Stoichiometry, Kinetics and Mechanism of the Oxidation of Hydroxyammonium Ion with Iron(III) in Acetate Buffers

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Iron(III) reacts with hydroxyammonium ion in acetate buffers and in diffuse light according to equation (i), where Fe^{III} represents the predominant form $[Fe_3O(O_2CMe)_6]^+$ and the rate law at 35 °C is (ii); k_1 and k_1k_3/k_2 were found to be $(4.6 \pm 0.2) \times 10^{-2}$ dm³ mol⁻¹ s⁻¹ and 0.31 ± 0.01 dm³ mol⁻¹ s⁻¹ respectively at 35 °C.

$$Fe^{III} + NH_3OH^+ \longrightarrow Fe^{II} + \tfrac{1}{2}N_2 + H_2O + 2H^+ \qquad (i)$$

$$-d[Fe^{III}]/dt = k_1k_3[Fe^{III}][NH_3OH^+][H^+]/(k_2[Fe^{II}] + k_3[H^+]) \qquad (ii)$$

The E_a for the k_1 step is 103 kJ mol⁻¹, but k_1k_3/k_2 varies little with temperature. The rate law has been verified by reducing it to simpler forms by working at different concentrations of Fe^{II} and H^+, at 60 °C, and 6 °C, and in the presence of methyl methacrylate. At 60 °C $k_2 \gg k_3$ and at 6 °C $k_2 \ll k_3$. The dark reaction stoichiometry is not fixed and the gaseous products are N_2 and N_2O.

The title reaction has long been known as a method[1] for the indirect determination of hydroxylamine at the boiling temperature according to equation (1), but several workers[2] have expressed doubt on the accuracy of the results. Kinetic studies[3–5] of the reaction in acid perchlorate and acid sulphate solutions have been made, but the reaction appeared to be complex from the viewpoint of stoichiometry[5] and kinetics.[4] There is yet no clear picture for the mechanism. There are conflicting reports[3–5] about the inhibition by iron(II) and it is further reported that different oxidation products are obtained in reactions carried out in the dark and light. A full reinvestigation therefore seemed worthwhile. A unique feature[3,5] of this reaction is its large temperature coefficient, and this fact has been used in verifying the mechanism.

$$4\,Fe^{III} + 2\,NH_3OH^+ \longrightarrow 4\,Fe^{II} + 6\,H^+ + N_2O + H_2O \qquad (1)$$

Experimental

Materials.—Loba hydroxyammonium sulphate and Fluka iron(III) perchlorate were employed as reactants. All other chemicals were either BDH AnalaR or E. Merck GR quality. Hydroxyammonium perchlorate was prepared by mixing equivalent amounts of hydroxyammonium sulphate and barium perchlorate and filtering off barium sulphate. Barium perchlorate was prepared from barium carbonate and perchloric acid. The hydroxylamine salt solution was standardised by the bromate method.[6] The concentration of iron(III) in solution was determined by adding a known excess (about four times) of sodium thiosulphate, allowing time (1 min) for completion of reaction, and back titrating the excess of thiosulphate with a standard iodine solution. This is a modification of the method given by Kolthoff and Tomicek.[7] Iron(III) perchlorate was always freshly prepared in order to avoid dimerisation[8] and to obtain reproducible results.[9]

The results were identical in the three types of light used, diffuse sunlight, light from a tungsten lamp and light from a mercury tube. Thus there was no necessity to standardise the light conditions and all reactions were carried out in diffuse sunlight. Some of the reactions were carried out in bottles wrapped in black paper to create conditions of darkness.

The reaction mixture on the addition of methyl methacrylate (mma) yields a white precipitate after some time, indicating polymerisation. Iron(III) and hydroxylamine separately do not respond to this test. A few kinetic runs were made in the presence of mma.

All solutions were prepared in doubly distilled water, the second distillation being from permanganate. All glass vessels were of Corning make. The ionic strength was adjusted to 1.0 mol dm⁻³ with $NaClO_4$.

Kinetic Procedure.—The reaction was initiated by adding thermally equilibrated iron(III) perchlorate solution to a flask containing known quantities of hydroxyammonium perchlorate, acetate buffer, and $NaClO_4$ at 35 ± 0.1 °C in a thermostat bath. The reaction was followed by removing aliquots (5 cm³) from the reaction mixture and determining iron(III) by the method described. The solution was acidified to 1.0 mol dm⁻³ with H_2SO_4 before titration to check any reaction[10] between hydroxylamine and iodine.

The data were processed for initial rates (v_0) by the plane-mirror method.[11] Pseudo-first-order plots were also made when hydroxyammonium ion was in excess and the pseudo-first-order rate constants were similar to those from the initial rates. Under pseudo-first-order conditions the kinetics was followed for three half-lives, whereas for initial rates 50% completion of reaction was followed. Since iron(II) inhibits the reaction, determination of initial rates was preferred. The results were reproducible to ±6%.

