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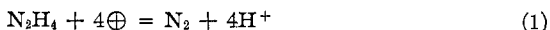
THE OXIDATION OF HYDRAZINE. III. THE LIMITING REACTION OF PERMANGANATE AND MANGANIC SALTS IN ACID SOLUTION WITH HYDRAZINE

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It has been known and recently confirmed^{1,2} that hydrazine is oxidized quantitatively according to the equation



by oxidizing agents, including such mild ones as iodine and ferricyanide and strong ones as hypochlorous acid and bromine. On the other hand, large deviations from this reaction have been observed³ with many oxidizing agents, as permanganate, dichromate, hydrogen peroxide and peroxysulfate. Even with the most powerful oxidizing agents the deviation is not in the direction that too much oxidizing agent is used, which would correspond to the oxidation of hydrazine beyond the nitrogen stage, but is always in the opposite direction, the amount of oxidizing agent varying from four to less than two equivalents for each mole of hydrazine. This ratio will be designated by the letter R.

With the hope of elucidating this striking phenomenon in at least one case, we undertook the study of some of these reactions. Our plan was to determine the effect of all variables on the results, and to find out whether by suitable variation of the experimental conditions the deviation from Reaction 1 could be increased until a definite limiting reaction was reached. In the preceding paper² the limit of R in the dichromate reaction was shown to be below three, but the limiting reaction was not actually identified. The present investigation of the permanganate reaction, however, has led to a more satisfactory conclusion.

Bach⁴ was the first to note the erratic nature of the results obtained in the permanganate-hydrazine reaction. "It was attempted to titrate hydrazine hydrochloride with potassium permanganate, but each titration gave a different result."

Roberto and Roncali⁵ state that in acid solution the reaction occurs according to Equation 1 and "for every four moles of permanganate five moles of nitrogen are liberated." Medri⁶ states that two instead of four equivalents of oxidizing agent are used up per mole of hydrazine.

¹ Bray and Cuy, *THIS JOURNAL*, **46**, 858 (1924).

² Cuy and Bray, *II*, *ibid.*, **46**, 1786 (1924).

³ Compare Browne and Shetterly, *ibid.*, **31**, 783 (1909).

⁴ Bach, *Z. physik. Chem.*, **9**, 253 (1892).

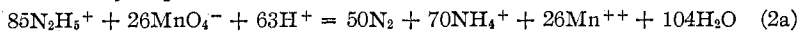
⁵ Roberto and Roncali, *Chem. Centr.*, **1904**, II, 616.

⁶ Medri, *Gazz. chim. ital.*, **36**, I, 373 (1906).

Petersen⁷ studied this reaction under a definite set of conditions and determined the amount of permanganate used up and nitrogen and ammonia formed. He represented his results by the equation



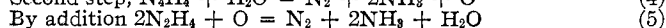
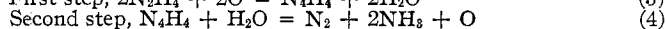
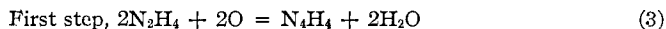
which we may express in the form⁸



The number of molecules involved in this reaction proves almost conclusively that it is not a "pure" reaction but a "mixture" of several, a fact which, apparently, Petersen realized, since he describes his equation as "wenig ansprechende." The conditions which he chose were: to a solution of hydrazine sulfate in 10% sulfuric acid at a temperature of 60–70° potassium permanganate was added in excess from a buret with stirring, oxalate was added at once, and the titration was completed in the usual way with permanganate. Petersen found also that more permanganate was required when the concentration of sulfuric acid was below 6% or above 12%, and that in boiling concd. sulfuric acid solution all the hydrazine was oxidized to nitrogen, since no ammonia could be detected. According to his equation the value of R is 1.53 equivalents per mole of hydrazine, instead of four as required by Equation 1.

