The Oxidation of Hydrazine in Aqueous Solution. Part III. Some Aspects of the Kinetics of Oxidation of Hydrazine by Iron*(III) *in Acid Solution.*

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Rates of formation of iron(II) and ammonia in the oxidation of hydrazine by iron(III) in acid solution have been measured. The results show that formation of ammonia proceeds through the dimerisation of N_2H_3 radicals. Under the conditions of these experiments, disproportionation of N_2H_3 radicals is unimportant. The latter finding is not in accord with the conclusions of other workers, and this disagreement is discussed.

THE mechanism of oxidation of hydrazine in acid solution can be partly established by using isotopically distinguished nitrogen (Higginson and Sutton, *J.*, 1953, 1402; Cahn and Powell, *J. Amer. Chem. Soc.*, 1954, **76**, 2568). The latter authors obtained further information by kinetic studies. We now report similar studies which lead us to somewhat different conclusions.

The experiments using labelled nitrogen show that oxidation by a 1-electron-transfer reagent can be expressed in terms of two limiting overall reactions :

$$\text{(i)}\quad N_2H_4 \xrightarrow{-(e)} \tfrac{1}{2}N_2 + NH_3$$

$$\text{(ii)}\quad N_2H_4 \xrightarrow{-4(e)} N_2$$

In (i), $NH_2\cdot NH\cdot NH\cdot NH_2$ is an intermediate, and successively loses two ammonia molecules, forming nitrogen gas. The experiments do not show how this intermediate is formed, although 1-electron oxidation of hydrazine, followed by dimerisation of the resulting N_2H_3 radicals, appears to be the most likely mechanism. Both atoms in a nitrogen molecule formed in (ii) come from the same hydrazine molecule, but it is not possible to decide whether the probable intermediate, N_2H_2 (cf. Part I, *J.*, 1953, 1380), is

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* Part II, *J.*, 1953, 1402.

formed by further oxidation of N_2H_3, or by disproportionation between two N_2H_3 radicals, or by both these routes.

These uncertain aspects of the oxidation mechanism can be investigated by kinetic experiments. Iron(III) appeared to be the only suitable 1-electron oxidant, although preliminary experiments showed that iron(II) retarded the reaction, presumably by reducing N_2H_3 to N_2H_4. The mechanism can thus be plausibly represented as :

$$\mathrm{Fe(III)} + N_2H_4 \xrightarrow{k_1} \mathrm{Fe(II)} + N_2H_3 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{Fe(II)} + N_2H_3 \xrightarrow{k_{-1}} \mathrm{Fe(III)} + N_2H_4 \quad . \quad . \quad . \quad . \quad . \quad (-1)$$

$$2N_2H_3 \xrightarrow{k_2} N_4H_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

followed by

$$N_4H_6 \xrightarrow{\text{fast}} N_2 + 2NH_3$$

$$2N_2H_3 \xrightarrow{k_3} N_2H_2 + N_2H_4 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

followed by

$$N_2H_2 \xrightarrow{-2(e),\ \text{fast}} N_2$$

$$\mathrm{Fe(III)} + N_2H_3 \xrightarrow{k_4} N_2H_2 + \mathrm{Fe(II)} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

followed by

$$N_2H_2 \xrightarrow{-2(e),\ \text{fast}} N_2$$

The reaction $N_2H_2 + N_2H_4 \longrightarrow N_4H_6$ is not included, since with 2-electron oxidants no ammonia is formed under conditions similar to those in our experiments, although N_2H_2 is thought to be the primary intermediate in such reactions (Part I, *loc. cit.*). Apart from the introduction of the back reaction (−1), this sequence is the same as that proposed by Cahn and Powell (*loc. cit.*). Unlike these workers, who measured overall stoicheiometries, we have investigated the dependence of the rates of formation of iron(II) and ammonia upon reactant concentrations. [For this purpose we include iron(II) as a reactant.] If the above mechanism is correct :

$$R(\mathrm{NH_3}) = k_2[N_2H_3]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$R(\mathrm{Fe}) = k_1[\mathrm{Fe(III)}][N_2H_4] - k_{-1}[\mathrm{Fe(II)}][N_2H_3] + k_3[N_2H_3]^2 + 3k_4[\mathrm{Fe(III)}][N_2H_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $R(\mathrm{NH_3}) = \mathrm{d}[\mathrm{NH_3}]/\mathrm{d}t$, $R(\mathrm{Fe}) = \mathrm{d}[\mathrm{Fe(II)}]/\mathrm{d}t = -\mathrm{d}[\mathrm{Fe(III)}]/\mathrm{d}t$