UV Spectrophotometric Measurements of the Reaction Mixture.—The absorption spectra of reaction mixtures containing different concentrations of reactants were recorded on a Cecil CE 599 automatic scanning spectrophotometer. The kinetics of decay of intermediates was followed by measuring the absorbance at 290 and 341 nm for the light-sensitive and dark reactions respectively.

Table 1 Stoichiometry and gaseous products of reaction between iron(III) and hydroxylamine at 35 °C, volume of reaction mixture 500 cm^3

10^3 [Fe^{III}]$_0$	10^3 [NH_3OH^+]$_0$	10^3 [Fe^{III}]$_t$	10^3 [NH_3OH^+]$_t$	pH or acid condition	Stoichiometry *	Volume of gas (cm^3) over water	Volume of gas (cm^3) over water saturated with N_2O
mol dm^{-3}							
In the light							
1.50	12.0	—	10.6	4.85	1.07	8.7 (8.96)	8.2 (8.96)
3.80	30.0	—	26.1	4.95	0.97	—	—
3.80	20.0	—	16.2	4.05	1.00	21 (21.3)	22 (21.3)
3.80	45.0	—	41.1	1.0 mol dm^{-3} $HClO_4$	0.97	—	—
7.60	30.0	—	22.6	1.0 mol dm^{-3} $HClO_4$	1.02	40 (41.4)	40 (41.4)
11.0	1.5	9.5	—	1.0 mol dm^{-3} $HClO_4$	0.97	—	—
16.0	3.0	13.1	—	4.55	0.97	15 (16.8)	16 (16.8)
11.0	3.0	8.0	—	4.55	1.00	—	
In the dark							
20.0	3.0	14.3	—	4.05	1.90	—	—
32.0	6.0	22.0	—	4.05	1.67	—	—
20.0	5.0	12.5	—	4.05	1.50	13 (14)	26 (28)
8.0	1.11	6.0	—	4.05	1.80	—	—
25.0	2.50	21.0	—	3.0 mol dm^{-3} $HClO_4$	1.00	—	—
35.0	7.50	23.8	—	3.0 mol dm^{-3} $HClO_4$	1.50	20 (21)	39 (42)

* [Fe^{III} reacted]/[NH_3OH^+] reacted. Subscripts 0 and t refer to initial and final concentrations. Values in parentheses for the reaction in light are the theoretical volumes. Values in parentheses for the dark reaction are calculated from the found stoichiometry. Stoichiometry 1.67 means that 67% reaction occurs by the N_2O path and 33% by the N_2 path.

Results

Stoichiometry.—Several reaction mixtures containing different concentrations of reactants were kept for 10–12 h. Excess of iron(III) was determined[7] as mentioned above and excess of hydroxyammonium ion was estimated bromometrically.[6] Evolved gases were collected in two ways: (1) over water, and (2) over water saturated with N_2O obtained[12] from concentrated solutions of hydroxyammonium sulphate and sodium nitrite. The former method gave nitrogen and the latter yielded both N_2 and N_2O. Nitric oxide and oxygen were not detected. These results are given in Table 1.

It has been reported[1,2] that 2 mol of iron(III) react with 1 mol of hydroxyammonium salt in acid solutions yielding N_2O as the gaseous products as per equation (1). Butler and Gordon[5] reported that in the dark the reaction is never complete and that some nitrogen-containing products other than N_2O are also formed. The stoichiometry in the oxidation of hydroxyammonium ion by different oxidants is never clean[13–19] and depends on the ratio of the concentrations of the reactants, acidity, and temperature; lately the role of light has also been mentioned.[5] One or more products from amongst NO_3^-, N_2O and N_2 are formed. Nitric oxide gas as product has also been reported in the oxidation with iodine.[10] Nitrogen is the major product in oxidations with excess of iodine,[10] iridium(IV)[20] $[Fe(CN)_6]^{3-}$[21] and vanadium(V).[22]

These results in Table 1 indicate that in the light the stoichiometry $\Delta[Fe^{III}]/\Delta[NH_3OH^+]$ is 1:1 [equation (2)] and the gaseous product is nitrogen, but in the dark the

$$Fe^{III} + NH_3OH^+ \longrightarrow Fe^{II} + \tfrac{1}{2}N_2 + H_2O + 2H^+ \quad (2)$$

stoichiometry is between 1:1 and 2:1 in accordance with what Butler and Gordon[5] found. The gaseous products are N_2 and N_2O in the latter case and hence both reactions (1) and (2) occur in the dark.

Kinetics.—The various rate dependences are in accordance with the rate law (3); [Fe^{III}] was varied in the range

$$\frac{-d[Fe^{III}]}{dt} = v_o = \frac{k_1k_3[Fe^{III}][NH_3OH^+][H^+]}{k_2[Fe^{II}] + k_3[H^+]} \quad (3)$$

(1.84–14.0) × 10^{-3} mol dm^{-3} at fixed [NH_3OH^+] = 5.0 × 10^{-2} mol dm^{-3} yielding a pseudo-first-order rate constant (k_0) of 2.35 × 10^{-3} s^{-1} and second-order rate constant (k_1) of (4.7 ± 0.2) × 10^{-2} dm^3 mol^{-1} s^{-1} at pH 4.05 and 35 °C.