Finally Browne and Shetterly⁹ in their study of the oxidation of hydrazine by a large number of oxidizing agents investigated this reaction also. They checked Petersen's result fairly well when working under similar conditions, but demonstrated that also a little hydronitric acid was formed when precautions were taken to prevent its reaction with permanganate, that is, when dilute permanganate was added gradually to the boiling hydrazine solution. In two other hydrazine reactions with manganese dioxide and ferric oxide in acid solution, the products were nitrogen and ammonia with little or no hydronitric acid.

From their results as a whole Browne and Shetterly⁹ concluded that at least three reactions must be assumed, which take place simultaneously but in widely different proportions. In these there are formed: nitrogen alone (compare Equation 1), hydronitric acid and probably ammonia, and finally nitrogen and ammonia but no hydronitric acid. For the last type they suggested Reaction 5 and the following theory of its mechanism.



This theory did not seem probable to us. One difficulty is that the second step involves the formation of two equivalents of the oxidizing agent used in the first step; this is a result of the assumption that each

⁷ Petersen, *Z. anorg. Chem.*, **5**, 1 (1894).

⁸ For the evidence that hydrazine is present mainly as N_2H_5^+ , see Ref. 2, Footnote 2.

⁹ Browne and Shetterly, *THIS JOURNAL*, **31**, 228 (1909).

molecule of hydrazine loses two atoms of hydrogen in the first step. Moreover, the experimental evidence in favor of Reaction 5 was not conclusive. Some such reaction must be assumed, but whether in the permanganate reaction the ratio R can be shown to approach 1 as a limit, as required by Equation 5, was not known.

Our experimental procedure was to titrate hydrazine and permanganate directly against each other in sulfuric acid solution, using the appearance or disappearance of the pink tint as the end-point. While we did not attain exact reproducibility under one set of conditions, the results in several duplicate experiments were sufficiently concordant to encourage us to use this simple method in searching for a variable that would produce a large and definite change in the results.

The permanganate was standardized against Bureau of Standards oxalate. The hydrazine solution was made by dissolving 0.1 mole of the sulfate to give one liter of solution and was not further analyzed, since our analytical methods had not yet been developed.

In a large number of experiments which will not be given in detail and in which the experimental conditions were varied one at a time, it was found that 1.5 to 1.8 equivalents of permanganate were sufficient to convert all of the hydrazine to nitrogen and ammonia. The results, however, were in general obstinately insensitive to large experimental variations. No definite trends were obtained when the following experimental conditions were varied: the temperature and the acidity of the solution during the reaction, the concentration and the order of mixing of the reagents (hydrazine and potassium permanganate), the presence or exclusion of atmospheric oxygen, and finally the presence of crushed glass (to increase the surface and favor catalytically any surface reactions). While the results were only roughly concordant, they showed that probably none of these factors was the cause of the lowering of R from 4 to between 1 and 2. It was evident that at least one variable had been overlooked which by adjusting itself automatically caused such large variations as to mask any relatively small effects which the above-mentioned variables have upon the results.

A clue to this determining factor was obtained when, after titrating a portion of permanganate and hydrazine sulfate solution, a second titration was performed in the beaker containing the reaction products of the first titration. The permanganate needed was about 10% less. A third titration in the same solution gave a still lower result by 3% and further titrations showed a decrease which became less and less marked. The results of three such series of experiments are given in Table I and Fig. 1.

In Table I, Col. 1 gives the number of the experiment, the amount of sulfuric acid present initially in each series, and the order of mixing the reagents; thus H to P in Series A and B means that the hydrazine sulfate

solution was added gradually to the permanganate until only a faint pink color remained. The volumes of permanganate and hydrazine used in the successive titrations are given in Cols. 2 and 3 and their ratio R in the fifth column. R is the number of equivalents of permanganate per mole of hydrazine. Col. 4 gives the total volume of 0.1 N potassium permanganate used by the end of the experiment in question, and is a rough measure of the amount of the reaction product, Mn^{++} (or NH_4^+) present in the solution. The approximate total volume of the solution in any experiment may be obtained by adding the volumes of the sulfuric acid, hydrazine and permanganate solutions already used, little or no water having been added.

