Kinetics and Mechanism of Oxidation of Hydrazine by Tri-iodide Ion in Aqueous Acidic Media

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The kinetics of oxidation of hydrazine (L) by I_3^- follows a pseudo-first-order rate law in aqueous acetic acid–sulphuric acid media in the range $[H^+]$ 2.0—1.58 × 10^{-3} mol dm^{-3}. The pseudo-first-order rate constants ($k_{obs.}$) exhibit: (1) at $[H^+]$ = 0.9 mol dm^{-3} a linear dependence on $[L]_0$ at low $[L]_0$, with a tendency to a limiting value at high relative $[L]_0$; (2) a decreasing and complex trend in $[I^-]$ and in $[H^+]$; (3) a decreasing trend with decreasing dielectric constant of the medium; and (4) negligible dependences on the ionic strength of the medium, on added Cu^{2+}(aq), and on added ethylenediaminetetra-acetate. The results are interpreted in terms of a mechanism which envisages (*a*) negligible reactivities of I_3^- and of HL^+ predominant in the medium, (*b*) an inner-complex mechanism of electron transfer (*i.e.* a 1 : 1 σ-charge-transfer co-ordination prior to the electron transfer) involving I_2 and L, and (*c*) an encounter reaction between IOH and L. Mechanistic ambiguities of some earlier reports of the same reaction are explained.

Although the oxidation of hydrazine by iodine has received much attention,[1-10] several mechanistic points of the reaction remain unclear. For example, two recent reports dealing with the kinetics of iodine oxidation of benzoylhydrazines[9] and of hydrazine[10] in aqueous acidic media suggest that the reactive species are hydrazine and hypoiodous acid (and also the tri-iodide ion in the case of the benzoyl derivative), without any quantitative evidence as to the relative reactivities of these species. Moreover, no reason has been given to explain why the unprotonated hydrazine species should be reactive only under conditions where the substrates essentially exist as the protonated species.

Here we report the kinetics of oxidation of hydrazine (L) using I_3^- in aqueous sulphuric acid–acetic acid mixtures in order to clarify some of the mechanistic implications.

Experimental

Guaranteed grade reagents were used. The concentration of the substrate (hydrazinium sulphate) was determined by bromatometric titrations in a strongly acidic medium; the oxidant (referred to as I_3^- and prepared using I_2 and I^-) was standardized by iodimetric titrations.[11] The $[H^+]$ was calculated by titration with a standard alkali solution or from the pH (±0.01 units) of the reaction solution recorded by an Elico LC-II digital pH meter, after applying corrections for the ionic strength effect.[12a]

The kinetics was studied by mixing equal volumes of the oxidant solution (I_3^-) and the substrate solution and by following the rate of disappearance of the oxidant by usual methods. While all the runs employing $[I_3^-]_0$ *ca.* 5 × 10^{-4} mol dm^{-3} were followed both spectrophotometrically (on a Pye Unicam SP 1800 instrument) at 460 nm [$\varepsilon(I_3^-)$ = 975 dm^3 mol^{-1} cm^{-1} [12b]] and iodimetrically, those employing other $[I_3^-]_0$ were followed iodimetrically; the agreement between results obtained by both methods was satisfactory. The pseudo-first-order rate constants ($k_{obs.}$) were reproducible to ±5%.

In experiments employing $[I_3^-]_0 \geqslant [L]_0$ ($[I_3^-]_0$ = 5 × 10^{-3}—20 × 10^{-3}, $[L]_0$ = 1 × 10^{-3}—3 × 10^{-3}, $[H^+]$ = 0.9 mol dm^{-3}) it was found that 1 mol of the substrate reacted with 2.0 ± 0.1 mol of the oxidant [equation (1)]. Nitrogen was

$$N_2H_5^+ + 2I_3^- \longrightarrow N_2 + 6I^- + 5H^+ \qquad (1)$$

qualitatively identified. Tests for ammonia[13] by Nessler's reagent gave negative results. Nitrogen was also obtained earlier[8,10] as the product of oxidation of hydrazine by this oxidant.