From the variation of [NH_3OH^+] in the range (2–21) × 10^{-2} mol dm^{-3} and fixed [Fe^{III}] = 4.6 × 10^{-3} mol dm^{-3}, the second-order rate constant (k_1) was found to be (4.6 ± 0.4) × 10^{-2} dm^{-3} mol^{-1} s^{-1} under the same conditions.

The results of pH variation at different temperatures and [Fe^{III}] are shown in Table 2. A plot of $(v_o)^{-1}$ *versus* $[H^+]^{-1}$ was linear with non-zero intercept in accordance with equation (3). In the presence of large [Fe^{II}], the results are in accordance with equation (4), which is the reduced form of (3) when

$$-d[Fe^{III}]/dt = k_1k_3[Fe^{III}][NH_3OH^+][H^+]/k_2[Fe^{II}] \quad (4)$$

$k_2[Fe^{II}] \gg k_3[H^+]$. A few reactions carried out in aqueous $HClO_4$ solutions (Table 3) gave results that are in accordance with equations (5) which is the reduced form of (3) when $k_3[H^+]$

$$-d[Fe^{III}]/dt = k_1[Fe^{III}][NH_3OH^+] \quad (5)$$

$\gg k_2[Fe^{II}]$; k_1 was found to be 0.23 dm^3 mol^{-1} s^{-1} at 35 °C in aqueous perchloric acid solutions.

The concentration of Fe^{II} was varied at pH 3.20, 4.15 and 4.50 at 35 °C and the results in the form of a plot of $(v_0)^{-1}$ *versus* [Fe^{II}] are given in Figure 1. The plots are linear with non-zero intercepts in accordance with equation (3).

There was no effect of acetate ions in the range 0.04–0.2 mol dm^{-3} and no effect of ionic strength ($NaNO_3$) in the range 0.1–1.0 mol dm^{-3}.

The description of various plots, intercepts and slopes of straight lines and the values of k_1 and k_1k_3/k_2 are given in Table 4, k_1 was found to be (4.6 ± 0.2) × 10^{-2} dm^3 mol^{-1} s^{-1} at 35 °C and has a large temperature coefficient, but the complex rate constant k_1k_3/k_2 does not vary much with temperature. Thus k_2 also varies much in the same way as k_1 or perhaps with a larger temperature coefficient.

Reactions at 6 *and* 60 °C. Since k_2 appears to have a large temperature coefficient, there seemed to be a possibility of verifying rate law (3) by studying the reaction at temperatures

Table 2 Initial rates (v_0 for the Fe^{III} + NH_3OH^+ reaction at different pH and temperatures in the presence of low and high $[Fe^{II}]$; $[Fe^{III}]$ = 4.8 × 10^{-3}, $[NH_3OH^+]$ = 5.0 × 10^{-2}, and I = 1.0 mol dm^{-3}

(*a*) 45 °C $[Fe^{II}]$ = 2.0 × 10^{-4} mol dm^{-3}

pH	3.30	3.70	4.08	4.35	4.80	4.85	5.18
$10^5 v_0$/mol dm^{-3} s^{-1}	2.9	2.6	2.1	1.8	1.0	0.90	0.48

(*b*) 35 °C $[Fe^{II}]$ = 1.0 × 10^{-4} mol dm^{-3}

pH	3.28	4.02	4.35	4.80	4.85	4.91	5.18
$10^5 v_0$/mol dm^{-3} s^{-1}	1.1	1.0	0.80	0.60	0.55	0.50	0.345

(*c*) 25 °C $[Fe^{II}]$ = 1.0 × 10^{-4} mol dm^{-3}

pH	3.70	4.10	4.35	4.70	4.98
$10^5 v_0$/mol dm^{-3} s^{-1}	0.33	0.30	0.27	0.21	0.15

(*d*) 35 °C $[Fe^{II}]$ = 7.5 × 10^{-3} mol dm^{-3}

pH	3.42	3.72	4.05	4.30
$10^5 v_0$/mol dm^{-3} s^{-1}	0.37	0.18	0.089	0.050

Table 3 Second-order rate constants (k_1) of the Fe^{III} + NH_3OH^+ reaction in aqueous $HClO_4$ solution at 35 °C; $[Fe^{III}]$ = 5.0 × 10^{-3} and $[NH_3OH^+]$ = 5.0 × 10^{-2} mol dm^{-3}

$[HClO_4]$/ mol dm^{-3}	pH	10^4 $[Fe^{II}]$/ mol dm^{-3}	10^5 v_0/ mol dm^{-3} s^{-1}	k_1/dm^3 mol^{-1} s^{-1}
0.01	1.91	—	5.9	0.24
0.01	1.91	5.0	5.6	0.22
0.01	1.91	7.5	6.0	0.24
0.01	1.91	10	5.8	0.23
0.02	1.71	—	5.8	0.23
0.05	1.32	—	5.8	0.23

