Kinetics and Mechanism of the Oxidation of Hydrazine with Iron(III) in Acidic Perchlorate Media

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The title reaction was investigated by determining iron(III) with thiosulphate under the condition $[N_2H_5^+]/[Fe^{III}] > 1$ and the stoicheiometry is 1 : 1. Reproducible results were obtained from the same stock solution of iron(III) perchlorate. The mechanism proposed for the reaction is shown in equations (i)—(iii), and the corresponding rate law is as in equation (iv); k_1 and k_2/k_3 were found to be

$$Fe^{3+} + H_2O \overset{K_H}{\rightleftharpoons} [Fe(OH)]^{2+} + H^+ \qquad \text{(i)}$$

$$[Fe(OH)]^{2+} + N_2H_5^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe^{2+} + N_2H_4^+ + H_2O \qquad \text{(ii)}$$

$$N_2H_4^+ + N_2H_5^+ \xrightarrow{k_3} \text{products} \qquad \text{(iii)}$$

$$\frac{-d[Fe^{III}]}{dt} = \frac{K_H k_1 k_3 [Fe^{III}][N_2H_5^+]^2}{[H^+](k_2[Fe^{II}] + k_3[N_2H_5^+])} \qquad \text{(iv)}$$

2.0 ± 0.2 s^{-1} and 0.66 ± 0.03 at 55 °C. The rate law has been verified under all conditions except that where $[Fe^{II}] \gg [N_2H_5^+]$ since Fe^{II} retards the rate and the lower limit of concentration of $N_2H_5^+$ is governed by $[Fe^{III}]$. The rate of reaction decreases in the presence of sulphate ions showing that sulphate complexes of iron(III) are not reactive.

We have previously [1] studied the iron(II)-catalyzed oxidation of hydrazine with peroxodisulphate, which proceeds very slowly in the absence of a catalyst. The oxidation of hydrazine with iron(III) is also slow and hence the role of iron(II) as catalyst [involved in iron(II)–iron(III) cycle] requires further probing as does the reaction of Fe^{III} with hydrazine. The latter reaction has been studied by several workers [2–5] and although the mechanism is not in dispute there are some aspects which merit further investigation: (1) no studies have been made under conditions of fixed stoicheiometry; (2) chloride and sulphate systems have been employed, but the reactive species of iron(III) has not been defined; (3) the inhibiting effect of iron(II) has not been studied systematically; (4) the effect of hydrogen ion has not been studied; (5) the extent of complex formation between iron(III) and hydrazine is unknown; although no such complexation has been reported in oxidations by Ce^{IV},[6] Mn^{III},[7] and Cr^{III},[8] complexes do form with Cu^{II},[9,10] Pt^{IV},[11] and many other metal ions.[12] Recently, an intermediate mixed complex has been suggested in the oxidation of hydrazine with tris(1,10-phenanthroline)-iron(III).[13]

Experimental

Materials.—All the chemicals used were either B.D.H. AnalaR or E. Merck G.R. quality. Iron(III) perchlorate was prepared by precipitating iron(III) carbonate from iron(III) nitrate, washing with hot water to free from nitrate, and dissolving in perchloric acid. 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.[14] Hydrazine perchlorate was prepared by mixing equivalent amounts of hydrazine hydrate and perchloric acid.

Kinetic Procedure.—The reaction was initiated by adding thermally equilibrated iron(III) perchlorate solution to a flask containing known concentrations of hydrazine perchlorate, perchloric acid, *etc.* at 55 ± 0.1 °C in a thermostat bath. The reaction was followed by removing aliquots (5 cm^3) from the mixture and adding to an excess of thiosulphate solution. The excess of thiosulphate was then titrated against standard iodine solution as above. The solution was acidified to 1.0 mol dm^{-3} with sulphuric acid before titration to check the reaction [15] of hydrazine with iodine.

All solutions were prepared in doubly distilled water, the second distillation being from permanganate. All glass vessels were of Corning glass.

