The theory of intermediate formation of manganic salt, developed to account for the above effect, was confirmed by an experimental study of the reaction between manganic acetate and hydrazine sulfate in acetic acid solution,

The reaction may be represented by the equation, $N_2H_5^+ + Mn^{+++} = NH_4^+ + 1/2N_2 + H^+ + Mn^{++}$, the amounts of nitrogen and ammonia formed and oxidizing agent used up differing only slightly from those demanded by this equation.

These deviations vary in such a way as to indicate that the above is a true stoichiometric (or "pure") reaction, which would be realized as a limit if the small deviations due to disturbing side reactions could be eliminated.

A theory of mechanism is proposed, according to which one hydrogen is removed from hydrazine in the first step, and the intermediate product is rapidly transformed into nitrogen and ammonium ion.

BERKELEY, CALIFORNIA

THE OXIDATION OF HYDRAZINE. IV
THE INTERACTION OF HYDRAZINE AND FERRIC SALT IN ACID SOLUTION

BY EUSTACE J. CUY

In the preceding paper it was shown that hydrazine reacts with a manganic salt in acid solution to form ammonium ion and nitrogen:

$$N_2H_5^+ + \oplus = NH_4^+ + 1/2N_2 + H^+ \tag{1}$$
$$\text{or} \quad N_2H_4 + \oplus = NH_4^+ + 1/2N_2 \tag{1a}$$
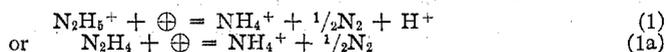
According to the mechanism there proposed, such a reaction is to be expected only with an oxidizing agent which on being reduced undergoes a change of one equivalent per mole, as $Mn^{+++} \longrightarrow Mn^{++}$. The converse is not necessarily true, since the intermediate product, N_2H_2, formed in the first step may react with the oxidizing agent more rapidly than it yields ammonium ion and nitrogen. It was therefore considered of interest to determine whether another oxidizing agent of the same type would react according to Reaction 1. Ferric ion was the oxidizing agent chosen.

Browne and Shetterly[1] state that at 100° with excess of hydrated ferric oxide in the presence of sulfuric acid (the concentration of acid in the solution varying from about 2 N to 8 N) large amounts of ammonia but no hydronitric acid were formed. From the results of their two quantitative experiments in approximately 3 N and 7 N acid, respectively, it may be

[1] Browne and Shetterly, THIS JOURNAL, 31, 791 (1909).

calculated that 1 mole of hydrazine reacted with 1.41 and 1.53 equivalents of ferric salt if ammonium ion and nitrogen are assumed to have been the only products. The values of this ratio R are low in comparison with the value 4 for the reaction,

$$N_2H_5^+ + 4 \oplus = N_2 + 5H^+ \tag{2}$$
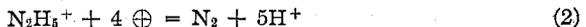
and therefore furnish evidence in support of Reaction 1 in this case. It seemed probable that the oxidizing agent was really ferric ion and not ferric hydroxide, and therefore that our experiments would yield similar results.

The reaction between Fe^{+++} and $N_2H_5^+$ is slow at room temperature, but is rapid at high temperature. Accordingly in our experiments each reaction mixture was heated to 80° or 90°, or the acid ferric sulfate solution was heated to this temperature and the hydrazine sulfate solution then added. In general a large excess of ferric sulfate was used, the quantity of sulfuric acid and the total volume were accurately known, the mixture was heated at 80–90° for ·ten minutes and cooled, and the ferrous salt formed in the reaction was determined by titration with permanganate.

The permanganate was standardized by the usual method against Bureau of Standards sodium oxalate and found to be 0.0904 N. The hydrazine sulfate, standardized by the iodic acid method,[2] was 0.0905 M. Since these concentrations are practically the same, the volume ratio, permanganate/hydrazine, is a measure of R, the number of equivalents of oxidizing agent required per mole of hydrazine. The stock ferric solution was 6 M ferric ammonium sulfate, $FeNH_4(SO_4)_2.12H_2O$, and contained enough sulfuric acid to make it 0.3 N.