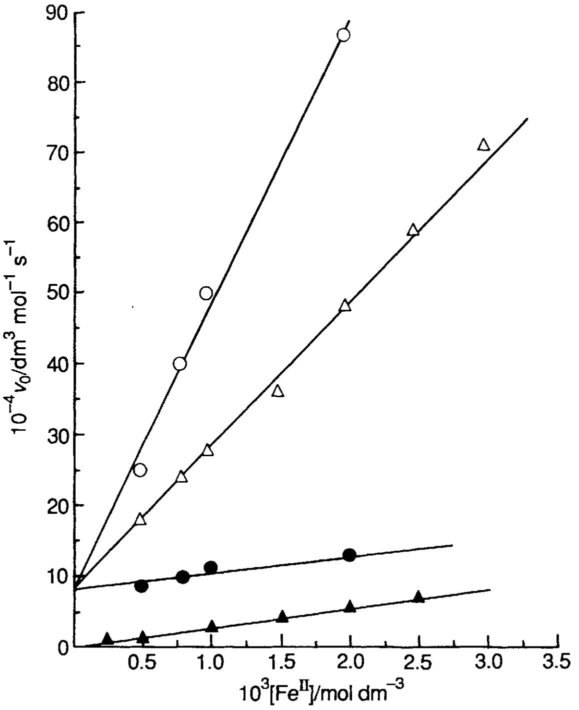


Fig. 1 Plot of v_0^{-1} *vs.* $[Fe^{II}]$ at $[Fe^{III}]$ = 4.8 × 10^{-3} and $[NH_3OH^+]$ = 0.05-pH = 4.5 (○), 4.15 (△) and 3.20 (●) at 35 °C; 4.05 (▲) at 60 °C

away from 35 °C. The results at 6 and 60 °C are shown in Tables 5 and 6. At 35 °C $k_2[Fe^{II}]$ and $k_3[H^+]$ are comparable and since $[Fe^{II}]$ and $[H^+]$ are also comparable $k_2 \approx k_3$ at 35 °C. At 6 °C $k_3 \gg k_2$ and hence the results are in accordance with equation (5) with comparable $[Fe^{II}]$ and $[H^+]$. At 60 °C $k_3 \ll k_2$ and hence the results are in accordance with equation (4) for comparable concentrations of $[Fe^{II}]$ and $[H^+]$.

Reaction in the dark. This reaction has already been studied.[5] We carried out only a few reactions to lend support to our results in the light. The results given in Table 7 seem to be a little more complicated than those in diffuse light. The order in $[Fe^{III}]$ in the absence of Fe^{II} is one, but it decreases and tends to zero in the presence of Fe^{II}. The results of variations of other parameters are similar to those in diffuse light. The second-order rate constant (k_1) in the absence of Fe^{II} is comparable to that obtained in diffuse light. These results were not better than ± 15%. The dark reaction was followed also spectrophotometrically at 341 nm as mentioned later in the spectrophotometric results.

Spectrophotometric Evidence for the Light-sensitive Intermediate.—Two representative spectra after 2.5 and 15 min of mixing of the reactants and with two different sets of concentrations are given in Figs. 2 and 3. Curves (*a*) and (*b*) of Fig. 3 show the spectra of the reaction mixtures ($[Fe^{III}]$ = 4.8 × 10^{-4}, $[NH_3OH^+]$ = 5.0 × 10^{-3}, $[Fe^{II}]$ = 2.0 × 10^{-4} mol dm^{-3}) after 15 min, in diffuse sunlight and the dark respectively. Some intermediate of the dark reaction seems to absorb strongly. The absorbance of the reaction mixture of the dark reaction after 2.5 min [Fig. 2(*a*)] also shows this. The corresponding absorption of the reaction mixture in diffuse sunlight is small and not shown. In order to get an idea of the absorption spectra of reactions carried out in diffuse sunlight, ten times larger concentrations of Fe^{III} and NH_3OH^+ were employed. Fig. 2(*b*) and Fig. 3(*c*) show spectra after 2.5 and 15 min respectively. The corresponding reaction mixtures at these concentrations in the dark show spectra beyond the scale of the figures. These results show that (1) reactions in the light and dark are accompanied by at least one intermediate in each case, (2) these intermediates have different absorption spectra, (3) the intermediate of the dark reaction absorbs strongly, and (4) formation of intermediate complexes is rapid.

