Mechanism of Oxidation of Azide by Periodate in Acid Medium

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The oxidation of azide by periodate in acid media shows second order dependence in azide ion and first order dependence in periodate under the condition $[H^+] >> [N_3^-]$. Increase in $[H^+]$ increase the pseudo-first order rate constant upto $[H^+] = [N_3^-]$ and beyond that the rate constant remains unchanged showing that HN_3 is the reacting species. Two mol of HN_3 require one mol of IO_4^- for oxidation. The reaction is independent of ionic strength. It is proposed that the hydrazoic acid forms a covalent complex with protonated periodate in the rate-determining step, which then further reacts with HN_3 in a fast step to give the product (N_2). The thermodynamic parameters have been calculated and the effects of added Fe^{2+}, Cr^{3+} and Mn^{2+} also studied.

In continuation of our earlier work[1-4] on the oxidation of azide, we report herein the results of oxidation kinetics of N_3^- by metaperiodate in acid media.

Materials and Methods

All the reagents used were of analytical grade. Deionised, doubly distilled over alkaline permanganate, water was used in preparing all solutions. Periodate solution was prepared by weight from $NaIO_4$ (BDH, AnalaR) and kept in flasks wrapped with aluminium foil to avoid photochemical decomposition[5]. Sodium azide solution was prepared afresh by dissolving a weighed amount of NaN_3 (E. Merck) and standardised by cerimetry. The pseudo-first order conditions ([azide] ⩾ [periodate]) were maintained in all kinetic runs which were carried out in flasks coated black from outside. The ionic strength was maintained by the addition of Na_2SO_4. The reaction was followed iodometrically.

Results and Discussion

It was found that for a smooth study of the reaction, a condition of $[N_3^-]$ and $[H^+]$ in excess was most suitable. The stoichiometry of the reaction was determined by mixing the reactants N_3^- and IO_4^- in various proportion and estimating the remaining N_3^- by cerimetry and IO_4^- and IO_3^- by iodometry. The results showed that, in acid medium, the stoichiometry could be expressed by Eq. (1).

$$IO_4^- + 2HN_3 \rightarrow IO_3^- + 3 N_2 + H_2O \qquad ...(1)$$
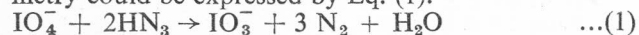
The reaction between IO_3^- and HN_3 is too slow to produce any complication as IO_4^- is quantitatively converted into IO_3^- and there is little decrease in $[IO_3^-]$ even after 24 hr. The gaseous product is found to be pure nitrogen by gas chromatographic analysis.

Dependence of rate on $[IO_4^-]$, $[N_3^-]$ *and* $[H^+]$—(i) At various initial $[IO_4^-]$ and fixed $[N_3^-]$, the rate was

Table 1—Pseudo-First Order Rate Constants k_{obs} under Various Conditions at 35° C

$[N_3^-]$ mol dm^{-3}	$[IO_4^-]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	μ	$k_{obs} \times 10^3$ min^{-1}
0.020	0.0015	0.10	0.50	1.34
0.025	0.0015	0.10	0.50	2.30
0.030	0.0015	0.10	0.50	3.15
0.0375	0.0015	0.10	0.50	4.72
0.045	0 0015	0.10	0.50	7.83
0.050	0.0015	0.10	0.50	9.67
0.0625	0.0015	0.10	0.50	14.56
0.075	0.0015	0.10	0.50	20.04
0.050	0.0005	0.10	0.35	9.44
0.05	0.0010	0.10	0.35	10.13
0.05	0.0015	0.10	0.35	9.67
0.05	0.0020	0.10	0.35	9.21
0.05	0.0015	0.10	0.75	10.02
0.05	0.0015	0.10	1.00	10.03
0.05	0.0015	0.10	1.25	9.86
0.05	0.0015	0.02	0.50	1.45
0.05	0.0015	0.03	0.50	3.11
0.05	0.0015	0.04	0.50	5.76
0.05	0.0015	0.05	0.50	9.50
0.05	0.0015	0.07	0.50	9.65
0.05	0.0015	0.09	0.50	9.90
0.05	0.0015	0.12	0.50	9.70

