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Kinetics & Mechanism of Oxidation of Hydroxylamine by Triiodide Ion in Aqueous Acid Medium

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The kinetics of oxidation of hydroxylamine (L) by I_3^- follow a pseudo-first order disappearance in $[I_3^-]$ in aqueous acetic acid-sulphuric acid media. While the pseudo-first order rate constant (k_{obs}) remains constant in $[I_3^-]_0$ range of 4.0×10^{-4} to 20×10^{-4} mol dm^{-3} at $[I_3^-]_0 < 4 \times 10^{-4}$ mol dm^{-3} k_{obs} increases progressively with decrease in $[I_3^-]_0$. The values of k_{obs} exhibit (i) a linear dependence on $[L]_0$ tending to attain limiting values at higher relative $[L]_0$, (ii) a decreasing and complex trend on increasing $[I^-]$ and on increasing $[H^+]$, (iii) a decreasing trend with decreasing dielectric constant of the medium, and (iv) a negligible dependence on ionic strength, on added Cu^{2+} aq and added disodium ethylenediaminetetraacetic acid. Results are interpreted in terms of a mechanism which envisages negligible reactivities of the I_3^- and of the LH^+ species predominant in the medium, an inner-complex mechanism of electron transfer involving the I_2 and L species, and an encounter-controlled reaction between the HOI and the L species.

The literature on the kinetics of oxidation of hydroxylamine by various oxidants is extensive[1-7]. In the hydroxylamine-iodine reaction reported earlier[6], many mechanistic details were lacking. Therefore, it was thought worthwhile to study the kinetics of oxidation of NH_2OH (L) by I_3^- under acidic conditions in detail with a view to getting a clear-cut mechanistic picture.

Materials and Methods

All the reagents used were of GR grade. Hydroxylammonium sulphate was standardised by bromate reaction. The experimental details were reported earlier[8]. Experiments in the presence of added metal ions or disodium EDTA etc, were conducted employing lower concentrations of these.

Stoichiometry and products

The stoichiometric experiments under the condition $[I_3^-]_0 > [L]_0$ showed that one mol of the substrate reacted with 0.9 ± 0.1 mol of the oxidant in accordance with Eq. (1), giving nitrous oxide as the major product.

$$2NH_3OH^+ + 2I_3^- \rightarrow N_2O + H_2O + 6I^- + 6H^+ \quad \ldots(1)$$

N_2O was also shown to be the major oxidation product of NH_3OH^+ in acidic medium by many workers[3,5,7].

Results

The reaction followed a pseudo-first order kinetics in the disappearance of oxidant (represented as $[I_3^-]_0$) for more than four half-lives, in individual runs and in the $[I_3^-]_0$ range of 4×10^{-4} to 20×10^{-4} mol dm^{-3} as seen from the linear plots of log $[I_3^-]_t$ versus t. However at $[I_3^-]_0 < 4 \times 10^{-4}$ mol dm^{-3} k_{obs} increased with decrease in $[I_3^-]_0$ although the pseudo-first order disappearance in oxidant was still observable in individual runs (Table 1).

The k_{obs} values were insensitive towards added acrylonitrile, Cu^{2+} and disodium ethylenediaminetetracetate and towards varying ionic strength (μ) of the medium (supporting electrolyte: $NaClO_4$ and/or $NaHSO_4$). These observations indicate that the

Table 1—Pseudo-first Order Rate Constants for Oxidation of Hydroxylamine by I_3^-

$[L]_0 = 1 \times 10^{-2}$; $[H^+]^a = 1 \times 10^{-2}$; $[I^-] = 1 \times 10^{-2}$ and $\mu = 1$ mol dm^{-3}, HOAc = 10%^{a} and temp. = 35°C)

$10^4[I_3^-]_0$ mol dm^{-3}	10^4 k_{obs} (s^{-1})	10^4 k_{obs} (s^{-1})
1.0	21.0	9.9
1.8	16.0(15)^b	34^c
2.4	14.0(13)^b	2.3^d
3.0	13.0	10^e
4.0	9.9(9.6)^b	9.9^f
4.4	9.6	10^g
5.0	9.9(8.9)^b	9.8^h
8.3	9.4(8.9)^b	9.9^i
10	9.4	10^j
20	9.5(8.5)^b	

(a) H_2SO_4 was used as a source of $[H^+]$; acetic acid-water = 10-90% (v/v).
(b) In the presence of 5×10^{-7} mol dm^{-3} of added Cu^{2+} aq.
(c,d) Aq. HOAc = 5% and 20% respectively.
(e, f) $\mu = 0.05$ and 2.0 mol dm^{-3} (supporting electrolyte: $NaClO_4$/$NaHSO_4$/$KHSO_4$).
(g,h,i) In the presence of 1×10^{-3}, 1×10^{-2}, 1.0 mol dm^{-3} of added KCl respectively.
(j) In the presence of 1×10^{-3} mol dm^{-3} of added acrylonitrile
$[I_3^-]_0$ ≃ Analytical initial concentration of the oxidant.