The data were processed for initial rates by the plane-mirror method,[16] and in some cases second-order plots of log $([N_2H_5^+]_t/[Fe^{III}]_t)$ *versus* time (t) were made to obtain second-order rate constants (k_2'). In a few other cases where hydrazine was present in excess over iron(III), first-order plots were also made to obtain first-order rate constants (k_1'). The three methods yielded results in good agreement.

Duplicate rate measurements were reproducible to ±10% for the same stock solution of iron(III) perchlorate, but different batches yielded different results. Four different solutions yielded rates which were 60—100% different from the one reported in this paper. A possible reason appears to be a difference in the concentrations of a reactive dimer [17a] of iron(III). Ondrus and Gordon [17b] have reported that a maximum of 5% dimer, depending on acidity and the concentration of iron(III), may be formed. The complete study of the present reaction was made with the same stock solution.

Stoicheiometry.—Several reaction mixtures with various concentrations of reactants were kept for 24 h. Excess of iron(III) was determined as above [14] and excess of hydrazine was estimated [18,19] by measuring the absorbance at 455 nm after its reaction with *p*-dimethylaminobenzaldehyde in dilute

Table 1. Initial rates (v_0) for the variation of Fe^{III} in the Fe^{III}–$N_2H_5^+$ reaction; $[N_2H_5^+] = 0.02$, $[H^+] = 0.3$ mol dm^{-3}, 55 °C

$10^3[Fe^{III}]$/mol dm^{-3}	2.0	4.0	6.0	8.0	12.0	16.0
10^6v_0/mol dm^{-3} s^{-1}	0.96	2.2	3.3	4.5	6.7	8.7
$10^3[Fe^{III}]$/mol dm^{-3}	18.0	19.0				
10^6v_0/mol dm^{-3} s^{-1}	9.0	9.0				

Table 2. Initial rates for the variation of $N_2H_5^+$ in the Fe^{III}–$N_2H_5^+$ reaction; $[Fe^{III}] = 4.0 \times 10^{-3}$, $[H^+] = 0.1$ mol dm^{-3}, 55 °C

(*a*) $[Fe^{II}] = 0.0$, $[SO_4^{2-}] = 0.0$						
$10^2[N_2H_5^+]$/mol dm^{-3}	0.5	1.0	5.0	10.0	14.0	16.0
10^6v_0/mol dm^{-3} s^{-1}	1.55	3.0	14.5	30.0	43	52
$10^2[N_2H_5^+]$/mol dm^{-3}	18.0					
10^6v_0/mol dm^{-3} s^{-1}	65					
(*b*) $[Fe^{II}] = 0.01$ mol dm^{-3}, $[SO_4^{2-}] = 0.01$ mol dm^{-3}						
$10^2[N_2H_5^+]$/mol dm^{-3}	0.5	0.8	1.0	1.2	1.5	2.0
10^6v_0/mol dm^{-3} s^{-1}	0.5	1.0	1.42	1.75	2.4	3.5
(*c*) $[Fe^{II}] = 0.003$ mol dm^{-3}, $[SO_4^{2-}] = 0.01$ mol dm^{-3}						
$10^2[N_2H_5^+]$/mol dm^{-3}	0.5	0.8	1.0	1.2	1.5	2.0
10^6v_0/mol dm^{-3} s^{-1}	0.83	1.5	1.9	2.4	3.05	4.2

Table 3. Second-order rate constant (k_2') for the variation of $[H^+]$ in the Fe^{II}–$N_2H_5^+$ reaction; $[Fe^{III}] = 4.0 \times 10^{-3}$, $[N_2H_5^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, 55 °C

$[H^+]$/mol dm^{-3}	0.1	0.15	0.2	0.3	0.4	0.6
$10^2k_2'$/dm^3 mol^{-1} s^{-1}	8.3	5.0	4.3	3.0	2.1	1.7
$[H^+]$/mol dm^{-3}	0.8	1.0				
$10^2k_2'$/dm^3 mol^{-1} s^{-1}	1.1	0.88				