directly proportional to the $[IO_4^-]$ (Table 1). (ii) The rate increased with the increase in $[N_3^-]$ at fixed $[IO_4^-]$ and excess $[H^+]$ (Table 1). A plot of $k_{obs}/[N_3^-]$ versus $[N_3^-]$ at constant $[H^+]$ was linear and passed through the origin (Fig. 1). This shows that the observed rate can be written as

$$-\frac{d [IO_4^-]}{d} = k \ [IO_4^-] [N_3^-]^2 \qquad ...(2)$$

(iii) An increase in $[H^+]$ increased the rate till $[H^+] = [N_3^-]$ and beyond this condition the observed rate constant remained unchanged (Table 1). A plot of $k_{obs}/[H^+]$ versus $[H^+]$ at constant $[N_3^-]$ upto $[H^+] = [N_3^-]$ was linear and passed through the origin. The
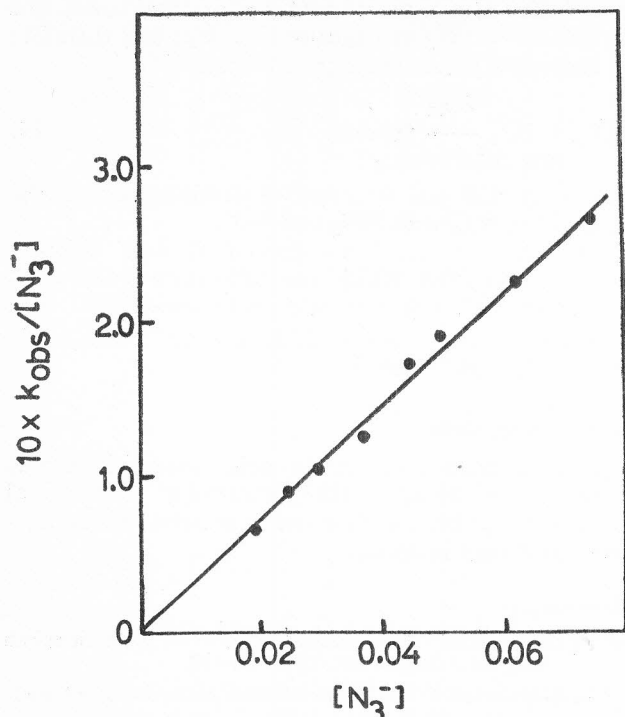
Fig. 1—A plot of $k_{obs}/[N_3^-]$ versus $[N_3^-]$ $[IO_4^-] = 0.0015$ mol dm^{-3}; $[H^+] = 0.10$ mol dm^{-3}; $\mu = 0.50$; temp. $= 35°$ C.

Table 2—Effect of Varying HN_3 on the Observed Rate $\{[IO_4^-] = 0.0015$ mol dm^{-3}; $[H^+]_{free} = 0.10$ mol dm^{-3}; $\mu = 0.775$; temp. $35°$ C$\}$

$[HN_3]$ mol dm^{-3}	$k_{obs} \times 10^3$ min^{-1}
0.02	1.34
0.03	3.20
0.04	6.08
0.05	9.50
0.0625	15.00
0.075	20.00
0.0875	28.10

Table 3—Effect of Cr^{3+}, Mn^{2+} and Fe^{2+} on Pseudo-First Order Rate Constant

$[N_3^-] = 0.05$ mol dm^{-3}; $[IO_4^-] = 0.0015$ mol dm^{-3}; $[H^+] = 0.10$ mol dm^{-3}; $\mu = 0.50$; temp. $35°$ C

$[Cr_2(SO_4)_3]$ mol dm^{-3}	$[MnSO_4]$ mol dm^{-3}	$[FeSO_4]$ mol dm^{-3}	$k_{obs} \times 10^3$ min^{-1}
0.0025	—	—	9.60
0.0050	—	—	10.02
0.0075	—	—	10 10
0.0100	—	—	9.80
—	0.0005	—	9.67
—	0.0010	—	10.00
—	0.0100	—	9.90
—	0.0200	—	9.98
—	—	0.00025	9.79
—	—	0.0005	9.68
—	—	0.0010	9.80
—	—	0.0100	very fast

slope of the linear plot was exactly equal to the slope of the linear plot in Fig. 1. This proves that HN_3 is the reactive species. The reaction was also studied by keeping the $[H^+]_{free}$ ($[H^+]_{free} = [H^+]_{total} -$

$[N_3^-]_{total}$) constant (Table 2) and varying $[HN_3]$. The linear plot of $k_{obs}/[HN_3]$ versus $[HN_3]$ also passed through origin with identical slope as that of the linear plot in Fig. 1. This clearly proves that the reaction is zero order with respect to free H^+.