Table 2—Pseudo-first Order Rate Constants for the Oxidation of Hydroxylamine by I_3^-

($[I_3^-]_0 = 5 \times 10^{-4}$, $[H^+] = 1 \times 10^{-2}$, $[I^-] = 1 \times 10^{-2}$ and $\mu = 1$ mol dm^{-3}, HOAc = 10%, temp. = 35°C)

10^2 $[L]_0$ (mol dm^{-3})	10^4 k_{obs} (s^{-1})
0.05	0.5[a]
0.5	5.0 (5.7)[b]
1.0	9.9(15.0)[c]
2.0	18 (4.9)[d]
8.0	50 (2.5)[e]
10.0	60(0.5)[f]
1.0	11[g](10.0)[h]
1.0	12[i](8.9)[j]
1.0	12[k](8.0)[l]

a) Calculated from the measured second order rate constant under the condition $[L]_0 \approxeq [I_3^-]_0$.

(b,c) At 30° and 40°C respectively; average values of activation parameters are: $\Delta H^{\neq} = 77$ kJ mol^{-1}; $\Delta S^{\neq} = -12.0$ JK^{-1} mol^{-1}; $\log_{10}A = 11.2$.

(d,e,f) In the presence of added $[I^-] = 2 \times 10^{-2}$, 4×10^{-2} and 20.0×10^{-2} mol dm^{-3} respectively.

(g,i,k) In the presence of added [EDTA] = 5×10^{-4}, 10×10^{-4} and 50×10^{-4} mol dm^{-3} respectively.

(h,j,l) In addition to added EDTA as in g, i, k, in the presence of added $[Cu^{2+}\ aq] = 1 \times 10^{-7}$, 5×10^{-7} and 10×10^{-7} mol dm^{-3} respectively.

reaction does not proceed by a free radical mechanism, does involve a neutral species as one of the reactants and there is no metal ion catalysis of the reaction. Under acid conditions the slight retarding effect of added Cu^{2+} aq (Tables 1 and 2) may possibly be traced to the formation of very small quantities of iodides of copper, which being less reactive, retard the reaction slightly. When Na_2EDTA is added to reaction systems containing Cu^{2+}, formation of iodides of copper is prevented and hence slight acceleration in rate (Tables 1 and 2).

Decrease in the dielectric constant of the medium retarded the rate. This suggests that the reaction may be of a dipole-dipole type; a plot of log k_{obs} versus $1/D$ was also linear. A plot of log k_{obs} versus $1/T$ was linear, from which the net activation parameters were calculated (Table 2).

The k_{obs} linearly increased with increase in $[L]_0$ in the lower concentration range (Table 2); however at higher relative $[L]_0$ the increase in k_{obs} with $[L]_0$ was somewhat non-linear as seen from the decrease in $k_{obs}/[L]_0$ values. A plot of $1/k_{obs}$ versus $1/[L]_0$ was linear with a definite intercept on the $1/k_{obs}$ axis.

Added iodide had a linear-inhibitory effect on k_{obs} at $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} (Table 2); however, at lower $[H^+]$ (*p*H 2.75) the inhibitory influence of $[I^-]$ on k_{obs} (Table 3) was such that a plot of k_{obs} $[I^-])^{-1}$ versus $[I^-]$ was linear with significant intercept and slope.

Table 3—Pseudo-first Order Rate Constants for Oxidation of Hydroxylamine by I_3^-

($[I_3^-]_0 = 5 \times 10^{-4}$, $[I^-] = 1 \times 10^{-2}$, $\mu = 1.07$ mol dm^{-3} and $L_0 = 5 \times 10^{-4}$ mol dm^{-3}; Medium H_2SO_4/HSO_4^-, $-CH_3COOH/CH_3COO^-$ and temp. = 35°C)

$10^3[H^+]$[a] mol dm^{-3}	$10^4 k_{obs}$ (s^{-1})[a]	$10^3[H^+]$ mol dm^{-3}	$10^4 k_{obs}$ (s^{-1})
100	1.0	10	0.5
20	5.0	8.91	0.6
10	9.9	4.47	1.5
6	16	2.51	4.0
5	20	1.78	7.0
			(3.0)[b]
			(1.0)[c]
			(0.3)[d]
		1.26	13
		1.00	20
		0.89	26
		0.79	31
		0.71	90

(a) $[L]_0 = 1 \times 10^{-2}$ mol dm^3, HOAc = 10%, H_2SO_4/HSO_4^- media.