Making the stationary state assumption, we have

$$0 = \mathrm{d}[N_2H_3]/\mathrm{d}t = k_1[\mathrm{Fe(III)}][N_2H_4] - k_{-1}[\mathrm{Fe(II)}][N_2H_3] - k_2[N_2H_3]^2 - k_3[N_2H_3]^2 - k_4[\mathrm{Fe(III)}][N_2H_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

k_1 and k_{-1} can be eliminated from (6), giving

$$R(\mathrm{Fe}) = k_2[N_2H_3]^2 + 2k_3[N_2H_3]^2 + 4k_4[\mathrm{Fe(III)}][N_2H_3] \quad . \quad . \quad . \quad (8)$$

Dividing (8) by (5), we have

$$R(\mathrm{Fe})/R(\mathrm{NH_3}) = 1 + 2k_3/k_2 + 4k_4[\mathrm{Fe(III)}]/k_2[N_2H_3] \quad . \quad . \quad . \quad (9)$$

and, eliminating $[N_2H_3]$ by use of (5) :

$$R(\mathrm{Fe})/R(\mathrm{NH_3}) = 1 + 2k_3/k_2 + 4k_4[\mathrm{Fe(III)}]/\sqrt{k_2R(\mathrm{NH_3})} \quad . \quad . \quad (10)$$

Fig. 1 shows a plot (full line) of $R(\mathrm{Fe})/R(\mathrm{NH_3})$ against $[\mathrm{Fe(III)}]/\sqrt{R(\mathrm{NH_3})}$ for experiments in chloride-ion solutions, summarised in Table 1. We consider that the resulting linear plot provides good evidence that the above reaction scheme is valid, for we are unable to suggest a different mechanism similarly consistent with our experimental results. The intercept, $(1 + 2k_3/k_2)$, is seen to be near to unity and was evaluated by rewriting equation (10) in the form :

$$\frac{R(\text{Fe})}{[\text{Fe(III)}]\sqrt{R(\text{NH}_3)}} = \left(1 + \frac{2k_3}{k_2}\right)\frac{\sqrt{R(\text{NH}_3)}}{[\text{Fe(III)}]} + \frac{4k_4}{\sqrt{k_2}} \quad . \quad . \quad . \quad (11)$$

a plot of the left-hand side against $\sqrt{R(\text{NH}_3)}/[\text{Fe(III)}]$ then giving as gradient $(1 + 2k_3/k_2) = 1{\cdot}03 \pm 0{\cdot}03$. Hence $k_3/k_2 = 0{\cdot}015 \pm 0{\cdot}015$.

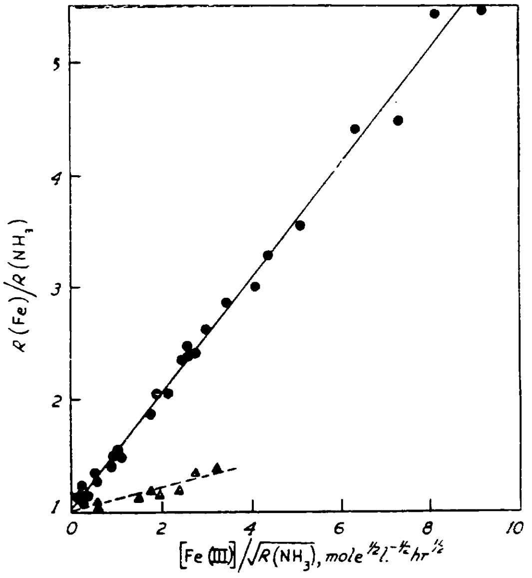

FIG. 1.
● *Chloride solution.*
▲ *Sulphate solutions.*

At sufficiently high concentrations of iron(II) the rate of disappearance of N_2H_3 by reactions (2), (3), and (4) will be very much less than by (—1), and as an approximation, if $K = k_1/k_{-1}$:

$$[\text{N}_2\text{H}_3] = K[\text{Fe(III)}][\text{N}_2\text{H}_4]/[\text{Fe(II)}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