In the preliminary experiments R was found to be between 1 and 2, as expected, but the results were not strictly reproducible. The disturbing factor was found to be the acidity of the solution, and in the later work the concentration of acid in each solution was carefully controlled.

Before discussing the results we shall consider whether the low values of R are inherent to the ferric-hydrazine reaction or due to the permanganate added later. If the ferric-hydrazine reaction were slow even at 90°, then the permanganate-hydrazine reaction would account for our results, as has been shown in the preceding paper. To decide this point the following method was devised. Two experiments were performed with 10 cc. of hydrazine solution, one by the above procedure, and the other identical, except that excess sodium vanadate was also added. In the latter case any hydrazine not oxidized by the ferric salt would have been oxidized by the vanadic acid according to Reaction 2,[3] and consequently more permanganate would have been required. However, the results were almost identical: for example, 13.85 and 13.80 cc. of permanganate

[2] Bray and Cuy, THIS JOURNAL, 46, 858 (1924).

[3] Compare Ref. 2, p. 873.

by the regular procedure, and 13.90 and 13.75 cc. when vanadate was added. (The corresponding value of R is 1.38 to 1.385.) It follows that the low results are due to the ferric-hydrazine reaction alone.

Three groups of results are summarized in Table I, the experiments in each group being arranged in the order of increasing concentration of acid, Col. 3. The experimental conditions are given at the head of the table. The last column shows the values of R, equivalents of oxidizing agent required per mole of hydrazine.

TABLE I

THE REACTION BETWEEN FERRIC SALT AND HYDRAZINE AT VARIOUS CONCENTRATIONS OF
SULFURIC ACID

10 cc. of 0.0905 M $N_2H_4.H_2SO_4$ in each experiment. 10 Cc. of 6 M $FeNH_4(SO_4)_2$ in Expts. 1–17; 30 cc. of 6 M $FeNH_4(SO_4)_2$ in Expts. 18–22.
Each mixture was heated at 80–90° for 10 minutes. The reagents were mixed at room temperature in Expts. 8–22. The hydrazine was added to the hot solution in Expts. 1–7.

Expt.	Total volume in cc.	Equiv. concn. of acid	0.0904 N KMnO$_4$ used Cc.	R
1	25	0.12	17.40	1.74
2	50	0.66	13.94	1.39
3	25	1.3	13.64	1.36
4	25	1.3	13.45	1.34
5	45	3.4	13.31	1.33
6	25	7.3	14.43	1.44
7	45	8.1	14.27	1.43
8	40	0.125	17.40	1.74
9	40	0.38	14.95	1.49
10	25	1.3	13.55	1.35
11	40	2.07	13.23	1.32
12	40	2.1	13.35	1.33
13	40	5.1	13.58	1.36
14	40	5.2	13.55	1.35
15	40	10.4	15.27	1.53
16	40	12.1	16.99	1.70
17	40	15.0	16.69	1.67
18	80	0.11	19.17	1.92
19	80	0.36	18.11	1.81
20	80	1.1	15.21	1.52
21	80	2.6	14.50	1.45
22	80	5.1	14.52	1.45

By plotting the values of R against the acid concentration it was shown that the results are fairly reproducible between 0.1 and 5 N acid, but only roughly so at higher concentrations, and that the points for Expts. 1–7 lie on the same curve as those for Expts. 8–17. From the latter fact it follows that it is immaterial whether the reagents are mixed at room temperature or the hydrazine sulfate solution is added to the hot ferric solution.

In these experiments with 10 cc. of the ferric solution, in which the

initial ratio of $Fe^{+++}/N_2H_5^+$ was about 66, R = 1.74 at 0.12 N acid, decreases rapidly with increasing acidity, passes through a rather flat minimum between 1 and 5 N acid, and increases gradually at higher concentration. The lowest value is about 1.32 in the neighborhood of 2 N acid.

The variation in the total volume between 25 and 50 cc. shown in the second column of the table seems to have little or no effect.