Table 1. Pseudo-first-order rate constants[a] for the oxidation of hydrazine by I_3^- at various $[I_3^-]_0$ and $[L]_0$ = 1 × 10^{-2}, $[H^+]$ = 0.9, $[I^-]$ = 1 × 10^{-2}, I = 1.0 mol dm^{-3}, and 35 °C

$10^4[I_3^-]_0$/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}	$10^4[I_3^-]$/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}
1.0	3.5	5	3.4[b]
2.6	3.3		3.5[c]
5.0	3.5		3.6[d]
5.3	3.5		3.5[e]
8.2	3.6		3.4[f]
13	3.4		3.6[g]
16	3.5		5.0[h]
20	3.6		1.8[i]
5	3.1[l]		1.5[j]
5	3.2[m]		0.9[k]

[a] In acetic acid–water (10:90 v/v). [b,c] In the presence of 1 × 10^{-7} and 1 × 10^{-6} mol dm^{-3} of Cu^{2+}(aq) respectively. [d,e,f] At I = 0.92, 1.5, and 2.0 mol dm^{-3} (using $NaHSO_4$ or $NaClO_4$). [g] At I = 2.0 mol dm^{-3} ($KHSO_4$ as supporting electrolyte). [h,i,j,k] In 5, 15, 20, and 30% acetic acid (aqueous). [l,m] In the presence of 1 × 10^{-3} and 5 × 10^{-3} mol dm^{-3} edta (the disodium salt was used).

Results

The kinetics of disappearance of I_3^- followed perfect pseudo-first-order behaviour for more than four half-lives in individual runs and in the range $[I_3^-]_0$ = 1 × 10^{-4}—20 × 10^{-4} mol dm^{-3} (Table 1). Earlier workers reported[10] rate decreases with increasing oxidant concentration; this was explained unconvincingly by higher concentrations of I_3^- formed at the expense of active oxygen. Our repeated experiments gave reproducible and constant $k_{obs.}$ in the oxidant concentration range employed.

The $k_{obs.}$ values were found to be practically insensitive to the presence of added ethylenediaminetetra-acetate (edta) or Cu^{2+}(aq) as well as to the ionic strength of the medium (maintained by a supporting electrolyte $NaClO_4$, $NaHSO_4$, or $KHSO_4$). Increasing proportions of acetic acid (*i.e.* decreasing

Table 2. Pseudo-first-order rate constants for the oxidation of hydrazine by I_3^- at various $[L]_o$ and $[I_3^-]_o = 5 \times 10^{-4}$, $I = 1.0$ mol dm^{-3}, 10% acetic acid, and 35 °C

$10^3[L]_o$/mol dm^{-3}	$10^4 k_{obs.}$^{a}/s^{-1}	$10 k_{obs.} [L]_o^{-1}$^{a}/dm^3 mol^{-1}s^{-1}	$10^4 k_{obs.}$^{b}/s^{-1}	$10^4 k_{obs.} [L]_o^{-1}$^{b}/dm^3 mol^{-1}s^{-1}
0.5	0.2	0.40	0.8	1.6
1.0	0.4	0.40		
2.0	0.8	0.40	3.0	1.5
2.5	1.0	0.40		
5.0	1.8	0.36		
10	3.5	0.35	15	1.5
15	4.9	0.33		
20	6.2	0.31	29	1.45
30	8.9	0.30		
50	12	0.24	75	1.5

[a] At $[H^+] = 0.9$, $[I^-] = 1 \times 10^{-2}$ mol dm^{-3}. [b] At $[H^+] = 4 \times 10^{-3}$ (pH 2.4), $[I^-] = 0.4$ mol dm^{-3}.

Table 3. Pseudo-first-order rate constants for the oxidation of hydrazine by I_3^- at various $[I^-]$ and $[I^-]_o = 5 \times 10^{-4}$, $I = 1.0$ mol dm^{-3}, 10% acetic acid, and 35 °C

	$10^4 k_{obs.}$/s^{-1}	
$10^2[I^-]$/mol dm^{-3}	*a*	*b*
0.2	18	500
1.0	3.5	100
2.0	1.8	48
4.0	0.9	23
10	0.4	8.3
20	0.2	3.5
40	0.1	1.3

[a] At $[H^+] = 0.9$, $[L]_o = 1 \times 10^{-2}$ mol dm^{-3}. [b] Calculated using (second-order rate constant) × $[L]_o$, assuming a linear dependence of $k_{obs.}$ at low $[L]_o$; the second-order rate constant was calculated from the usual expression. At $[H^+] = 2 \times 10^{-3}$ (pH 2.7), $[L]_o = 5 \times 10^{-4}$ mol dm^{-3}.