Table 4. Initial rates for the variation of Fe^{II} in the Fe^{III}–$N_2H_5^+$ reaction; $[Fe^{III}] = 4.0 \times 10^{-3}$, $[H^+] = 0.1$, $[SO_4^{2-}] = 1.0 \times 10^{-2}$ mol dm^{-3}, 55 °C

(*a*) $[N_2H_5^+] = 5.0 \times 10^{-3}$ mol dm^{-3}						
$10^3[Fe^{II}]$/mol dm^{-3}	1.0	2.0	4.0	6.0	8.0	10.0
10^6v_0/mol dm^{-3} s^{-1}	0.80	0.71	0.58	0.50	0.43	0.38
(*b*) $[N_2H_5^+] = 10.0 \times 10^{-3}$ mol dm^{-3}						
$10^3[Fe^{II}]$/mol dm^{-3}	1.0	2.0	4.0	6.0	8.0	10.0
10^6v_0/mol dm^{-3} s^{-1}	1.8	1.65	1.5	1.30	1.25	1.15
(*c*) $[N_2H_5^+] = 0.1$ mol dm^{-3}						
$10^3[Fe^{II}]$/mol dm^{-3}	0.0	2.0	4.0	8.0	10.0	
$10^3k_1'$/s^{-1} *	4.9	4.9	5.2	5.1	5.0	

* k_1' is the pseudo-first-order rate constant.

Table 5. Initial rates for the variation of SO_4^{2-} in the Fe^{III}–$N_2H_5^+$ reaction; $[Fe^{III}] = 4.0 \times 10^{-3}$, $[N_2H_5^+] = 1.0 \times 10^{-2}$, $[H^+] = 0.1$ mol dm^{-3}, 55 °C

$10^3[SO_4^{2-}]$/mol dm^{-3}	0.0	2.0	4.0	8.0	10.0
10^6v_0/mol dm^{-3} s^{-1}	3.1	2.2	2.0	1.7	1.5

HCl solution. Iron(II) was estimated colorimetrically with 1,10-phenanthroline as the complexing ligand at pH ≈ 3 using acetate buffer. The stoicheiometry was found to be 1 : 1 when $[N_2H_5^+]/[Fe^{III}] > 1$, according to equation (1). However, the number of moles of iron(III) which react increases with increasing ratio $[Fe^{III}]/[N_2H_5^+]$. An attempt to determine the stoicheiometry in the presence of excess Fe^{II} (more than 50 times the concentration of hydrazine) in a nitrogen atmosphere was also made. The reaction was not complete even after 96 h, *i.e.* it is very slow in the presence of Fe^{II}. All reactions using iron(II) were performed under a stream of nitrogen.

$$Fe^{III} + N_2H_5^+ \longrightarrow Fe^{II} + \tfrac{1}{2}N_2 + NH_4^+ + H^+ \quad (1)$$

Results

Iron(III) *Dependence*.—The concentration of iron(III) was varied from 2.0×10^{-3} to 1.9×10^{-2} mol dm^{-3} at fixed concentrations of the other reactants. The results are given in Table 1. A plot of initial rate *versus* $[Fe^{III}]$ was a straight line passing through the origin, denoting a first-order dependence on $[Fe^{III}]$. However, for higher concentrations of Fe^{III} this plot deviated from linearity towards the $[Fe^{III}]$ axis. The second-order rate constant (k_2') obtained by dividing the initial rate by the concentrations of Fe^{III} and $N_2H_5^+$ was found to be 2.8×10^{-2} dm^3 mol^{-1} s^{-1} at 55 °C and $[H^+] = 0.3$ mol dm^{-3}.