From (12) and (5) :

$$R(\text{NH}_3) = k_2K^2[\text{Fe(III)}]^2[\text{N}_2\text{H}_4]^2/[\text{Fe(II)}]^2 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and from (12) and (9) :

$$R(\text{Fe})/R(\text{NH}_3) = 1 + 2k_3/k_2 + 4k_4[\text{Fe(II)}]/Kk_2[\text{N}_2\text{H}_4] \quad . \quad . \quad . \quad (14)$$

The expression $R(\text{N}_2\text{H}_4)/\{k_1[\text{Fe(III)}][\text{N}_2\text{H}_4] - R(\text{N}_2\text{H}_4)\}$, represented by $R(2,3,4)/R(-1)$, gives the ratio of the rate of disappearance of N_2H_3 radicals by reactions (2), (3), and (4) to the rate of disappearance by (—1), and its value can be used to indicate whether (12) is an allowable approximation. $R(\text{N}_2\text{H}_4)$ can be obtained from $R(\text{NH}_3)$ and $R(\text{Fe})$, since $R(\text{N}_2\text{H}_4) = \frac{3}{4}R(\text{NH}_3) + \frac{1}{4}R(\text{Fe})$. It is difficult to find k_1 directly at 60°; however, experiments at 25° and 35° with low iron(II) concentrations and under otherwise similar conditions gave $k_1 = 0{\cdot}06$ and $0{\cdot}35$ l. mole^{-1} hr.$^{-1}$, whence at 60° $k_1 \simeq 18$ l. mole^{-1} hr.$^{-1}$. The experiments in Table 1 are arranged in increasing order of the $R(2,3,4)/R(-1)$ values which vary from 5×10^{-3} to $5{\cdot}4 \times 10^{-2}$. These approximate figures suggest that (12) is a reasonable assumption for the first experiments in Table 1. Figs. 2 and 3 show that equations (13) and (14) hold well for experiments 1—6. Equation (14) holds fairly well for all the experiments in Table 1, and gives an intercept similar to that obtained by using equation (10), but deviations, increasing with $R(2,3,4)/R(-1)$, of up to 35% in $R(\text{NH}_3)$ occur from equation (13). These plots give additional evidence for the validity of the proposed reaction mechanism. The effect of iron(II) when in concentrations comparable with those of the other reactants is also emphasised, whereas (10) should hold even in the absence of reaction (—1).

The value of 0·015 for k_3/k_2 obtained by using chloride-ion solutions at 60° compares poorly with Cahn and Powell's value of 0·15 found at 50° by using sulphate solutions.

FIG. 2.

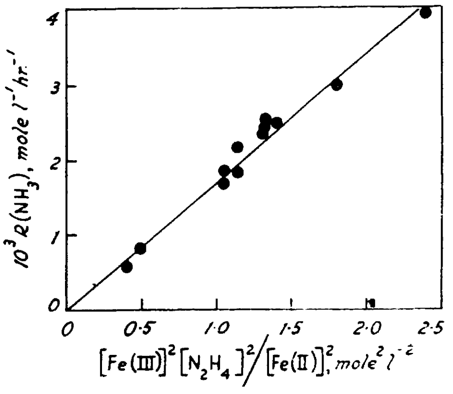

FIG. 3.

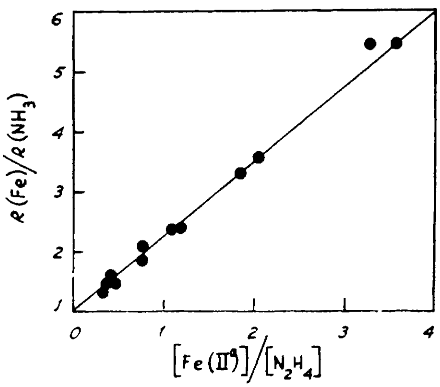

TABLE 1. $[H^+]$ = 1·00M; $[Cl^-]_{total}$ = 3·50M; Temp. = 60°.