The results of Expts. 18–22, with a larger excess of ferric salt, 200 fold instead of 66, lie on a similar curve, but R is larger at all concentrations of acid. The minimum value is 1.45 in this series. The increase in the excess of the oxidizing agent thus favors Reaction 2 at the expense of Reaction 1. Confirmatory evidence was given by the results of another series of experiments (not included in the table), in which the excess was 33 fold: the minimum value of R was lower, between 1.25 and 1.27.

It is therefore to be expected that R will continue to decrease as the ratio of the ferric to hydrazine concentration in the reaction mixture is made smaller and smaller. The extreme condition would be to add the ferric solution drop by drop to a hot, acidified hydrazine solution. This investigation was interrupted (in the summer of 1922) before the experiment could be performed. Conclusive proof that Reaction 1 is the limiting reaction in this case is therefore lacking, but the present results and especially the analogy to the manganic-hydrazine reaction furnish strong evidence in favor of this conclusion.

The effect of the excess of ferric salt in increasing R is in accord with the assumption that some of the primary intermediate product, N_2H_3 or $N_2H_4^+$, reacts with ferric salt while the remainder is decomposing. The proportion oxidized would be expected to increase with the excess of ferric salt.

The observed increase of R at low acid concentration is probably related to the fact, referred to in earlier papers, that Reaction 2 is usually the main reaction in the presence of alkali, and thus appears to be the beginning of the transition to R = 4 in alkaline solution. The alkaline ferricyanide reaction, discussed in the second paper of this series, is of interest in this connection. Although the change from ferri- to ferrocyanide involves only one equivalent per mole of the oxidizing agent (compare the Fe^{+++}-Fe^{++} change), nevertheless the reaction requires four equivalents per mole of hydrazine. The apparently general effect of alkali may be due to a relatively high rate of reduction by intermediate hydrazine compounds, as N_2H_3 and N_2H_2, in alkaline solution, or to a relatively high rate of decomposition of these intermediate compounds in acid solution.

Summary

In the reaction between hydrazine and ferric salt in sulfuric acid solution, the amount of oxidizing agent required is between 1 and 2 equivalents per

mole of hydrazine. With constant large excess of ferric salt it varies with the acid concentration, and passes through a minimum in the neighborhood of 2 N acid. With constant acid concentration the value decreases with decreasing excess of the ferric salt. The results obtained and the analogy with the manganic-hydrazine reaction indicate that the limiting reaction is $N_2H_5^+ + Fe^{+++} = NH_4^+ + \frac{1}{2}N_2 + H^+ + Fe^{++}$.

The conclusion that this type of reaction is not likely to occur in alkaline solution is supported by the fact that the amount of ferric salt required increases with decreasing acid concentration, and by the behavior of hydrazine in alkaline solution towards ferricyanide and other oxidizing agents.

BERKELEY, CALIFORNIA

INVESTIGATIONS ON THE PLATINUM METALS. V
THE ANALYTICAL SEPARATION OF COPPER FROM THE PLATINUM METALS[1]

BY WM. H. SWANGER[2] AND EDWARD WICHERS[3]

The various methods that have been proposed for the analysis of crude platinum and of platinum alloys containing copper usually provide for the determination of copper in the solutions from which silver and gold and the bulk of the platinum metals have been previously removed.

From such solutions copper is precipitated by hydrogen sulfide together with all of the remaining quantity of the platinum metals. The precipitate usually includes most of the rhodium that was in the sample. This mixture of sulfides is ignited strongly in air and then leached with nitric acid. It is the supposition that copper dissolves completely while the platinum metals remain as the undissolved residue.

It has been the experience in this Laboratory that nitric acid does not separate the copper completely from such an ignited mixture, leaving as a residue all of the platinum, iridium and rhodium. The following experiments were made in order to determine to what extent this separation may be in error.

Extraction with Nitric Acid.—Solutions were prepared containing approximately 50 mg. of copper with the amount of noble metal indicated in Col. 2 of Table I. The metals were precipitated by hydrogen sulfide. The mixed sulfides were ignited strongly in air and then leached with 20 cc. of nitric acid (1 volume of nitric acid, d. 1.42, diluted with 1 volume of