Table 4. Pseudo-first-order rate constants for the oxidation of hydrazine by I_3^- at various $[H^+]$ and $[I_3^-]_o = 5 \times 10^{-4}$, $[I^-] = 1 \times 10^{-2}$, $I = 1.0$ mol dm^{-3}, 10% acetic acid, and 35 °C

$[H^+]$/mol dm^{-3}	$10^4 k_{obs.}$^{a}/s^{-1}	pH	$10^3[H^+]$/mol dm^{-3}	$10^4 k_{obs.}$^{b}/s^{-1}
2.0	1.6	1.60	25	6
1.3	2.5	2.35	4.47	40
0.9	3.5	2.60	2.51	72
0.7	4.8	2.68	2.09	87
0.67	5.1	2.70	2.0	100
0.45	7.5	2.80	1.58	117
0.2	17			

[a] At $[L]_o = 1 \times 10^{-2}$ mol dm^{-3}. [b] At $[L]_o = 5 \times 10^{-4}$ mol dm^{-3}; $k_{obs.}$ calculated from the measured second-order rate constants; pH (corrected) (±0.01 unit); buffer H_2SO_4–HSO_4^- + $MeCO_2H$–$MeCO_2^-$.

Table 5. Pseudo-first-order rate constants for the oxidation of hydrazine by I_3^- at various temperatures and $[I_3^-]_o = 5 \times 10^{-4}$, $I = 1.0$ mol dm^{-3}, and 10% acetic acid

	θ$_c$/°C					
$10^4 k_{obs.}$/s^{-1}	30	35	40	45	Av. Δ*H*/kJ mol^{-1}	Av. Δ*S*/J K^{-1} mol^{-1}
a	1.7	3.5	4.6	7.1	74^c	−71^c
b	0.5	0.8	2.0	3.2	93	−9

[a] At $[H^+] = 0.9$, $[I^-] = 1 \times 10^{-2}$, and $[L]_o = 1 \times 10^{-2}$ mol dm^{-3}. [b] At $[H^+] = 4 \times 10^{-3}$ (pH 2.4), $[I^-] = 0.4$, and $[L]_o = 5 \times 10^{-4}$ mol dm^{-3}. [c] Activation parameters pertaining to the I_2 + L reaction (the k_2 step).

dielectric constant *D* of the medium) at constant $[H^+]$ had a retarding effect on $k_{obs.}$ (Table 1); a plot of log $k_{obs.}$ *vs.* $1/D$ was linear suggesting that the reaction might be of a dipole–dipole type.

At $[H^+] = 0.9$ mol dm^{-3}, $k_{obs.}$ linearly increased with $[L]_o$ for low $[L]_o$, with a tendency to a limiting value at higher relative $[L]_o$, as seen by the departure of $k_{obs.}/[L]_o$ values from the near-constant values at low $[L]_o$; a plot of $(k_{obs.})^{-1}$ *vs.* $([L]_o)^{-1}$ was linear with a significant intercept on the $(k_{obs.})^{-1}$ axis. However, at relatively lower $[H^+]$ (4×10^{-3} mol dm^{-3}, pH 2.4), the $k_{obs.}/[L]_o$ values were almost constant showing a linear dependence of $k_{obs.}$ on $[L]_o$ in the same concentration range (Table 2). Still higher $[L]_o$ could not be employed because of solubility problems.

Iodide had an inhibitory influence on $k_{obs.}$ at $[H^+] = 0.9$ and at 2×10^{-3} mol dm^{-3} (pH 2.7) as shown in Table 3. While at the former $[H^+]$, the $k_{obs.}$ *vs.* $1/[I^-]$ plot was linear passing almost through the origin, at the latter $[H^+]$ the dependence was complex and the $(k_{obs.}[I^-])^{-1}$ *vs.* $[I^-]$ plot was linear with a significant intercept and slope.

Table 4 shows the retarding effect of $[H^+]$ on $k_{obs.}$. At higher $[H^+]$ (2.0—0.2 mol dm^{-3}), the $k_{obs.}$ *vs.* $1/[H^+]$ plot was linear passing almost through the origin. At $[H^+] = 25 \times 10^{-3}$—$1.58 \times 10^{-3}$ mol dm^{-3} the reactions were relatively rapid; the runs were conducted at low $[L]_o$ ($= [I_3^-]_o = 5 \times 10^{-4}$ mol dm^{-3}) and second-order rate constants were calculated from the usual expression and then converted into first-order rate constants by multiplication with $[L]_o$. The $k_{obs.}$ values thus obtained showed a complex dependence on $[H^+]$ at lower $[H^+]$; the $(k_{obs.}[H^+])^{-1}$ *vs.* $[H^+]$ plot was linear with a significant intercept and slope.