Expt.	Time, hr.	10^2[Fe(III)], M	10^2[Fe(II)], M	$10^2[N_2H_4]$, M	$10^3R(NH_3)$	10^3R(Fe) (all in mole l.$^{-1}$ hr.$^{-1}$)	$10^3R(N_2H_4)$
1	1½	12·94	29·51	26·29	2·51	5·98	3·38
	2½	12·40	30·05	25·97	2·15	5·15	2·90
2	1½	8·60	19·70	26·37	2·43	4·57	2·97
	2½	8·16	20·15	26·11	1·84	3·75	2·32
3	1	4·27	9·89	26·60	2·38	3·35	2·62
	2	3·96	10·20	26·36	1·82	2·73	2·05
4	1½	22·93	10·02	3·07	0·80	4·33	1·68
	2½	22·54	10·41	2·92	0·60	3·30	1·23
5	1½	6·33	10·60	25·92	3·95	5·99	4·46
	2½	5·83	11·10	25·55	3·00	4·50	3·38
6	1½	21·73	11·02	6·00	2·47	8·11	3·88
	2½	21·06	11·69	5·69	1·70	6·06	2·79
7	1½	2·31	5·22	26·46	1·90	2·50	2·05
	2½	2·09	5·43	26·29	1·42	1·83	1·52
8	1½	22·35	7·51	2·93	1·23	5·42	2·28
	2½	21·92	7·94	2·74	0·90	4·04	1·69
9	1½	17·15	8·09	5·93	2·45	7·00	3·59
	2½	16·56	8·68	5·63	1·66	5·00	2·50
10	1½	12·76	5·95	6·02	2·44	6·01	3·33
	2½	12·25	6·47	5·74	1·66	4·34	2·33
11	1½	12·19	4·59	5·65	3·28	6·73	4·14
	2½	11·63	5·15	5·31	2·12	5·00	2·84
12	1½	0·77	2·23	26·56	1·32	1·57	1·41
	2½	0·64	2·36	26·45	0·82	1·01	0·87
13	1	1·42	2·35	26·47	3·15	3·40	3·21
	2	1·15	2·61	26·22	1·75	2·00	1·81
14	1½	0·54	1·35	26·54	1·29	1·46	1·33
	2½	0·43	1·47	26·44	0·73	0·83	0·76

TABLE 2. $[H^+] + [HSO_4^-]$ = 1·60M; $[SO_4^{--}] + [HSO_4^-]$ = 1·10M; Temp. = 50°.

Expt.	Time, hr.	10^2[Fe(III)], M	10^2[Fe(II)], M	$10^2[N_2H_4]$, M	$10^3R(NH_3)$	10^3R(Fe) (all in mole l.$^{-1}$ hr.$^{-1}$)	$10^3R(N_2H_4)$
15	1½	16·08	5·75	3·17	3·44	4·62	3·74
	2½	15·68	6·15	2·86	2·38	3·28	2·61
16	1	13·71	3·30	3·17	5·13	5·88	5·32
	2	13·23	3·77	2·75	3·13	3·70	3·27
17	1	9·18	2·91	3·42	3·81	4·25	3·92
	2	8·81	3·28	3·10	2·55	3·01	2·67
18	1½	2·76	2·06	7·13	2·84	3·02	2·89
	2½	2·50	2·32	6·87	2·20	2·28	2·22

Although it seemed to us that such a variation in conditions could not cause so big a change in the ratio of velocity constants involving only one reactant species, we completed four experiments, summarised in Table 2, under similar conditions to certain of Cahn and Powell's experiments. The corresponding plot of $R(\text{Fe})/R(\text{NH}_3)$ against $[\text{Fe(III)}]/\sqrt{R(\text{NH}_3)}$ is shown as the broken line in Fig. 1. In a similar manner to the interpretation of the chloride-ion experiments, we conclude that $k_3/k_2 = -0{\cdot}005 \pm 0{\cdot}025$. Since negative values are inadmissible, k_3/k_2 must lie between 0 and 0·02. Comparison of the rates of hydrazine disappearance at 1 (or 1½) and 2 (or 2½) hours in experiments 15—19 shows that there is a very much bigger change than can be accounted for by the change in the product of iron(III) and hydrazine concentrations, and hence that retardation by iron(II) is important at these concentrations in sulphate solutions.