TABLE I
VARIATION OF THE PERMANGANATE-HYDRAZINE REACTION IN ACID SOLUTION AS A
FUNCTION OF THE AMOUNT OF REACTION PRODUCTS PRESENT

Compare Fig. 1

	Expt.	0.1 N $KMnO_4$ Cc.	0.1 M $N_2H_4SO_4$ Cc.	0.1 N $KMnO_4$ already used Cc.	Ratio, R , $KMnO_4$ to $N_2H_4SO_4$
Series A	1	8.91	5.20	8.91	1.71
30 cc. of 6 N H_2SO_4 (and crushed glass)	2	9.85	6.35	18.76	1.55
	3	9.39	6.25	28.15	1.50
Order H to P	4	10.07	7.05	38.22	1.43
	5	11.15	7.70	49.39	1.45
	6	10.33	7.10	59.72	1.45
	7	7.11	4.95	66.83	1.44
Series B	1	11.22	7.00	11.22	1.60
15 cc. of 6 N H_2SO_4	2	11.22	7.45	22.44	1.51
Order H to P	3	11.49	8.10	33.93	1.42
	4	11.75	8.05	45.68	1.46
	5	10.38	7.15	56.06	1.45
	6	10.59	7.30	66.65	1.45
Series C	1	9.12	5.40	9.12	1.69
15 cc. of 6 N H_2SO_4	2	8.38	5.30	17.50	1.58
Order P to H	3	8.48	5.45	25.98	1.55
	4	8.22	5.55	34.20	1.48
	5	7.53	5.10	41.73	1.47
	6	7.64	5.25	49.37	1.45
	7	8.59	5.95	57.96	1.45
	8	7.91	5.40	65.87	1.46

In Fig. 1 the values in Col. 5 of Table I are plotted as ordinates against those of the fourth as the abscissas. The single curve corresponds closely with the data of Series A, and also represents fairly well the results of the two other series. The permanganate-hydrazine ratio R decreases very rapidly at first and then more slowly, approaching asymptotically a value only slightly higher than 1.4.

It is almost superfluous to mention that the order of mixing (contrast Series C with A or B) is, at most, of secondary importance.

In each series of experiments there was a steady increase in the volume and decrease in the acidity of the solution, but it had been found in earlier experiments that these factors had little influence. This was confirmed as follows. Between Expts. 5 and 6 of Series B, 45 cc. of 6 *N* sulfuric acid was added, thereby increasing the volume from 105 to 150 cc. and the acidity from 0.9 *N* to 2.4 *N*. The ratio, however, remained constant.

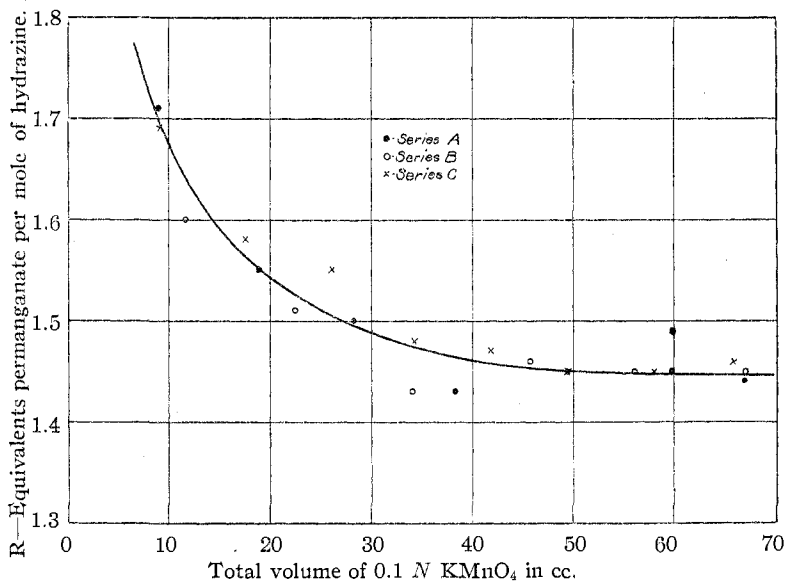


Fig. 1.—Compare Table I.