The kinetics of the decomposition of the complex in the light-sensitive reaction was followed by measuring the absorption at 290 nm (Table 8). Assuming that it is a first-order decomposition, a plot of log *A versus* time yields a first-order rate constant of 1.25 × 10^{-3} s^{-1} for a mixture containing $[Fe^{III}]$ = 5.0 × 10^{-3} mol dm^{-3} and $[NH_3OH^+]$ = 5.0 × 10^{-2} mol dm^{-3} at pH 4.05 and 30 °C. This yielded a second-order rate constant of 2.5 × 10^{-2} dm^3 mol^{-1} s^{-1} at 30 °C. The dark reaction was studied at 341 nm (Table 8) and the same procedure yielded a first-order rate constant of 5.0 × 10^{-4} s^{-1} (for a mixture containing $[Fe^{III}]$ = 5.0 × 10^{-4} mol dm^{-3} and $[NH_3OH^+]$ = 2.0 × 10^{-2} mol dm^{-3}) and a second-order rate constant of 2.4 × 10^{-2} dm^3 mol^{-1} s^{-1} at pH 4.05 and 30 °C. Thus the

Table 4 Values of the intercepts and slopes of different linear plots, and of k_1 and k_1k_3/k_2 in the Fe^{III} + NH_3OH^+ reaction; $[NH_3OH^+]$ = 5.00 × 10^{-2} mol dm^{-3}

10^3 $[Fe^{III}]$/ mol dm^{-3}	pH	10^3 $[Fe^{II}]$/ mol dm^{-3}	Plot	Intercept	Slope	T/°C	10^2k_1/ dm^3 mol^{-1} s^{-1}	$k_1k_3/k_2{}^{-1}$/ dm^3 mol^{-1} s^{-1}
1.80–14.0	4.05	—	v_0 *vs.* $[Fe^{III}]$	Zero	2.35 × 10^{-3}	35	4.7	—
4.60*	4.05	—	v_0 *vs.* $[NH_3OH^+]$	Zero	2.08 × 10^{-4}	35	4.5	—
5.00	3.42–4.05	7.5	v_0 *vs.* $[H^+]$	Zero	1.0 × 10^{-2}	35	—	0.32
4.80	3.20	0.50–2.00	$(v_0)^{-1}$ *vs.* $[Fe^{II}]$	0.85 × 10^5	2.25 × 10^7	35	5.0	0.29
4.80	4.15	0.50–3.00	$(v_0)^{-1}$ *vs.* $[Fe^{II}]$	0.85 × 10^5	2.0 × 10^8	35	4.6	0.29
4.80	4.50	0.50–2.50	$(v_0)^{-1}$ *vs.* $[Fe^{II}]$	0.85 × 10^5	4.0 × 10^9	35	4.2	0.33
4.80	3.28–5.18	0.100	$(v_0)^{-1}$ *vs.* $[H^+]^{-1}$	0.90 × 10^5	1.32	35	4.6	0.31
4.75	3.30–5.18	0.200	$(v_0)^{-1}$ *vs.* $[H^+]^{-1}$	0.30 × 10^5	1.17	45	16	0.68
4.80	3.70–4.98	0.100	$(v_0)^{-1}$ *vs.* $[H^+]^{-1}$	2.9 × 10^5	2.0	25	1.4	0.13
4.80	4.05	0.50–2.00	(v_0) *vs.* $[Fe^{II}]^{-1}$	2.1 × 10^7	Zero	6	0.084	—
4.70	3.72–5.23	0.200	(v_0) *vs.* $[H^+]$	2.1 × 10^7	Zero	6	0.084	—
4.80	4.35–5.18	0.100	(v_0) *vs.* $[H^+]$	Zero	4.9	60	—	2.0
4.80	4.05	0.50–2.00	(v_0) *vs.* $[Fe^{II}]^{-1}$	Zero	3.5 × 10^{-8}	60	—	1.6
				Average 10^2k_1 at 35 °C 4.6 ± 0.2				

* $[NH_3OH^+]$ = (2.00–21.0) × 10^{-2} mol dm^{-3}.

Table 5 Variation of pH and $[Fe^{II}]$ in the Fe^{III} + NH_3OH^+ reaction at 6 °C, $[NH_3OH^+]$ = 5.0 × 10^{-2} mol dm^{-3} and $[Fe^{III}]$ = 4.8 × 10^{-3} mol dm^{-3}

pH	$10^3[Fe^{II}]$/ mol dm^{-3}	10^7v_0/ mol dm^{-3} s^{-1}
3.72	2.0	2.1
4.05	2.0	2.0
4.42	2.0	2.2
4.60	2.0	2.1
4.82	2.0	2.2
5.23	2.0	2.0
4.05	0.50	2.0
4.05	1.00	2.1
4.05	1.5	2.0
4.05	2.0	2.1

Table 6 Variation of pH and $[Fe^{II}]$ in the Fe^{III} + NH_3OH^+ reaction at 60 °C, $[Fe^{III}]$ = 4.8 × 10^{-3} and $[NH_3OH^+]$ = 5.0 × 10^{-2} mol dm^{-3}

Variation of pH at $[Fe^{II}]$ = 1.0 × 10^{-4} mol dm^{-3}

pH	4.64	4.77	4.85	4.98	5.18
10^5v_0/mol dm^{-3} s^{-1}	11.0	8.2	6.8	5.2	3.2

Variation of $[Fe^{II}]$ at pH 4.05

$10^5[Fe^{II}]$/mol dm^{-3}	0.25	0.50	1.0	1.5	2.0	2.5
10^5v_0/mol dm^{-3} s^{-1}	14	7.0	3.1	2.4	1.8	1.4

intermediate complexes of light-sensitive and dark reactions have similar rates under identical conditions. These rate constants are similar to that (2.3 × 10^{-2} dm^3 mol^{-1} s^{-1}) found at 30 °C under the same conditions by the volumetric method. Thus the redox reaction and decomposition of the intermediate are kinetically the same processes.