We ascribe the difference between our value of k_3/k_2 and that of Cahn and Powell to their neglect of reaction (—1) in the interpretation of their results. As the concentration of iron(II) increases during their experiments, the stationary concentration of N_2H_3 radicals will fall relatively to the value to be expected in the absence of reaction (—1). Reference to equation (9) then shows that, as the overall reaction proceeds, $R(\text{Fe})/R(\text{NH}_3)$ values in the presence of reaction (—1) will increase relatively to the corresponding $R(\text{Fe})/R(\text{NH}_3)$ values in the absence of this reaction. The instantaneous stoicheiometry, $R(\text{Fe})/R(\text{N}_2\text{H}_4)$, is related to $R(\text{Fe})/R(\text{NH}_3)$ by the expression :

$$R(\text{Fe})/R(\text{N}_2\text{H}_4) = 4/\{1 + 3R(\text{NH}_3)/R(\text{Fe})\} \quad . \quad . \quad . \quad . \quad (15)$$

and hence will increase more rapidly than their treatment suggests. The overall stoicheiometry is therefore higher than would be observed if reaction (—1) did not take place. Since Cahn and Powell do not allow for this effect, they can only ascribe their limiting overall stoicheiometry of 1·21 to a significant contribution by the disproportionation reaction (3).

At *ca.* 20° in sulphate solutions we have observed overall stoicheiometries as low as 1·03 when using cerium(IV) and cobalt(III). Simple calculation using (15) and (9) shows that under these conditions k_3/k_2 cannot exceed 0·02.

The experiments discussed above do not give any information about the charge on the various radicals and intermediates, which may act as acids or bases. We have therefore represented them as uncharged, and, for convenience, hydrazine as N_2H_4 although in our conditions $N_2H_5^+$ and $N_2H_6^{++}$ are present.

EXPERIMENTAL

Hydrazine dihydrochloride (from B.D.H.) was twice recrystallised. In stock solutions, hydrazine, chloride ion, and hydrogen ion in excess of that bound as $N_2H_5^+$ were determined by appropriate titrations. Iron(II) chloride and iron(II) sulphate stock solutions were prepared by dissolving weighed amounts of Hilger H.H.P. iron in excess of hydrochloric or sulphuric acid. Iron(III) chloride and iron(III) sulphate stock solutions were prepared by oxidation of the corresponding iron(II) solutions with inhibitor-free hydrogen peroxide, the excess of which was removed by gentle heating. Iron(II), iron(III), and hydrogen ion were determined in these stock solutions by appropriate methods. These iron solutions were kept in absence of light, the iron(II) solutions under nitrogen. All other stock solutions were made up from " AnalaR " reagents, and concentrations were determined where necessary by appropriate methods.

In the kinetic experiments in chloride-ion solutions a constant initial hydrogen-ion concentration was desired, and hence it was necessary to know the second dissociation constant of hydrazine, $K_2 = [\text{H}^+][\text{N}_2\text{H}_5^+]/[\text{N}_2\text{H}_6^{++}]$, since the initial concentration of this reagent was varied from 0·269M to 0·0336M in different experiments. By using picric acid as an indicator, K_2 was estimated as 6 ± 2 mole l.$^{-1}$ at 60° and ionic strength 3·5 by measurement of the optical density of solutions at 360 mμ. A Unicam SP500 spectrophotometer was used for these and other optical measurements. The initial hydrogen-ion concentration was 1·00; the error due to the uncertainty in K_2 is ±0·012M. Changes due to liberation of hydrogen ions during reaction were not greater than 0·03M-H$^+$.