That ammonium salt, whose concentration increased steadily in successive experiments, was not the determining factor was proved by separate determinations in which an excess of solid ammonium sulfate was added, but no effect on the ratio was observed.

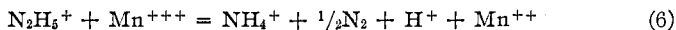
After eliminating the volume, acidity and ammonium salt concentration, the only variable remaining, namely, the manganous salt concentration was shown to be the factor responsible for the trend by the results of a number of experiments in which manganous salt was added initially; the permanganate-hydrazine ratio was always smaller than when no manganous salt had been added, and in general a sudden decrease in the ratio could be caused by a sudden increase in the concentration of the manganous salt.

Regardless of any theory, it can be stated that the amount of permanganate used up per mole of hydrazine depends primarily upon the concentration of manganous salt present in the reaction medium during the reaction.

The results can be accounted for as follows. It is well known that permanganate in acid solution oxidizes manganous salts fairly rapidly to manganic salts. It is therefore evident that in the case of the permanganate-hydrazine reaction, except for the first instant, we really have two distinctly different oxidizing agents acting simultaneously on the hydrazine, namely, the manganic salt and the permanganate.

How permanganate, *per se*, would oxidize hydrazine in acid solution if the manganous salt could by some means be removed as fast as it was formed is not known; but by analogy with the behavior of iodate, vanadate and dichromate it seems justifiable to assume that it would oxidize hydrazine mainly to nitrogen¹⁰ corresponding to the ratio $R = 4$.

The manganic salt, on the other hand, must react with hydrazine so as to give a value of R much lower than 4 if it is responsible for the low values found in the permanganate experiments in acid solution. The simplest possible reaction is



in which $R =$ one equivalent of the oxidizing agent per mole of hydrazine.

¹⁰ This assumption is supported by the behavior of permanganate towards hydrazine in alkaline solution. Here the oxidation of hydrazine to nitrogen, Reaction 1, is practically quantitative. The results of Sabanejeff [*Z. anorg. Chem.*, **17**, 480 (1898); **20**, 21 (1899)] are on the average only about 1% low. Browne and Shetterly,⁹ were able to obtain only small amounts of hydronitric acid, and this only when an excess of permanganate was avoided. We performed three experiments in which the hydrazine (accurately standardized),¹ was added to an excess of permanganate, and the excess determined by adding iodide and acid and titrating with thiosulfate. In 1, 3 and 6 *N* sodium hydroxide solution the ratio, R , was found to be 3.87, 3.89 and 3.91 equivalents per mole of hydrazine. No precautions were taken to exclude air in our experiments.

Both *manganate* and *manganese dioxide*, in the presence of an excess of alkali, also oxidize hydrazine mainly to nitrogen. This could have been deduced from the above experiments with permanganate, since the color changes during the addition of hydrazine showed the presence of these substances during the reaction; but the same conclusion was reached from a large number of experiments with an excess of each substance. (These experiments will not be described in detail.) The chief source of error was shown to be the presence of oxygen of the air, which oxidized the product manganous hydroxide (and possibly also the hydrazine), thus yielding low results. The more completely this error was eliminated, the more closely was the value $R = 4$ approached. This limit was actually reached in the manganate experiments. It is therefore evident that the limiting value $R = 4$ would have been approached or even realized in the *permanganate* experiments if the air had been excluded.

