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Kinetics of Oxidation of Hydrazine by Iodine

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The kinetics of oxidation of hydrazine by iodine in aqueous acetic acid containing sulphuric acid have been investigated. The reaction is first order in [oxidant], first order in [substrate] and inverse first order in [H+]. I− ion markedly impedes the reaction due to the formation of the less effective oxidant, I_3^-. HOI appears to be the active oxidant.

THE oxidation of hydrazine by iodine in aqueous acetic acid has been investigated from the kinetic standpoint and the results are reported in this note. This reaction does not seem to have been studied earlier mechanistically.

Hydrazine sulphate (BDH) was repeatedly recrystallised from hot water, and acetic acid purified by the conventional method[1]. All other chemicals used were of AR grade.

The kinetic runs were carried out in aq. acetic acid medium containing a fixed concentration of sulphuric acid and the course of the reaction followed by quenching the aliquot in a large volume of ice-cold water and estimating the unreacted iodine by titrating with sodium thiosulphate. Each reaction was conducted under pseudo-first order conditions. One mol of hydrazine, when reacted with a large excess of iodine consumed two mol of iodine. For all the reactions, log (a-x) versus time plots were linear and the pseudo-first order rate constant (k_1) varied linearly with [substrate] indicating that the reaction is first order in substrate. However, k_1 values decreased with increasing [iodine]. This curious observation indicates that iodine is a more effective

oxidant in dilute than in concentrated solution. It is likely that $[I_3^-]$, which is weak oxidant increases as $[I_2]$ increased.

Thus the formation of I_3^- at the expense of the active oxidant may be responsible for the decreased reaction rate at higher iodine. The oxidation was considerably impeded by an increase in [H+] when other experimental conditions were the same. The reaction was inverse first order in [H+] as evident from the constancy of $k_1 \times$ [H+] values (Table 1). A significant decrease in the rate constant occurred when [I−] was increased (Table 2). This substantiates that increasing [I−] forms the less effective oxidant I_3^- at the expense of the more effective oxidant, HOI. A similar observation was reported by Edwards and co-workers on the oxidation of hydrocyanic acid by iodine[2]. An increase in acetic acid content of the reaction medium (upto 40% HOAC) decreased the rate constant (Table 2). Beyond this concentration of acetic acid, the substrate was insoluble. The increase in the rate with increase in dielectric constant of the solvent indicates a polar transition state in which the charges are separated. Added salts such as KHSO4 have negligible effect on the reaction rate.

Activation parameters have been obtained from the Arrhenius plot in the temperature range, 30°-45°C, and the values are:

$$E_a = 30.56 \text{ kJ mol}^{-1}, \quad \triangle S\dagger = -155.3 \text{ JK}^{-1}$$
$$\text{and } \triangle G\ddagger (35°C) = 75.77 \text{ kJ mol}^{-1}$$

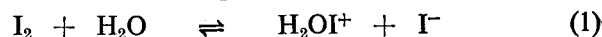The equilibria (1) and (2) are known to exist when iodine is in dilute aqueous acidic solution[3].

$$I_2 + H_2O \rightleftharpoons H_2OI^+ + I^- \qquad (1)$$
$$H_2OI^+ \rightleftharpoons HOI + H^+ \qquad (2)$$

TABLE 1 — EFFECT OF H+ CONCENTRATION ON THE FIRST ORDER RATE CONSTANTS

[[Substrate] = 0.02M; [KI] = 0.02M; temp. = 30°C; [Oxidant] = 0.002M; solvent = HOAc 25% (v/v)]

$[H^+] \times 10^2$ (M)	$k_1 \times 10^2$ (min^{-1})	$k_1 \times [H^+] \times 10^3$
7.5	9.30	6.98
10.0	6.46	6.47
15.0	4.98	7.49
20.0	3.00	6.00
30.0	2.12	6.37
50.0	1.21	6.16
75.0	0.90	6.77

TABLE 2 — EFFECT OF ACETIC ACID AND KI ON THE RATE CONSTANTS

[Substrate]=0.02M; [H$_2$SO$_4$] = 0.05M; temp. =30°C; [I$_2$] = 0.002M]

HOAc (%, v/v)	$k_1 \times 10^2$ (min^{-1})	$[KI] \times 10^2$ (M)	$k_1 \times 10^2$ (min^{-1})
20	34.5	2.0	3.45
25	12.6	3.0	2.33
30	9.78	4.0	1.91
35	4.36	5.0	1.25
40	2.66	6.0	1.04

Since [H$^+$] sharply reduces the reaction rate it is axiomatic that H$_2$OI$^+$ is not the active oxidant species. Hence it is likely that HOI is the active species involved in the oxidation of hydrazine. The concentration of HOI is expected to decrease with increase in [H$^+$] or [I$^-$]. I$_3^-$ cannot be the active oxidant because increasing [I$^-$] is found to decrease the reaction rate.