Hydrazine Dependence.—The concentration of hydrazine perchlorate was varied from 0.005 to 0.20 mol dm^{-3} (Table 2). A plot of initial rates *versus* $[N_2H_5^+]$ was a straight line passing through the origin, showing a first-order dependence on hydrazine concentration and no significant complexing of Fe^{III} and hydrazine. The second-order rate constant calculated as in the previous paragraph was found to be 7.8×10^{-2} dm^3 mol^{-1} s^{-1}. If we take into account the different $[H^+]$ and multiply the second-order rate constant by the latter, the rate constants in the two cases were found to be 8.5×10^{-3} and 7.8×10^{-3} s^{-1}. The variation of hydrazine was also carried out in the presence of the different concentrations of iron(II) sulphate at constant $[SO_4^{2-}]$ since the reaction is retarded by sulphate ions. These results are also given in Table 2.

Variation of Hydrogen-ion Concentration.—The effect of $[H^+]$ was studied at fixed concentrations of the other reactants. The rate decreases with increasing hydrogen-ion concentration (Table 3). A plot of the second-order rate constant (k_2') *versus* $[H^+]^{-1}$ yielded a straight line passing through the origin. It thus appears that there is probably one term in the rate law with an inverse hydrogen-ion dependence. The slope of the line is 8.3×10^{-3} s^{-1}, which is similar to the value of the rate constant derived in the previous section.

Effect of Iron(II).—The iron(II) sulphate concentration was varied from 1×10^{-3} to 1×10^{-2} mol dm^{-3} at constant total $[SO_4^{2-}] = 0.01$ mol dm^{-3} and different concentrations of hydrazine. All the results are given in Table 4. The rate decreases with increasing $[Fe^{II}]$, except when excess of hydrazine is present where it appears to be independent of $[Fe^{II}]$. In the first two cases (Table 4), a plot of (rate)$^{-1}$ *versus* $[Fe^{II}]$ gives a straight line with an intercept.

Effect of Sulphate and Hydrogensulphate.—The sulphate-ion concentration was varied from 5×10^{-4} to 1.0×10^{-2} mol dm^{-3} by employing sodium sulphate at fixed concentrations of the other reactants (Table 5). The rate decreases with increasing $[SO_4^{2-}]$. A plot of (rate)$^{-1}$ *versus* $[SO_4^{2-}]$ gave a straight line with an intercept. Since the hydrogen-ion concentration was at least $10[SO_4^{2-}]$, the variation in $[H^+]$ was considered negligible. The concentration of hydrogen-

Table 6. Initial rates in the oxidation of hydrazine with Fe^{III} in the presence of peroxodisulphate; $[Fe^{III}] = 5.0 \times 10^{-3}$, $[N_2H_5^+] = 1.0 \times 10^{-2}$, $[H^+] = 0.1$ mol dm^{-3}, 55 °C

$10^3[S_2O_8^{2-}]$/mol dm^{-3}	0.0	2.0	4.0	8.0	10.0
10^6v_0/mol dm^{-3} s^{-1}	3.8	24	23	23	24

sulphate was varied from 1×10^{-3} to 1×10^{-2} mol dm^{-3} but without any effect.

Effect of Ionic Strength.—The ionic strength was varied with $LiClO_4$ in the range 0.1—1.0 mol dm^{-3} but there was no effect.

Reaction in the Presence of Peroxodisulphate.—As stated in the introduction, the reason for investigating the present reaction was its relevance to the catalysis by Fe^{II} or Fe^{III} of the oxidation of hydrazine with peroxodisulphate. Since peroxodisulphate would interfere with the method of determination of Fe^{III} employed, the kinetics were studied by estimating hydrazine with potassium bromate using indigo carmine as indicator.[20] The results given in Table 6 are in accord with earlier findings,[1] showing that the mechanism in the presence of peroxodisulphate is different from that of a simple iron(II)–iron(III) cycle.