The temperature dependence of $k_{obs.}$ is shown in Table 5.

Rate Law and Mechanism.—The observed kinetic data can be interpreted in terms of a probable mechanism (Scheme 1). At low $[L]_o$, where a linear dependence of $k_{obs.}$ on $[L]_o$ was observed, the rate law (2) derived from Scheme 1 satisfies the observed kinetics, assuming that K_1 in the denominator is

$$HL^+ \rightleftharpoons L + H^+,\ K_1 = 10^{-8.1}\ \text{mol dm}^{-3}\ \text{at } 35\ ^\circ\text{C}^{13}$$

$$I_3^- \rightleftharpoons I_2 + I^-,\ K_2 = 1/782 = 1.28 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{at } 25\ ^\circ\text{C}^{14a}$$

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^-,\ K_3 = 4.6 \times 10^{-13}\ \text{mol}^2\ \text{dm}^{-6}\ \text{at } 25\ ^\circ\text{C}^{14a}$$

$$I_2 + L \xrightarrow{k_2} \text{Intermediate products}$$

$$HOI + L \xrightarrow{k_3} \text{Intermediate products}$$

Scheme 1. L = H_2NNH_2; the reactivities of other species are considered to be negligible

$$\frac{-d[I_3^-]/dt}{[I_3^-]} = k_{obs.} = \frac{(k_2K_1K_2[H^+][I^-] + k_3K_1K_2K_3)[L]}{(K_1 + [H^+])([H^+][I^-]^2 + K_2[H^+][I^-] + K_2K_3)} \approx \frac{k_2K_1K_2[L]_o}{[H^+][I^-]} + \frac{k_3K_1K_2K_3[L]_o}{[H^+]^2[I^-]^2} \quad (2)$$

negligible in comparison with $[H^+]$ ($[H^+] \gg K_1$) and that the terms $K_2[H^+][I^-]$ and K_2K_3 are negligible in comparison with $[H^+][I^-]^2$ under the present experimental conditions. In the range $[H^+]$ 2.0—0.2 mol dm^{-3}, the effective oxidant species is I_2 so that $k_{obs.} \approx (k_2K_1K_2)[L]_o/[H^+][I^-]$. At lower $[H^+]$, $k_{obs.}$ is composed of a negligible contribution from the most abundant species I_3^-, a major contribution from the I_2 species of some abundance, and a small contribution from the minor species HOI. Although the concentration and the contribution to overall reactivity of the HOI species are small at low $[H^+]$, HOI is the most reactive of the three species; therefore, the rate law (2) could not be further simplified at lower $[H^+]$.

Assuming the enthalpy variation of K_1, K_2, and K_3 to be negligible over the small temperature range, data treatment resulted in average values of k_2 and k_3 of 3.5×10^7 and 7.9×10^{10} dm^3 mol^{-1} s^{-1} respectively at 35 °C. The pseudo-first-order rate constants calculated using these values were in agreement with the experimental $k_{obs.}$ values.

At $[H^+] = 0.9$ and $[I^-] = 1 \times 10^{-2}$ mol dm^{-3} where a tendency to a limiting $k_{obs.}$ was observed at higher $[L]_o$, the data could be fitted by equation (4) in accordance with the sequence (3). Data treatment furnished average values of the pseudo-formation constant (K') and the pseudo-decomposition rate constant (k') of the $[I_2{\cdot}L]$ complex intermediate as 2.3×10^9 dm^3 mol^{-1} and 1.5×10^{-2} s^{-1} at 35 °C, respectively. At lower $[L]_o$ (and high $[H^+]$) where a near-linear dependence of $k_{obs.}$ on $[L]_o$ was observed, $k'K'$ approached the computed k_2 value (3.5×10^7 dm^3 mol^{-1} s^{-1}).

$$I_2 + L \xrightarrow{K'} [I_2{\cdot}L] \xrightarrow{k'} \text{Products} \qquad (3)$$

$$k_{obs.} \approx \frac{k'K'K_1K_2[L]_o}{[I^-]([H^+] + K'K_1[L]_o)} \qquad (4)$$

The earlier kinetic data[10] can be treated in terms of the $I_2 + L$ reaction (the k_2 step), but not as shown.