(b,c,d) At 2×10^{-2}, 4×10^{-2} and 10×10^{-2} mol dm^{-3} of I^- respectively.

Table 3 presents the retarding effect of $[H^+]$ on k_{obs}. At higher $[H^+]$ region, the k_{obs} versus $1/[H^+]$ plot was linear passing almost through the origin whereas at relatively low $[H^+]$ range (corresponding to *p*H range 2.0 to 3.15) the reactions were relatively fast. The k_{obs} depended on $[H^+]$ at lower $[H^+]$ in a complex manner; the k_{obs} $[H^+])^{-1}$ versus $[H^+]$ plot was linear with significant intercept and slope.

Rate law, mechanism and data treatment

The observed kinetic data can be interpreted in terms of a probable mechanism presented in Scheme 1. (L = NH_2OH, $LH^+ = NH_3OH^+$; the reactivities of other species were considered negligible).

$$LH^+ \rightleftharpoons L + H^+, \quad \underline{K}_a = 10^{-5.8}\ \text{mol dm}^{-3} \quad \text{(ref. 7)}$$

$$I_3^- \rightleftharpoons I_2 + I^-, \quad \underline{K}_2 = 1/782 = 1.28 \times 10^{-3}\ \text{mol dm}^{-3} \quad \text{(ref. 9a)}$$

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^-, \quad \underline{K}_3 = 4.6 \times 10^{-13}\ \text{mol}^2\text{dm}^{-6} \quad \text{(ref. 9a)}$$

$$I_2 + L \xrightarrow{\underline{k}_{2X}} \text{Intermediateproducts} \xrightarrow{\text{fast}} \text{Products}$$

$$HOI + L \xrightarrow{\underline{k}_{3x}} \text{Intermediate products} \xrightarrow{\text{fast}} \text{Products}$$

(L = NH_2OH, $LH^+ = NH_3OH^+$; the reactivities of other species were considered negligible)

Scheme 1

At low $[L]_0$ and $[I_3^-]_0 = 5 \times 10^{-4}$ mol dm^{-3} where a linear dependence of k_{obs} on $[L]_0$ and $[I_3^-]_0$ was observed respectively, the rate law (Eq. 2) derived based on Scheme 1 satisfies the observed kinetics.

$$\frac{-d[I_3^-]/dt}{[I_3^-]} = k_{obs} =$$

$$\frac{(k_{2x}K_aK_2[H^+][I^-] + k_{3x}K_aK_2K_3)[L]_0}{(K_a+[H^+])([H^+][I^-]^2 + K_2[H^+][I^-] + K_2K_3)} \quad \ldots(2)$$

Since $[H^+] \gg K_a$ and that the terms $K_2[H^+][I^-]$ and K_2K_3 in Eq. (2) are negligible in comparison to $[H^+][I^-]^2$ in the denominator under the present experimental conditions, rate law (2) reduces to expression (3).

$$k_{obs} \approx \frac{k_{2x}K_aK_2[L]_0}{[H^+][I^-]} + \frac{k_{3x}K_aK_2K_3[L]_0}{[H^+]^2[I^-]^2} \quad \ldots(3)$$

At higher $[H^+]$ range the effective reacting oxidant species is I_2 so that $k_{obs} \approx (k_{2x}K_aK_2)[L]_0/([H^+][I^-])$. At lower $[H^+]$ region (pH range 2.0 to 3.15), the k_{obs} is composed of a negligible contribution from the most abundant species I_3^-, a major contribution from the molecular I_2 species and a small contribution from HOI. Although the concentration, and the contribution to the overall reactivity of the HOI species are small at lower $[H^+]$ range employed, individually HOI is the most reactive of the three species; therefore, the rate law (Eq. 3) could not be further simplified at lower $[H^+]$ region.

Assuming the enthalpy variation of K_a, K_2 and K_3 (the latter two values shown in the Scheme 1 refer to those at 25°C) to be negligible in the small temperature range, data treatment as discussed somewhere else in the paper, in accordance with Eq. (2) results in the average values of k_{2x} and k_{3x} as 4.6×10^3 dm^3 mol^{-1} s^{-1} and 3.5×10^{11} dm^3 mol^{-1} s^{-1}, respectively, at 35°C in 10% aqueous acetic acid (Table 4). The pseudo-first order rate constants calculated using these values are in agreement with the experimental k_{obs} values.