Discussion

The present reaction is first order in the concentrations of Fe^{III} and hydrazine, and inversely proportional to the first power of the hydrogen ion concentration. Thus, so far as the main reactants are concerned, the reaction and its mechanism appear to be simple. The role of hydrogen ion could be explained by the reactive hydrazine species being N_2H_4, although the predominant species would be $N_2H_5^+$ since the protonation equilibrium constant[21] is large. It could also be explained by assuming $[Fe(OH)]^{2+}$ to be the reactive species, but the predominant form would be Fe^{3+} since the hydrolysis constant of Fe^{3+} is small[22] compared to the hydrogen-ion concentrations employed in this investigation. There is no way to distinguish kinetically between the two situations. However, since $[N_2H_4]$ would be small and the hydrolyzed species of Fe^{III} are considered[23] to be more reactive than the unhydrolyzed species, the reactive species in the present case are probably $[Fe(OH)]^{2+}$ and $N_2H_5^+$.

One important observation in the present investigation is the deviation from first-order behaviour at high concentrations of Fe^{III}. This could be due either to dimer[17] formation or inhibition by one of the products. Since the reaction is retarded by the presence of added iron(II) and dimer formation is small, the reaction seems to involve an equilibrium between Fe^{III} and Fe^{II}. The fact that the reaction is not complete in the presence of Fe^{II} even after 96 h and the stoicheiometry could not be determined also suggests that iron(II) reacts to yield iron(III). Secondly, the inhibiting effect of iron(II) is not found at high concentrations of hydrazine (Table 4). All these facts taken together lead to the formulation of the mechanism in equations (2)—(4). With $[H^+] \gg K_H$ the rate law (5) is obtained.

$$Fe^{3+} + H_2O \overset{K_H}{\rightleftharpoons} [Fe(OH)]^{2+} + H^+ \qquad (2)$$

$$[Fe(OH)]^{2+} + N_2H_5^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe^{2+} + N_2H_4^+ + H_2O \qquad (3)$$

$$N_2H_4^+ + N_2H_5^+ \xrightarrow{k_3} \text{products} \qquad (4)$$

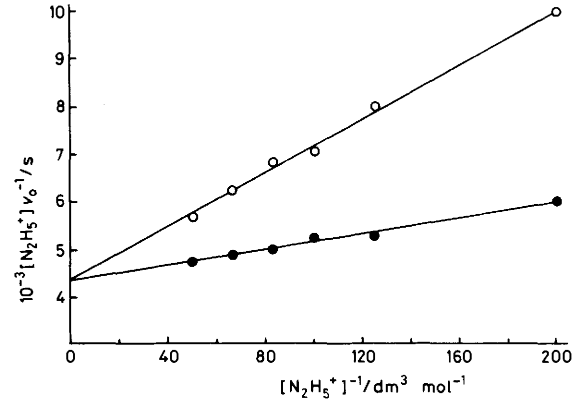

Figure 1. Plot of $[N_2H_5^+]v_0^{-1}$ *versus* $[N_2H_5^+]^{-1}$ at $[Fe^{III}] = 4.0 \times 10^{-3}$, $[H^+] = 0.1$, $[SO_4^{2-}] = 0.01$ mol dm^{-3}, 55 °C; $[Fe^{II}] = 0.01$ (○) and 0.003 mol dm^{-3} (●)

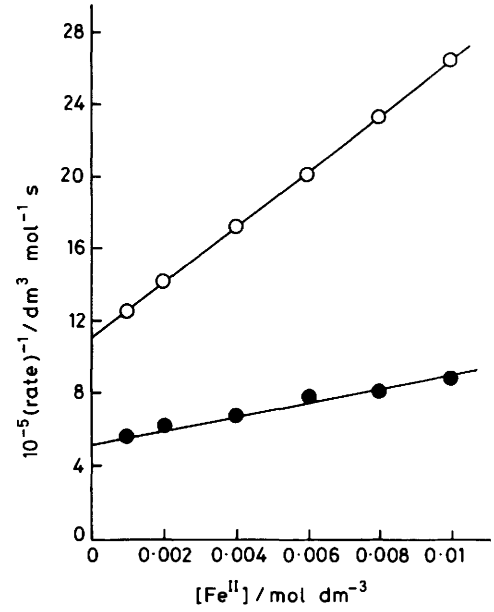

Figure 2. Plot of (rate)$^{-1}$ *versus* $[Fe^{II}]$ at $[Fe^{III}] = 4.0 \times 10^{-3}$, $[H^+] = 0.1$, $[SO_4^{2-}] = 0.01$ mol dm^{-3}, 55 °C; $[N_2H_5^+] = 0.005$ (○) and 0.01 mol dm^{-3} (●)