Discussion

It is well established that hydrazine transfers two electrons to an oxidant to form a diazene intermediate which on further very rapid two-electron loss gives nitrogen;[15] the overall stoicheiometry for this process should be $e/[N_2H_4] = 4$. On the other hand, the loss of one electron (hydrogen atom) from hydrazine results in a hydrazyl radical,[16] two of which give nitrogen and ammonia as products with a stoicheiometry of $e/[N_2H_4] = 1$ (Scheme 2).

$$N_2H_4 - 2e \longrightarrow N_2H_2 + 2H^+$$

$$N_2H_2 - 2e \longrightarrow N_2 + 2H^+$$

$$N_2H_4 - e \longrightarrow N_2H_4^{\cdot +} \longrightarrow N_2H_3 + H^+$$

$$2N_2H_3 \longrightarrow 2NH_3 + N_2$$

Scheme 2.

Inasmuch as the oxidizing iodine species are essentially two-electron acceptors, the stoicheiometry and products of the reaction indicate that a two-electron transfer might have taken place in the rate-determining step. Furthermore, had there been a discernible one-electron loss, two reactive species (iodine radical and hydrazyl radical) would have been produced in the rate-limiting step for which the activation enthalpy would have been much higher[17] than what has been observed here.

The kinetic observations have most plausibly been explained in terms of the Schemes and the rate laws, but there are several mechanistic implications.

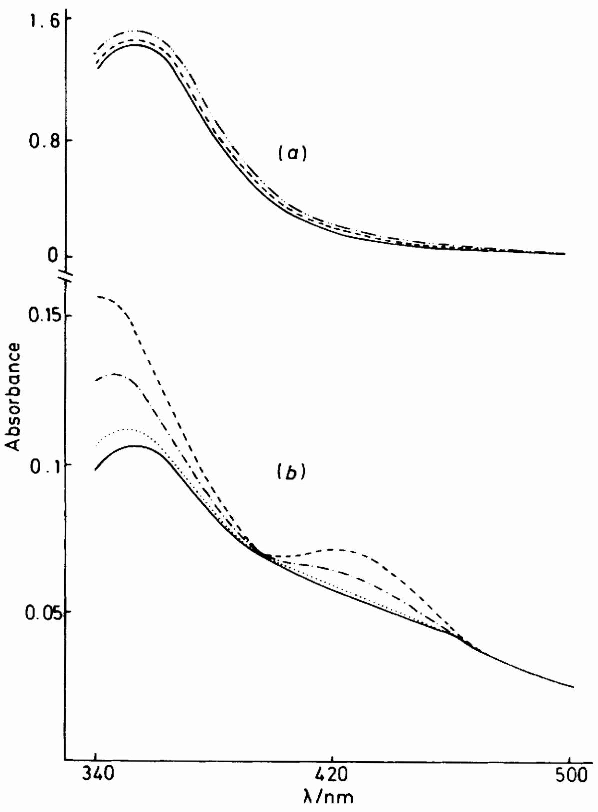

Figure. Spectral scans of reaction mixtures containing hydrazine and iodine. ($[H^+] = 1$ mol dm^{-3}, 10% aqueous acetic acid, 35 °C): (*a*) $[I^-] = 0.2$, $[I_2]_o = [I_3^-] = 5.5 \times 10^{-5}$; $10^5[L]_o = 0$ (——), 5 (– – –), and 15 mol dm^{-3} (–·–·–). (*b*) $[I^-] = 1 \times 10^{-4}$, $[I_3^-]_o = 5.5 \times 10^{-5}$, $[I_3^-] = 0.4 \times 10^{-5}$, $[I_2] = 5.1 \times 10^{-5}$, $10^5[L]_o = 0$ (——), 1 (· · · ·), 2.5 (–·–·–), and 5 mol dm^{-3} (– – –)

(1) The estimated redox potentials (pertaining to two-electron changes) for various couples involving the reacting species are: $N_2H_5^+$–N_2 = 0.23,[14b] I_3^-–I^- = −0.54, I_2–I^- = −0.54, and IOH–I^- = −0.91 V.[14a] While the concentration of the oxidizing iodine species decreases in the order $I_3^- \gg I_2 \gg$ IOH, the reactivity order increases in the opposite direction, I_3^- being of negligible reactivity as seen from the linear plot of $k_{obs.}$ *vs.* $1/[I^-]$ passing through the origin. The reactivities of IOH and I_2 ($k_3/k_2 \approx 2 \times 10^3$) might be approximately in accord with their redox potentials, but the lack of reactivity of the I_3^- species (*vis-à-vis* the reactivity of the I_2) is not explicable on the basis of redox potential considerations. The lack of reactivity of I_3^- can, however, be explained if the oxidant is thought of being involved in a complexation process with the substrate prior to the rate-determining step; the species I_3^-, in which iodine is strongly bonded with I^-, will probably not be available for such a process.