Under the pseudo-first order conditions, the rate was independent of the ionic strength (Table 1).

Addition of Mn^{2+} and Cr^{3+} had no effect on the rate of the reaction. In the presence of added Fe^{2+}, the rate was constant only when $[Fe^{2+}] < [IO_4^-]$. Under the condition $[Fe^{2+}] > [IO_4^-]$ the reaction was very fast. Table 3 summarizes the results of Mn^{2+}, Cr^{3+} and Fe^{2+} addition on the rate of the reaction.

Mechanism—Generally the azide ion, in acidic solution; exists predominantly as HN_3 (HN_3 is a weak acid $K_a = 2.1 \times 10^{-5}$ mol dm^{-3} at $20°$ C with high thermal stability[6]). Therefore the reacting species is the protonated species i.e. hydrazoic acid and as a first approximation $[HN_3] = [N_3^-]_{total}$ at excess $[H^+]$ over $[N_3^-]$.

The behaviour of the periodate ion in aqueous solution is best described[7,8] by Eqs (3–5)

$$H^+ + H_4IO_6^- \underset{K_H}{\overset{K_1}{\rightleftharpoons}} H_5IO_6^- \ (K^1 = 1.98 \times 10^3 \ M^{-1}) \ ...(3)$$

$$2 \ H_2O + IO_4^- \rightleftharpoons H_4IO_6^- \ (K_H = 0.025) \qquad ...(4)$$

$$H^+ + H_3IO_6^{2-} \overset{K_2}{\rightleftharpoons} H_4IO_6^- \ (K_2 = 5.0 \times 10^6 \ M^{-1}) \ ...(5)$$
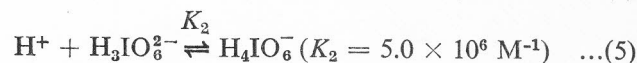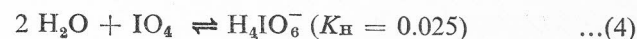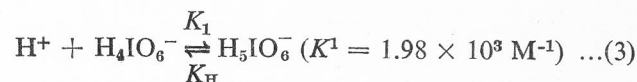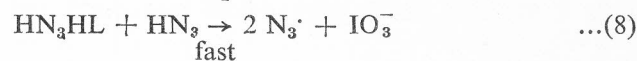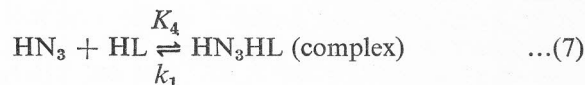
where the values of the equilibrium constant are those at zero ionic strength and $25°$ C. From these equilibria it is possible to conclude that at the $[H^+]$ employed, the periodate species exist as HIO_4 and H_5IO_6. It is perhaps worth mentioning that the rapid equilibrium between periodate and hydrogen ions.

$$H^+ + L^- \overset{K_3}{\rightleftharpoons} HL \qquad ...(6)$$

($L^- = IO_4^- + H_4IO_6^- = [IO_4^-]_{total}$ — total [periodate]) should be considered. The thermodynamic value of K_3 is reported[9] as 200 dm^3 mol^{-1} at $25°$ C. K_3 was determined as 150 ± 10 dm^3 mol^{-1} at ionic strength 1.0 at $25°$ C.

Taking into consideration all the experimental facts the mechanism in scheme 1 is proposed.

$$HN_3 + HL \overset{K_4}{\underset{k_1}{\rightleftharpoons}} HN_3HL \text{ (complex)} \qquad ...(7)$$

$$HN_3HL + HN_3 \rightarrow 2 \ N_3^{\cdot} + IO_3^- \qquad ...(8)$$
fast

$$2 \ N_3^{\cdot} \rightarrow 3 \ N_2 \qquad ...(9)$$

Scheme 1

The rate law derived from Scheme 1 assuming that K_4 is small, an assumption warranted by the adherence of the rate law to first order dependence on $[IO_4^-]_{total}$ is

$$\text{Rate} = \{1 + 1/K_3[H^+]\}^{-1} \ K_4 \ k_1 \ ]HN_3]^2 \ [IO_4^-]_{total} \ ...(10)$$