$$\frac{-d[Fe^{III}]}{dt} = \frac{K_Hk_1k_3[Fe^{III}][N_2H_5^+]^2}{[H^+]\,(k_2[Fe^{II}] + k_3[N_2H_5^+])} \qquad (5)$$

According to equation (5), plots of $[N_2H_5^+]$/rate *versus* $[N_2H_5^+]^{-1}$, and those of (rate)$^{-1}$ *versus* $[Fe^{II}]$, should yield straight lines with intercepts (Figures 1 and 2). This is actually found and from these plots values of k_1 and k_2/k_3 (Table 7) were calculated using 4.84×10^{-3} for the value of K_H. The agreement amongst the values can be considered satisfactory in view of the complexity of the reaction. The order in $[N_2H_5^+]^2$ at high concentrations of Fe^{II} could not be demonstrated since the reaction becomes very slow. However, the fact that the plot of $[N_2H_5^+]$/rate *versus* $[N_2H_5^+]^{-1}$ contained an intercept shows that the order varies between one and two. The order in $[N_2H_5^+]$ is one when Fe^{II} is not present. A close look at Table 4 reveals that the ratio of the rates at $[N_2H_5^+] = 0.01$ and 0.005 mol dm^{-3} increases from 2.3 to 3.2 as the concentration of iron(II) is increased, *i.e.* the order in $[N_2H_5^+]$ increases from one towards two.

Table 7. Values of k_1 and k_2/k_3 at 55 °C in the oxidation of hydrazine with Fe^{III} in acidic perchlorate media from the variation of $N_2H_5^+$ and Fe^{II} at $I = 1.0$ mol dm^{-3} and 55 °C

$10^3[Fe^{II}]$	$10^3[N_2H_5^+]$	$[H^+]$				
	mol dm^{-3}		Intercept	Slope	k_1/s^{-1}	k_2/k_3
10.0	5.0—20.0	0.1	$4.4 \times 10^{3\,a}$	8.0^{a}	2.19	0.64
3.0	5.0—20.0	0.1	$4.4 \times 10^{3\,a}$	28.0^{a}	2.19	0.61
1.0—10.0	10.0	0.1	$5.2 \times 10^{5\,b}$	$3.6 \times 10^{7\,b}$	1.86	0.69
1.0—10.0	5.0	0.1	$11.1 \times 10^{5\,b}$	$15.1 \times 10^{7\,b}$	1.75	0.68
				Average	2.0 ± 0.2	0.66 ± 0.03

[a] From the plot of $[N_2H_5^+]/v_0$ *versus* $[N_2H_5^+]^{-1}$. [b] From the plot of v_0^{-1} *versus* $[Fe^{II}]$.

In the presence of sulphate ions, the reaction rate decreases perhaps owing to the formation of less reactive species, $[Fe(SO_4)]^+$ and $[Fe(SO_4)_2]^-$. The values of the formation constants [24] of these complexes suggest that the concentration of $[Fe(SO_4)_2]^-$ would be negligible. The sulphate-ion concentration would be controlled by its complex formation with Fe^{3+} and also by its protonation. The extent of the latter would be small [25] at the temperature and the ionic strength employed. Without defining the various species and considering the gross picture, it is found that a plot of (rate)$^{-1}$ *versus* $[SO_4^{2-}]$ yields a straight line with an intercept and hence the empirical relationship (6) should hold, where A is an unspecified constant for a particular set of concentrations of reactants and K is a sort of equilibrium constant involving sulphate ions. From this one can estimate K separate from A. Although the value obtained is only approximate, it enables one to compare the values of k_1 obtained under different conditions. An average value of about 88 dm^3 mol^{-1} found for K may prompt one to relate it with the equilibrium (7) which has an equilibrium constant [25] of the same order of magnitude at 55 °C and the ionic strength employed.