Discussion

An outline of the reaction scheme that corresponds to rate law (3) is shown in equations (6) and (7), but the actual mechanism may be quite complex.

$$Fe^{III}OH + NH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe^{II} + NHOH + H_2O \quad (6)$$

$$NHOH + H^+ \xrightarrow{k_3} \text{products} \quad (7)$$

In acetate buffers several mononuclear and polymeric species of iron(III) are reported[23] and the species[24] $[Fe_3O(O_2CMe)_6]^+$ is said to be 99% present along with 1% monomer under the conditions employed in our investigation. The formation constant[23,25] of this complex is large (*ca.* 10^{22}). Hydroxylamine has a protonation constant[26] of about 1 × 10^6 dm^3 mol^{-1} and hence NH_3OH^+ would be the predominant species of hydroxylamine. Hydrolysed metal ions and un-ionised hydroxylamine are generally the reactive species in redox reactions and also where co-ordination is involved, though their concentrations may be small. Since there is positive spectrophotometric evidence for an intermediate in the present reaction, a precursor complex of Fe^{III} and NH_2OH is likely to be formed and thus reaction occurs by an inner-sphere mechanism. Since the light-sensitive and dark reactions differ in giving the products (and hence in the transition states), these reactions should differ by the intermediacy of one more complex in addition to the above-mentioned common precursor complex. Thus the forward reaction (6) is not as simple as shown. It may involve three steps: (1) rapid formation of the first precursor complex, (2) rapid formation of another precursor complex, and then (3) slow redox reaction yielding Fe^{II} and still another reactive short-lived complex species of Fe^{III} and the oxidised moiety of NH_2OH. There is no eivdence for the compositions of these complexes, but a guess can be made from the composition of the acetate trimer[24] and the sequence of reactions mentioned above. A possible mechanism is shown in Scheme 1.

It may seem unlikely that complexes **5** and **6** have a structure and composition related to those of the original trimer, but one fact has to be highlighted and explained. These complexes contain N in the zero oxidation state. One, **5**, is protonated and yields N_2 and the other, **6**, undergoes redox reaction to yield nitrogen in oxidation state I and finally N_2O. This would be facile only when Fe^{III} and nitrogen(0) are in some sort of co-ordination. Hence the complex is likely to retain its polymeric form even after redox reaction. In any case they are reactive intermediates and shortlived. Secondly the equilibrium reaction (6) would be retarded by acetate ions if we were to assume the break up of complexes **3** and **4** after redox reaction. Acetate ion has no effect and hence it appears that complexes **5** and **6** are not much different from the original trimer. Complexes **2**–**6** are not unique in composition and charge. The only point of interest is the presence of three or two iron(III) atoms with nitrogen in different oxidation states.

The absorption spectra in Figs. 2 and 3 may refer to complexes **3** and **4** under the conditions of darkness and light respectively. It is likely that even these two complexes are formed through mixed-valence complexes[27] $[Fe^{III}{}_2Fe^{II}O(N)(O_2CMe)_6]$ and $[Fe^{III}{}_2Fe^{II}O(NHOH)(O_2CMe)_6]$ which may not be stable in solution. Mixed-valence complexes are known

Table 7 Reaction of Fe^{III} and NH_3OH^+ in the dark at 35 °C

$10^3[Fe^{III}]$	$10^2[NH_3OH^+]$	$10^3[Fe^{II}]$	pH	$10^6 v_0$/ mol dm^{-3} s^{-1}	$10^2 k_1$/ dm^3 mol^{-1} s^{-1}
mol dm^{-3}					
0.50	5.00	—	4.05	0.85	3.4
1.00	5.00	—	4.05	1.8	3.6
2.00	5.00	—	4.05	3.6	3.6
5.00	5.00	—	4.05	10	4.0
4.00	5.00	—	4.05	15.5	3.9
4.80	10.0	—	4.05	17	3.5
4.80	15.0	—	4.05	29	4.0
0.50	5.00	5.00	4.05	0.58	—
1.00	5.00	5.00	4.05	0.65	—
2.00	5.00	5.00	4.05	0.77	—
4.00	5.00	5.00	4.05	0.87	—
6.00	5.00	5.00	4.05	0.94	—
8.00	5.00	5.00	4.05	0.96	—
4.80	5.00	—	3.72	11	—
4.80	5.00	—	4.05	10	—
4.80	5.00	—	4.40	9.2	—
5.00	5.00	0.200	4.05	8.5	—
5.00	5.00	0.400	4.05	7.3	—
5.00	5.00	0.600	4.05	6.0	—
5.00	5.00	5.00	3.72	1.0	—
5.00	5.00	5.00	4.05	0.90	—
5.00	5.00	5.00	4.80	0.83	—
5.00	5.00	5.00	5.18	0.66	—

