$$

the equilibrium constant in the case of iodine[15] is extremely small (2.0×10^{-13}). Hence HOI would not be present in any significant concentration to be regarded as the oxidant.

Mechanism of the Reaction

From the various foregoing observations it was reasonable to infer that N_2H_4 and I_2 were the reacting species and that one molecule of each was involved in the rate determining step although, according to stoïchiometry, one molecule of hydrazine reacted with two molecules of iodine. The reaction most probably occurred by the following mechanism:

$$N_2H_4 + I_2 \xrightarrow[\text{r.d.s.}]{\text{slow}} N_2H_4I^+ + I^-$$

$$N_2H_4I^+ + I_2 \xrightarrow{\text{fast}} N_2 + 3I^- + 4H^+$$

Since both species involved in the rate determining step were uncharged, the reaction would be unaffected by the ionic strength of the medium. Further, the rate-determining step did not involve any abstraction of H^+ and therefore, the reaction was not base catalysed. Further, according to the proposed mechanism, the rate of the reaction would be given by the equation

$$\text{Rate} = k\,[N_2H_4]\,[I_2].$$

If K_a was the dissociation constant of $N_2H_5^+$ and K was the stability constant of I_3^-, then

$$[N_2H_4] = \frac{K_a\,[N_2H_5^+]}{[H^+_{aq}]} \text{ and } [I_2] = \frac{1}{K}\,\frac{[I_3^-]}{[I^-]}$$

$$\text{Hence, Rate} = \frac{k\cdot K_a\,[N_2H_5^+]}{[H^+_{aq}]}\,\frac{1}{K}\cdot\frac{[I_3^-]}{[I^-]}$$

$$= k_2\,[N_2H_5^+]\,[I_3^-],$$

$$\text{where}\quad k_2 = \frac{k\cdot K_a}{[H^+_{aq}]\,K[I^-]}$$

Here k_2 was the experimentally determined specific rate and k was the specific rate of the rate determining step. Further, at constant iodide ion concentration,

$$\log k_2 = \log\frac{kK_a}{K\,[I^-]} + \log\frac{1}{[H^+_{aq}]}$$

$$\text{i.e., } \log k_2 = \text{constant} + pH.$$

The above equations clearly showed that the specific rate varied inversely with the iodide ion concentration and also that a plot of log k_2 *vs.* pH was a straight line.

In the equation for k_2, the dissociation constant K_a was in the numerator while the stability constant K was in the denominator and, over a short temperature range, their ratio may not change significantly. Hence, at constant pH and iodide ion concentration, the quantity $\frac{K_a}{[H^+_{aq}]\,K[I^-]}$ may be regarded as nearly constant. Therefore, any variation in k_2 due to temperature would be due to a corresponding variation in k. Hence,

$$\frac{k_2\,(T_2)}{k_2(T_1)} \approx \frac{k(T_2)}{k(T_1)}$$

Therefore, the experimentally determined energy of activation was also nearly the energy of activation of the rate-determining step.

The mechanism proposed above was simple, yet was able to account for all the observed features of the reaction.