$$\frac{-d[Fe^{III}]}{dt} = \frac{A}{(1 + K[SO_4^{2-}])} \qquad (6)$$

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons [Fe(SO_4)]^+ \qquad (7)$$

The data of Table 1 and set (*a*) of Table 2 correspond to the rate law (8) under the condition that no Fe^{II} or SO_4^{2-} is initially added and hence k_1 can be obtained. The average value of k_1 from Table 7 is 2.0 ± 0.2 s^{-1}, that from Table 1 is 1.76 s^{-1}, and from the hydrazine and hydrogen-ion dependences the values are 1.65 and 1.70 s^{-1} respectively. At high concentration of hydrazine [set (*c*), Table 4] when the rate is independent of iron(II), k_1 is found to be 1.9 s^{-1}. In view of the complicated rate law, the agreement among these values can be considered satisfactory. In all these calculations the value [26] of K_H employed was 4.84×10^{-3}. From the values of k_2/k_3 it is obvious that k_2 and k_3 are of comparable magnitude.

$$-d[Fe^{III}]/dt = K_H k_1[Fe^{III}][N_2H_5^+]/[H^+] \qquad (8)$$

Although iron(III) forms strong complexes with oxygen-containing compounds,[27] it does not seem to form complexes in general with nitrogen compounds in aqueous acidic media. There is no evidence for such complexation in the present investigation, nor is there any spectrophotometric evidence. However, mixed complexes of Fe^{III} in which nitrogen-containing compounds are also present are known [13,28] to be formed as intermediates in the redox reactions of Fe^{III}. Since complexes of metal ions with hydrazine are formed [12] in neutral or slightly acidic media, the only inhibiting factor for complex formation appears to be the protonation of hydrazine in the acidic medium and the very low concentration of neutral hydrazine available for co-ordination. The formation of mixed complexes with hydrazine even in acidic media shows that after complexing by the other ligands there are still vacant orbitals on the iron(III) ion available for co-ordination. It appears that the existence of similar charges on the metal ion and the ligand is a significant inhibiting factor. With the formation of a complex between $[Fe(OH)]^{2+}$ and $S_2O_8^{2-}$ there is charge neutralization and redistribution, and the charge no longer remains a hurdle for complexation of hydrazinium ion. The increased rate of oxidation of hydrazine in the presence of peroxodisulphate (Table 6), which could also be regarded as an iron(III)-catalyzed oxidation of hydrazine with peroxodisulphate, thus shows the intermediacy of a reactive iron(III)–peroxodisulphate–hydrazine ternary complex.

A comparison of the present results with those of earlier workers [3,5] shows that the equilibrium step involving Fe^{III} and Fe^{II} is essentially the same. The previous studies considered the dimerization of N_2H_3 and its subsequent decomposition in two different ways [equation (9)] and that these steps are rate controlling. Large concentrations of iron(III) were employed which would make the stoicheiometry variable. Since the retardation by Fe^{II} is not observed at high hydrazine concentration, step (3) of the present mechanism is more realistic. Quantitative comparison of our results with those of earlier workers [3,5] is not possible because of the lack of reproducibility between different samples of iron(III); even the order of magnitude cannot be compared since the earlier workers did not specify the species of iron(III) and hydrogen-ion dependence, both of which are significant as found in the present investigation. However, retardation by iron(II) is well established and is also reported in the oxidation of hydroxylamine.[29]

$$\begin{tikzcd} & & 2NH_3 + N_2 & & \text{(9a)} \\ 2N_2H_3 \arrow[r] & N_4H_6 \arrow[ur] \arrow[dr] & & & \\ & & N_2H_4 + N_2H_2 \arrow[r] & N_2 & \text{(9b)} \end{tikzcd}$$

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