In the experiments with *manganese dioxide*, colloidal solutions (see below) were used. While the results were not as reproducible and R was usually not as large as in the manganate experiments, there was no doubt that Reaction 1 was the main reaction in alkaline, neutral and slightly acid solutions. The results of Browne and Shetterly⁹ with solid manganese dioxide in sulfuric acid solution show wide variations. The values of R , which have been calculated, were nearly all between 2 and 3, but one was as low as 1.7 and another as high as 3.2. We have concluded that there is no evidence against the possibility that manganese dioxide itself can react with hydrazine mainly according to Reaction 1.

If the above theories are accepted, then at the first instant in the permanganate-hydrazine reaction, when the concentration of Mn^{++} is zero, R is practically 4 (Reaction 1). As the reaction proceeds and the concentration of Mn^{++} increases, R decreases greatly, provided that MnO_4^- reacts with Mn^{++} more rapidly than with $N_2H_5^+$. It is at once evident that the presence of Mn^{++} initially will produce a lower average value of R , since this favors the formation of Mn^{+++} and consequently Reaction 6. In other words, the relatively slow reaction in which $R = 4$ is outdistanced by the two successive reactions for which $R = 1$. It may even be said that manganous salt catalyzes Reaction 6 at the expense of Reaction 1.

A satisfactory basis for explaining the vagaries of the permanganate-hydrazine reaction in acid solution has thus been attained. The lack of reproducibility of supposedly duplicate experiments is no longer mysterious, since the final result depends upon the relative rates of three reactions, two of which probably take place in steps. It seems probable that the rate of mixing the reagents will have a definite effect on the result, but we have no reliable data on this point.

Instead of continuing our work with permanganate, we decided to undertake a quantitative study of the manganic-hydrazine reaction, with the twofold object of testing the above explanation and of attempting to isolate the "pure" manganic reaction (Equation 6).

Quantitative Study of the Reaction between Manganic and Hydrazine Salts in Acid Solution

Of the various manganic salts reported in the literature, manganic acetate was chosen because it could easily be prepared in a pure crystalline form. The solid salt was prepared according to Christensen¹¹ by interaction of manganous acetate and potassium permanganate in proper proportions in glacial acetic acid solution; it was then washed with glacial acetic acid and kept in the dark. Small amounts of a solution in glacial acetic acid were prepared for each day's work, since the solution changes strength on standing. The mixture was heated for a short time not above 50° and was then filtered. This seemed necessary since the solid dissolved rather slowly and owing to its very deep color it was impossible to be sure that the solution was homogeneous and did not contain suspended solid salt.

The solution was standardized at the beginning and end of each day according to the method of Skrabal¹² by adding an excess of iodide and determining the liberated iodine by means of thiosulfate. The solution remained essentially unchanged during the day.

The thiosulfate was standardized as usual against standard perman-

¹¹ Christensen, *Z. anorg. Chem.*, **27**, 321 (1901).

¹² Skrabal, *ibid.*, **42**, 3 (1904).

ganate after the latter had reacted with an excess of potassium iodide in acid solution. The hydrazine was analyzed according to the iodic acid method of Bray and Cuy.¹

The usual procedure was to pipet into a glass-stoppered vessel definite volumes of the two analyzed solutions, hydrazine sulfate and manganic acetate, the latter in excess, and after three or more minutes to determine this excess by adding potassium iodide and titrating with thiosulfate solution.

The results are collected in Table II. Col. 1 gives the number of the experiment; Col. 2, the volume of manganic acetate calculated in cc. of 0.1 *N* solution; and Col. 3, the volume of thiosulfate, also calculated in cc. of 0.1 *N* solution, equivalent to the excess of manganic salt. The results are shown in Col. 4, *R* being the number of moles (or equivalents) of manganic salt used up per mole of hydrazine. The last column is reserved for remarks; it shows for example the amounts of manganous salt added initially in various experiments in Series C and D and the corresponding molal ratio of manganous salt to hydrazine.

TABLE II

THE REACTION BETWEEN MANGANIC ACETATE AND HYDRAZINE SULFATE IN ACETIC ACID SOLUTION

9.02 Cc. of 0.1 *M* hydrazine used in Series A, B and C except in Expts. 7, 8 and 9 of Series B, in which 8.99 cc. was used; 5.86 cc. was used in Series D and E.