At $[H^+] = 1 \times 10^{-2}$, $[I^-] = 1 \times 10^{-2}$ and $[I_3^-]_0 = 5 \times 10^{-4}$ mol dm^{-3} where a tendency to a limiting k_{obs} is observed at higher $[L]_0$, the data fits Eq. (5) in accordance with the reaction sequence in Eq. (4).

$$I_2 + L \overset{K'}{\rightleftharpoons} [I_2L] \overset{k'}{\rightarrow} \text{Products} \quad \ldots(4)$$

$$k_{obs} \approx \frac{k'K'K_aK_2[L]_0}{[I^-]([H^+] + K'K_a[L]_0)} \quad \ldots(5)$$

Data treatment furnishes the average values of the pseudo-formation constant (K') and the pseudo-decomposition rate constant (k') of the $[I_2L]$ complex intermediate as 4.6×10^4 dm^3 mol^{-1} and 0.1 s^{-1}, respectively at 35°C in 10% aqueous acetic acid. At lower $[L]_0$ (and high $[H^+]$) where a near linear dependence of k_{obs} on $[L]_0$ is observed, $k'K'$ approaches the computed value of k_{2x} (4.6×10^3 dm^3 mol^{-1} s^{-1}).

Table 4—Average Values of Resolved Constants for Oxidation of Hydroxylamine (L) by I_3^- in Aqueous Acid (H_2SO_4) Medium

(HOAc = 10%; temp. = 35°C; μ = 1 mol dm^3)

Constant	Value	Reaction step/ Effective reactant species
k_{2x} (dm^3 mol^{-1} s^{-1})	4.6×10^3	I_2, NH_2OH
k_{3x} (dm^3 mol^{-1} s^{-1})	3.5×10^{11}	HOI, NH_2OH
K' (dm^3 mol^{-1})	4.6×10^4	$[I_2L]$ complex formation constant
k' (s^{-1})	0.1	$[I_2L]$ complex decomposition rate constant
$k'K'$ (dm^3 mol^{-1} s^{-1})	4.6×10^3	Overall second order rate constant for $I_2 + NH_2OH$ reaction
k'_1(dm^3 mol^{-1} s^{-1})	0.4	Forward rate constant for $[I_2L]$ complex formation
k'_{-1}(s^{-1})	*9×10^{-6}	Reversal rate constant for $[I_2L]$ complex reversal

Although the reaction followed a strict pseudo-first order kinetics in I_3^- disappearance at $[I_3^-]_0$ in the range of 4×10^{-4} to 20×10^{-4} mol dm^{-3}, there was a progressive increase in the k_{obs} value when the $[I_3^-]_0$ was lowered below 4×10^{-4} mol dm^{-3}. This increase does not appear to have any relationship with trace metal ion participation as seen from experiments in the presence of small amounts of added Cu^{2+} aq. On the other hand, at low $[I_3^-]_0$, if a reasonable assumption is made that when $k'[I_2] < k'_{-1}$ (Eqs 4 and 5; $K' = k'_1/k'_{-1}$) i.e. when the $[I_2L]$ complex decomposition constant is not so slow compared to the complex reversibility, Eq. (6) can be derived from which, the pertinent values can be obtained.

$$k_{obs} = \frac{k'k'_1K_2K_a[L]}{k'_1[H^+][I^-] + k'K_2[I_3^-][H^+] + k'_1K_a[L][I^-]} \quad \ldots(6)$$

The average values of k'_1 and k'_{-1} as obtained from the plot of $1/k_{obs}$ versus $[I_3^-]_0$, where 0.4 dm^3 mol^{-1} s^{-1} and 9×10^{-6} s^{-1} respectively under the conditions specified earlier. The above contention appears valid as the value of the $[I_2L]$ complex decomposition constant k' (= 0.1 s^{-1}) is much too larger than the complex reversal constant k'_{-1}.

Iodine (or HOI) is well known to be an effective two-electron acceptor in aqueous solutions as also seen from the present study. This is because if a rate-determining one-electron change were to take place it would have resulted in the formation of atomic iodine and NH_2O radical (viz. two reactive species) for which the activation enthalpy would have been much higher[10] than what is observed here, and which would have resulted in induced polymerisation of added acrylonitrile.