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Kinetics of Benzidine-induced Decomposition of Dibenzoyl Peroxide in Viscous Media

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The kinetics of decomposition of dibenzoyl peroxide in the presence of benzidine has been studied at various temperatures in three polymeric viscous media of softening temperature of about 50°C. The reaction is found to be pseudo-first order. The intrinsic activation energies have been calculated. The effect of viscosity on activation parameters, E_a, $\triangle H\ddagger$ and $\triangle S\ddagger$ has also been examined.

THE published data on the kinetics of amine-induced decomposition of dibenzoyl peroxide (DBP) have revealed that the rate of decomposition depends on the solvent[1] and the degree of basicity of amine[2]. The influence of diphenylamine and benzidine on the rate of decomposition of DBP has also been studied in non-restricted fluid medium[3]. Recently[4] the kinetics of unimolecular spontaneous and bimolecular amine (diphenylamine) induced decomposition of DBP in partially restricted media have been studied.

In the present investigation the kinetics of benzidine-induced decomposition of DBP has been studied in partially restricted fluid media. One of the objectives of this investigation has been to characterise the effect of solvent viscosity on the activation parameters, E_a, $\triangle H\ddagger$ and $\triangle S\ddagger$.

Three polymeric viscous media, chosen in the present investigation, were prepared by the condensation of ethylene glycol with adipic acid[5]. The degree of viscosity of each medium was dependent upon the time of preparation. The absolute viscosities of these polymeric media were measured by the co-axial cylinder method[6] at four various temperatures between 60° and 72° ± 0.1°C. The experimental procedure for kinetic measurements was similar to the one described elsewhere[4]. All reagents were of either AR or CP grade.
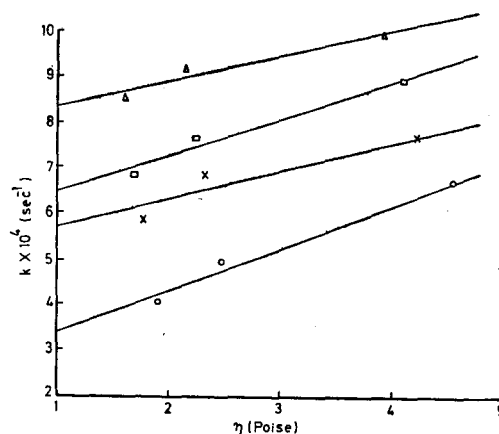

Fig. 1 — Variation of initial reaction rate with initial benzidine concentration in viscous medium (3) at constant initial DBP concentration of 0.145 × 10^{-2}M and at various temperatures [(○) 60°, (×) 65°; (□) 68°; and (△) 72°C].

The initial rate method was used to reveal the O—O bond cleavage under the working conditions of the present investigation. To obtain quantitative measurements on the cage effect[4], a restriction in the medium was imposed by carrying out rate measurements in polymer media of various viscosities.

The concentration of DBP was kept constant (0.145×10^{-2} M) while that of benzidine was varied in the range of 0.231 to 0.75×10^{-3} M. From the decomposition-time curves, the concentration of the undecomposed DBP was calculated and plotted against time. From the latter plots (concentration-time curves) reaction velocities were found graphically and initial rates were obtained by extrapolation. The initial rate versus benzidine concentration was plotted at various temperatures for the three media (Fig. 1) from which the rate constants were evaluated. The values of reaction rate constant (k) together with the measured values of viscosity, η at various temperatures for the three polymeric media are given in Table 1. It is clear that the rate constant increases with increase in the solvent viscosity. The activation energies for the viscosity-induced decomposition have been deduced from the plots of log η versus $1/T$ and found to be 10.4, 10.4 and 10.1 kJ mol^{-1} for media 1, 2 and 3 respectively. The activation energy for the amine-induced decomposition of DBP is found to decrease with increase in visco-

TABLE 1 — REACTION RATE CONSTANT (k) FOR DECOMPOSITION OF DBP IN PRESENCE OF BENZIDINE IN DIFFERENT VISCOUS MEDIA (1-3)

Temp. °C	(1)		(2)		(3)	
	η (Poise)	$k \times 10^4$ (sec^{-1})	η (Poise)	$k \times 10^4$ (sec^{-1})	η (Poise)	$k \times 10^4$ (sec^{-1})
60	1.9	4.1	2.5	5.0	4.6	6.7
65	1.8	5.9	2.3	6.9	4.2	7.7
68	1.7	6.9	2.2	7.7	4.1	9.0
72	1.6	8.6	2.1	9.2	3.9	10.0