Iron(III) forms various complexes with chloride ions (Gamlin and Jordan, *J.*, 1953, **1435**) and a high concentration of chloride ions was therefore used to minimise changes in the proportion of these complexes and to maintain a high ionic strength. Sodium chloride was used to bring the total concentration of chloride ions to 3·50M. The maximum concentration of iron(III) used was 0·23M, and experiments showed that, with such an excess of chloride over iron(III), alterations of the order 10% in the chloride-ion concentration, with consequent changes in the ionic strength, caused negligible changes in the rate of reaction. The ionic strength of the solutions cannot be estimated accurately but is probably slightly less than 3·5 and does not vary greatly from one experiment to another.

In the reactions in sulphate solutions a large excess of sulphate could not be used. From Whiteker and Davidson's results (*J. Amer. Chem. Soc.*, 1953, **75**, 3081) we conclude that in these solutions iron(III) is mainly in the form $Fe(SO_4)_2^-$. Accordingly, solutions were made up 1·60M in hydrogen ion, and twice the corresponding concentration of iron(III) plus 1·10M in sulphate ion, giving a concentration of free sulphate plus bisulphate of 1·10M. The second dissociation constant of sulphuric acid increases considerably with ionic strength (Bray and Liebhafsky, *ibid.*, 1935, **57**, 51), and under our conditions is probably of the order 0·1—0·3 mole $l.^{-1}$. Hence the free hydrogen-ion concentration lies within the range 0·5—0·8M.

Reactions were carried out under pure nitrogen in absence of light. A mixture of all the reagents except the appropriate hydrazine stock solution was outgassed with nitrogen and allowed to come to equilibrium in a thermostat, and the reaction was started by adding the outgassed hydrazine solution. Two samples were withdrawn for ammonia and iron analyses within a few minutes of mixing. For most of the experiments four other pairs of samples were withdrawn at hourly intervals.

Ammonia was estimated in one of the samples in the following manner. Hydrazine was removed by addition of a small excess of potassium iodate and the iodine so formed by sodium sulphite. Excess of sulphite was removed by boiling. The solution was transferred to a small distillation apparatus and made alkaline with sodium hydroxide. Ammonia was distilled into 2% boric acid solution and titrated with 0·01M-hydrochloric acid with mixed bromocresol-green and methyl-red indicator following Ma and Zuazaga's method (*Ind. Eng. Chem. Anal.*, 1942, **14**, 280).

Iron(II) or iron(III), depending on which was present in smaller amount, was estimated in the second sample. Iron(II) was estimated by measurement of the optical density at 510 mμ of the tris-*o*-phenanthroline complex in a citrate buffer (Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313). Iron(III) was estimated by measurement of the optical density at 303 mμ of a sample diluted in 0·4M-sulphuric acid. The extinction coefficient of such iron(III) sulphate solutions varies with temperature (Dewhurst, *Trans. Faraday Soc.*, 1953, **49**, 1175), and is affected slightly by the presence of low concentrations of chloride ions as obtained in diluted samples from the experiments in chloride-ion solutions. Appropriate calibration curves were made to correct for these two effects. Iron(II), iron(III), and ammonia were analysed by using the above methods in solutions of known composition, similar in all respects to those of the reaction solutions. We conclude that iron(II) and iron(III) can be determined in the reaction solutions with an accuracy of ±1%, and ammonia with an accuracy of ±2%.

Plots of the iron and ammonia concentrations against time were made from these results, and the gradients found at the times quoted in Tables 1 and 2. Since only a part of the reaction was followed, the changes in rates were not large in a given experiment. In most cases these changes were not greater than three-fold and were never larger than six-fold. We consider that $R(NH_3)$ can be estimated to ±5% and R(Fe) to ±6% from these plots. Since there is a comparatively small change in $R(Fe)/R(NH_3)$ over a given experiment, this quantity can be compared with $\Delta[Fe(II)]/\Delta[NH_3]$ values taken over hourly intervals, and we conclude that $R(Fe)/R(NH_3)$ can be obtained to ±5%.

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