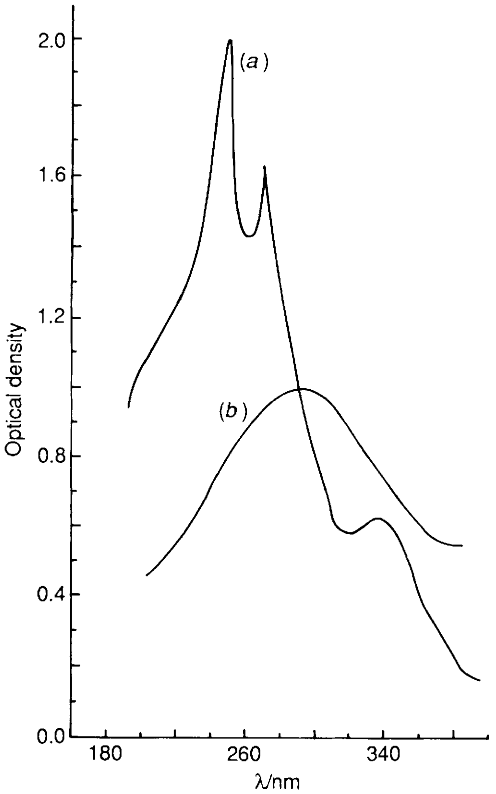


Fig. 2 UV spectrum of reaction mixtures 2.5 min after mixing at pH 4.05, $[NH_3OH^+] = 5.0 \times 10^{-3}$ and $[Fe^{II}] = 2.0 \times 10^{-4}$ mol dm^{-3}. (*a*) In the dark, $[Fe^{III}] = 4.8 \times 10^{-4}$ mol dm^{-3}; (*b*) in the light, $[Fe^{III}] = 4.8 \times 10^{-3}$ mol dm^{-3}

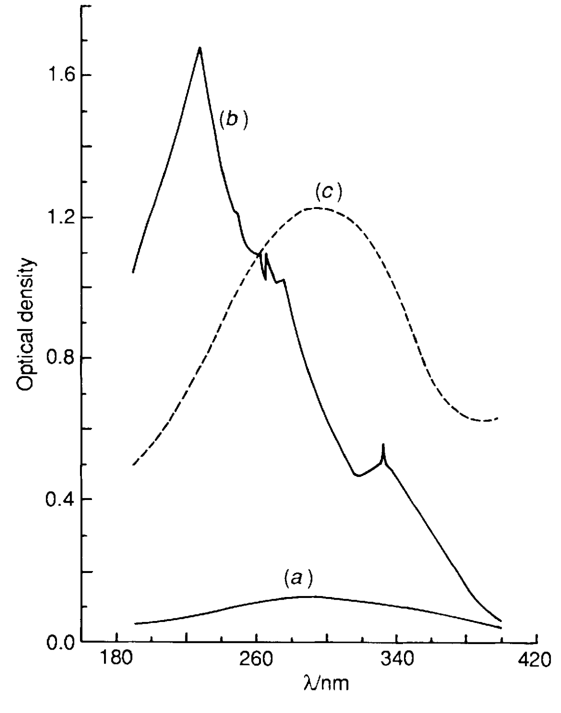


Fig. 3 UV spectrum of reaction mixtures 15 min after mixing at pH 4.05 and $[Fe^{II}] = 2.0 \times 10^{-4}$ mol dm^{-3}. (*a*) (light) and (*b*) (dark), $[Fe^{III}] = 4.8 \times 10^{-4}$ and $[NH_3OH^+] = 5.0 \times 10^{-3}$; (*c*) (light), $[Fe^{III}] = 4.8 \times 10^{-3}$, and $[NH_3OH^+] = 5.0 \times 10^{-2}$, mol dm^{-3}

to absorb strongly[28] in the UV region on account of double excitation.

The second-order rate constants for the decomposition (spectrophotometric) of the intermediate complex and for the redox reaction followed by volumetric determination of Fe^{III} are similar. This shows that the two processes are one and the same. However, more significant is the finding that the rates of the light-sensitive and dark reactions are similar using three altogether different methods for following the kinetics, *viz*, volumetric estimation of Fe^{III} and UV absorption measurement by us, and gas analysis of N_2O by Butler and Gordon.[5] This only lends credibility to the fact that the two reactions (light-sensitive and dark) have essentially the same mechanism and must differ only in part to explain the formation of N_2 in the light-sensitive reaction, and N_2O in the dark reaction. Further the dark reaction is not really a dark reaction, being composite and yielding a mixture of N_2 and N_2O. It is also worth

Table 8 Absorbance of the intermediate complexes in the light-sensitive and dark reactions at different times. $[Fe^{II}] = 2.0 \times 10^{-4}$ mol dm^{-3}, pH 4.05, 30 °C