(2) It is well known that iodine possesses significant σ-acceptor properties because of the availability of a more diffuse σ_u^* orbital (compared to the bonding σ_g orbital) and thus forms charge-transfer (c.t.) complexes with a number of ligands by σ donation from the latter to the σ_u^* orbital of the former.[18] For example, with tetramethylhydrazine iodine forms an 'outer complex' (with little c.t.) which, in a polar solvent, becomes an 'inner complex' (with significant c.t.); the transformation of the former to the latter, which weakens the I–I bond, eventually results in a complete electron transfer and dissociation.[19a] The facility with which such processes occur depends a great deal on the nature of the constituents involved in the donor–acceptor

interaction and on the medium. While for the [$I_2 \cdot N_2Me_4$] complex there is complete c.t. (*i.e.* formation of an 'inner complex'),[19a] for the $I_2 \cdot I^-$ interaction the complex is of the 'outer' type without appreciable c.t.[18b]

Spectral evidence (in the visible region) on the c.t. interaction between iodine and hydrazine has also been qualitatively obtained under the conditions of the present study. While the original c.t. band of I_3^- at 353 nm [Figure (*a*)] did not change in the presence of hydrazine in an acidic medium (there was a small increase in absorbance in the presence of hydrazine), the bands at 353 and 460 nm (both due to the brown colour of iodine and the latter appearing as a shoulder) were considerably altered both in intensity and position [Figure (*b*)]. The spectra of solutions containing different $[L]_o$ and fixed $[I_2]_o$ ($[I_2]$ = *ca.* 93%, $[I_3^-]$ = *ca.* 7%) showed that there was a common wavelength (392 ± 2 nm) at which all the spectra had the same absorbance (but without intersection) and that both the original bands of I_2 at 353 and 460 nm became more intense and appeared to shift towards higher energy in the presence of $[L]_o$; in the range 480—540 nm, however, the absorbances were very small and showed no further spectral change. An attempt to calculate, using a Benesi–Hildebrand type formula,[19b] the equilibrium constant (K') and ε of the $I_2 \cdot L$ complex on the basis of observed spectral changes was not successful as the absorbance changes were small and the interference from the I_3^- absorbance could not be avoided under the experimental conditions employed. (The solutions of hydrazine, in the absence of the oxidant, were almost transparent in the range 340—540 nm; the oxidation of hydrazine under the conditions employed was negligible during the spectral scans.)

(3) The σ-c.t. interaction will naturally be more facile for a more nucleophilic donor as seen from a qualitative comparison of the magnitudes of the formation constants of 1:1 σ-c.t. complexes of I_2 with a number of nucleophiles;[18a] that is probably why the unprotonated L is more reactive than HL^+ although the abundance of the latter is almost 100% under the present conditions. It has also been shown earlier for the reaction system containing I_3^- and HCN ($pK_a = 9.1$) in the range pH 3.30—4.96 that the effective substrate species is CN^- and that the formation constant of I_2CN^- is $> 10^9$ dm^3 mol^{-1} at 25 °C (as the forward reaction constant $k_{I_2\text{-}CN^-} = 3 \times 10^9$ dm^3 mol^{-1} s^{-1} and the reverse rate constant is negligible).[20] The formation constant involving I_2 and N_2H_4 (pK_a of $N_2H_5^+ = 8.1$) is 2.3×10^9 dm^3 mol^{-1} and is quite compatible with the above argument.

Thus the oxidation of hydrazine using I_3^- most probably proceeds essentially by an inner-complex electron-transfer mechanism with a pre-equilibrium 1:1 σ-c.t. interaction involving I_2 and L, the reaction of HOI and L most probably approaches the encounter rate, and the reactivities of the predominant species I_3^- and of HL^+ are negligible under the present conditions.

Acknowledgements

One of us (N. K. R.) is grateful to Khallikote College and Berhampur University, Berhampur for permission and facilities to carry out this project.

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Received 23*rd May* 1985; *Paper* 5/863