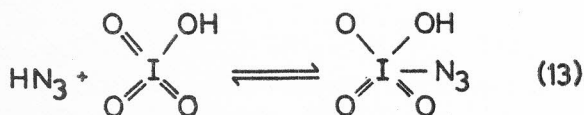Eq. (10) will reduce to the observed rate equation for the limiting conditions $K_5 [H^+] \gg 1$.

$$\text{Rate} = K_4\, k_1\, [HN_3]^2\, [IO_4^-]_{total} \qquad \ldots(11)$$

$$k_{obs} = K_4\, k_1\, [HN_3]^2 \qquad \ldots(12)$$

The proposed mechanism implies that two-electron transfer operates in the reduction of periodate by HN_3 and this transfer of electrons from two molecules of HN_3 to I(VII) precludes the formation of a high energy free radical I(VI). This mechanism also indicates that two-electron transfer is associated with the acid forms, HIO_4 and/or H_5IO_6 in accord with the observation of El-Eziri[10]. Two-electron transfer is commonly proposed for periodate oxidation of organic substrates[11] and iodide[12]. Finally the azide radicals produced disproportionate to give N_2. This reaction is shown to be very fast[13] ($k = 1.3 \times 10^{10}$ dm³ mol⁻¹ s⁻¹) and similar observations were proposed by various authors in the oxidation of N_3^- (ref. 14, 15).

The mechanism involving L^- ($[IO_4^-]_{total}$) with HN_3, could be eliminated as this would involve an inverse dependence of k_{obs} on $[H^+]$ which is not observed in our experimental conditions.

The oxidant species which is involved in the oxidation of HN_3 has not been specified. It is tempting to view HIO_4 as the reactive species because of its smaller size compared to H_5IO_6; it is involved in complex formation with protonated periodate and HN_3 forming a covalent bond (Eq. 13).

$$HN_3 + \begin{array}{c}O\\ \backslash \\ O\end{array}\!\!\!\begin{array}{c}OH\\ I \\ O\end{array} \rightleftharpoons \begin{array}{c}O\\ \backslash \\ O\end{array}\!\!\!\begin{array}{c}OH\\ I-N_3 \\ O\end{array} \qquad (13)$$

Similar observations have also been observed in the periodate oxidation of glycol[16]. In the oxidation of I^- by iodate[17] and bromate[18], in the presence of H^+ also a complex intermediate involving a covalent link was proposed. Therefore it would be logical that this is the complex intermediate which is proposed in Eq. (7).

The effect of Fe^{2+} can be explained by the fact that the reaction between Fe^{2+} and IO_4^- is very fast

$$Fe^{2+} + IO_4^- \xrightarrow[\text{fast}]{k_2} Fe^{3+} + IO_3^- \qquad \ldots(14)$$
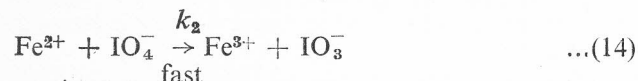
Such an observation has been recorded in the presence of H^+ by El-Eziri and Sulfab[10] in the oxidation of hexaaquoiron(II) and the observed rate was $k_{pseudo} = 1.06$ s⁻¹ at $[Fe^{2+}] = 5.0 \times 10^{-4}$ mol dm⁻³; $[IO_4^-] = 0.25 \times 10^{-2}$ mol dm⁻³; $[H^+] = 0.10$ mol dm⁻³ and $\mu = 1.00$. Under the present experimental conditions k_2 will be ~ 10^4 times greater than k_{obs} and therefore of these two parallel reaction (14) and (15)

$$HN_3 + IO_4^- \xrightarrow[\text{rate determining}]{k_{obs}} \text{product} \qquad \ldots(15)$$
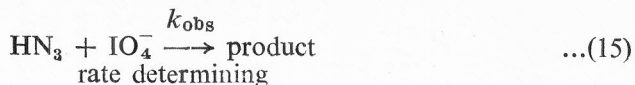
step (14) will not be a rate determining step in the reaction of IO_4^- with HN_3 and Fe^{2+}.

The reaction has been studied at four different temperatures from which the activation parameters for the overall reaction rate were calculated. The values found for $\triangle H^{\neq} = 25.83$ k J mol⁻¹ and $\triangle S^{\neq} = -361.95$ JK⁻¹ mol⁻¹.

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