(*a*) At 290 nm for light-sensitive reaction[a]

t/min	2	6	12	18	24	30
A	3.70	2.75	1.79	1.13	0.722	0.440

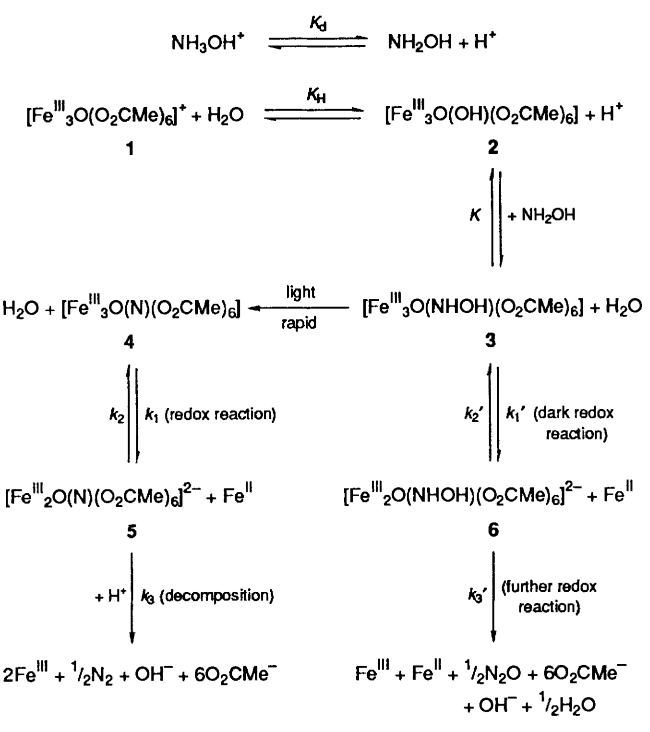
(*b*) At 341 nm for dark reaction[b]

t/min	1	3	5	7	12	18	28
A	2.63	2.48	2.30	2.16	1.92	1.58	1.20

[a] $[Fe^{III}] = 5.0 \times 10^{-3}$ mol dm^{-3} and $[NH_3OH^+] = 5.0 \times 10^{-2}$ mol dm^{-3} [b] $[Fe^{III}] = 5.0 \times 10^{-4}$ mol dm^{-3} and $[NH_3OH^+] = 2.0 \times 10^{-2}$ mol dm^{-3}

Table 9 Reaction of $Fe^{III} + NH_3OH^+$ in the presence of methylmethacrylate (2 cm^3 added to each reaction mixture)

$10^3[Fe^{III}]$/ mol dm^{-3}	$10^2[NH_3OH^+]$/ mol dm^{-3}	pH	$10^4[Fe^{II}]$/ mol dm^{-3}	$10^6 v_0$/ mol dm^{-3} s^{-1}	$10^2 k_1$/ dm^3 mol^{-1} s^{-1}
4.80	5.00	4.05	—	4.6	1.9
4.80	5.00	4.05	2.00	4.3	1.8
2.40	5.00	4.05	2.00	2.2	1.9
4.70	10.0	4.05	2.00	8.2	1.8
4.80	5.00	4.05	4.00	4.2	1.7
4.80	5.00	4.05	6.00	4.4	1.8
4.80	5.00	3.42	2.00	4.6	1.9
4.80	5.00	3.72	2.00	4.4	1.8



Scheme 1

mentioning that the decomposition rate constants of the two complexes **3** and **4** are almost the same, but it is not surprising since the two complexes may not be much different in their compositions and structures.

The reactions carried out in aqueous $HClO_4$ solutions (Table 3) show that the second-order rate constant is about five times larger than that obtained in acetate buffers. The species likely to be present in 0.01 mol dm^{-3} $HClO_4$ will be the aqua complex of Fe^{3+} (*ca.* 78%) using a value[29] of 1.84×10^{-3} for the hydrolysis constant. Other species[30] present may be $[Fe(OH)]^{2+}$ and $[(H_2O)_5FeOFe(H_2O)_5]^{4+}$. These species may be more reactive than the oxo-centred trimeric acetate complex. No detailed study in aqueous $HClO_4$ was made since our purpose was limited to the verification of rate law (3) with respect to $[H^+]$ and $[Fe^{II}]$ dependences.

Reaction in the Presence of Methyl Methacrylate (*mma*).—The reaction mixture if treated with mma yields a white precipitate indicating polymerisation and the intermediacy of some reactive free radical. The results of reactions carried out in the presence of 2% mma are shown in Table 9. The rate is first order in $[Fe^{III}]$ and $[NH_3OH^+]$ and independent of H^+ and Fe^{II} as per rate law (5). The most significant observation is that no gas is evolved in the presence of mma, though Fe^{III} is reduced. Since a gas is obtained only after reaction (7) has taken place, it is obvious that the reactive intermediate formed in the forward reaction (6) is consumed by mma. The failure to obtain a gas and the kinetic results show that the mechanism is limited to the forward reaction only, in the presence of mma. The rate constant in the presence of mma, though not equal, is similar to k_1 in Table 4 and thus reaction in presence of mma can be regarded as a direct approach to the forward reaction (6). The difference in the rate constants of a factor of 2 may be due to the change in iron(III) species in the presence of mma.

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