The overall mechanism of product formation in acid medium can be visualised in terms of Scheme 2.

$$I_2(aq) + 2e \rightarrow 2\,I^-(aq)$$
$$\text{or} \quad HOI\,(aq) + H^+ + 2e \rightarrow I^-(aq) + H_2O$$
$$2\,NH_2OH - 2e \rightarrow 2\,NH_2\dot{O} + 2H^+$$
$$2\,NH_2O - 2e \rightarrow H_2N_2O_2 + 2H^+$$
$$H_2N_2O_2 \rightarrow N_2O + H_2O$$
$$\text{or} \quad HON + NH_2OH \rightarrow N_2 + 2\,H_2O$$
$$2\,NH_2O \rightarrow N_2 + 2\,H_2O$$

Scheme 2

While the stoichiometry ratio, $\Delta[I_2]/\Delta[NH_2OH]$, is $2/2 = 1$ for the formation of N_2O (through the intermediacy of hyponitrous acid, $H_2N_2O_2$), the same ratio should be $1/2 = 0.5$ for the formation of N_2. In the majority of oxidation reactions of NH_2OH in acid medium, N_2O has been obtained predominantly and often almost quantitatively[3,5,7]. Evidences for the intermediacy of $H_2N_2O_2$ have also been presented in a number of instances[3,7]. In our previous work on NH_2OH-Ni(IV)-Cu(II) reaction we made a gas chromatographic analysis of the products and found that when the acidity of the reaction medium is less formation of N_2 is favoured, while in acid solutions N_2O formation is favoured[7]. Hyponitrous acid, $HO-N=N-OH$, which is a dimeric form of reactive nitroxyl HON, easily loses a molecule of water, by internal dehydration, to produce N_2O(NON). This can also be seen from a consideration of reported redox potentials $E_{25} = 0.44$ V and $E_{25} = -0.54$ V for the couples $2\,NH_2OH - 4\,e \rightarrow H_2N_2O_2 + 4\,H^+$ (ref. 9b) and, $I_2(aq) + 2e \rightarrow 2I^-(aq)$ respectively, and $\Delta F^\circ_{25} = 38$ kcal mol^{-1} for the reaction $H_2N_2O_2 \rightarrow N_2O + H_2O$. These data suggest that the formation of N_2O by oxidation of NH_2OH by I_2 is thermodynamically favourable. (On the other hand, the redox potential $E^\circ_{25} = -2.65$ V (see ref. 9b) for the couple, $H_2N_2O_2 + 2H^+ + 2e \rightarrow N_2 + 2H_2O$ suggests a high energy barrier accompanying the formation of N_2 from $H_2N_2O_2$ intermediate, although the two nitrogens in the later are presumably linked). Even though we have not made any detailed analysis on distribution of N_2O, the overwhelming evidence presented in other investigations[3,5,7] lead us to believe that N_2O is the product of oxidation of NH_2OH under the present conditions.

The oxidation of hydroxylamine often exhibits extensive metal ion catalysis via complex formation; the complex may undergo decomposition with intramolecular and concomitant electron transfer prior to product formation step(s). But in the present reactions added Cu^{2+} aq did not have any significant effect on the rate.

The reactivity of the most abundant reducing substrate species LH^+ was negligible in comparison to that of the less abundant unprotonated L species, since the k_{obs} versus $1/[H^+]$ plot was linear passing almost through the origin. Similarly while the abundance of the oxidising iodine species decreased in the order: $I_3^- \gg I_2 \gg IOH$, the individual reactivity order increased in a reverse pattern: $I_3^- \ll I_2 \ll HOI$.

The reactivities of the two important oxidant species HOI and I_2 might approximately be in consonance with their redox potentials (e.g., $k_{3x} \gg k_{2x}$), but the lack of reactivity of the most abundant I_3^- species is not explicable on the basis of redox potential considerations (viz. both I_2 and I_3^- have the same redox potentials in aqueous solutions[9a]; $E^\circ_{HOI/I} = -0.91$ V, $E^\circ_{I_3^-/I^-} = -0.54$ V, $E^\circ_{I_2/I^-} = -0.54$ V). The latter can, however, be explained if it is assumed that the oxidant is involved in a complexation reaction with the substrate prior to the rate-determining step; the oxidant I_3^- species, in which iodine is strongly bonded with I^-, will not most likely be available for such a process. This has been evidenced in the oxidation of hydrazine using I_3^- both from kinetic and spectral measurements[8].

The mechanisms and rate laws which satisfactorily explain the kinetic data, lead us to conclude that the oxidation of hydroxylamine by I_3^-, resulting in the formation of N_2O and I^-(aq), proceeds by an inner-complex mechanism of electron-transfer(s) with a pre-equilibrium 1:1 σ-CT interaction involving I_2 and L species. Further the reaction of the HOI and L species approaches the encounter-rate limit, and the reactivities of the predominant species I_3^- and of LH^+ are negligible under the conditions of the present work.

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