Expt.	Cc. of 0.1 <i>N</i> Mn ⁺⁺⁺	Cc. of 0.1 <i>N</i> thiosulfate	<i>R</i>	Remarks
SERIES A				
1	24.69	12.75	1.32	In Series A Mn ⁺⁺⁺ was added to N ₂ H ₅ ⁺ except in Expts. 3 and 4
2	24.69	12.77	1.32	
3	24.69	12.76	1.32	
4	24.69	12.81	1.32	
5	24.69	12.80	1.32	
SERIES B				
1	12.43	1.74	1.185	In Series B Mn ⁺⁺⁺ was added to N ₂ H ₅ ⁺ except in Expt. 5
2	16.44	5.74	1.19	
3	12.43	1.66	1.19	105 min., time of addition
4	12.43	1.68	1.19	
5	12.43	1.77	1.18	
6	20.63	9.84	1.20	100 min., time of addition
7	12.47	1.65	1.20	
8	12.47	1.62	1.21	
9	16.44	5.63	1.20	
SERIES C				
1	13.29	1.77	1.28	In Series C, D and E, N ₂ H ₅ ⁺ was added to Mn ⁺⁺⁺
2	13.29	1.77	1.28	
3	13.29	1.62	1.29	10 cc. of 3% Mn(Ac) ₂ .Mn ⁺⁺ /N ₂ H ₄ =3.32
4	13.29	1.17	1.34	
5	13.29	0.96	1.37	

TABLE II (Concluded)

Expt.	Cc. of 0.1 N Mn ⁺⁺⁺	Cc. of 0.1 N thiosulfate	R	Remarks
6	13.29	2.45	1.20	10 cc. of 0.33 M MnSO ₄ .Mn ⁺⁺ /N ₂ H ₄ = 3.66 25 cc. of 0.33 M MnSO ₄ .Mn/N ₂ H ₄ =9.15
7	13.29	1.79	1.28	
8	13.29	1.77	1.28	
9	13.29	1.64	1.29	
10	13.29	1.87	1.27	
SERIES D				
1	14.49	6.75	1.32	10 cc. of 0.225 M MnSO ₄ .Mn ⁺⁺ /N ₂ H ₄ = 0.95 25 cc. of 0.225 M MnSO ₄ .Mn ⁺⁺ /N ₂ H ₄ = 2.37 Excess of solid MnSO ₄ .Mn ⁺⁺ /N ₂ H ₄ is large 60 cc. of glacial acetic acid Manganic solution was made alkaline and heated 10 cc. of 0.1 N NaOH added, but solution still acid
2	14.49	6.75	1.32	
3	14.49	6.86	1.30	
4	14.49	6.79	1.31	
5	14.49	6.74	1.32	
6	14.49	6.74	1.32	
7	14.49	6.80	1.31	
8	14.49	6.83	1.31	
9	14.49	8.12	1.09	
10	14.49	7.64	1.17	
11	28.98	12.68	2.78	
12	14.49	5.90	1.47	
SERIES E				
1	13.74	6.27	1.28	Usual procedure Manganic solution was heated just to boiling Boiled for 4 min. A black ppte. formed
2	13.74	6.24	1.28	
3	16.63	8.96	1.31	
4	16.63	8.93	1.31	
5	16.89	0.75	2.75	
6	16.89	.37	2.82	

For reasons to be discussed later, the results of one series (obtained in one day) do not check numerically with those of another series. However, the results within each series are reproducible, and the trends and conclusions obtained, if not the numerical values, could be checked on the next day with a new manganic solution.

In Series A the time allowed for the reaction before the addition of potassium iodide was three minutes in the first four experiments and ten in the fifth. Similarly in Series B the time was three minutes in Expts. 1 and 2, 25 minutes in Expt. 3, 105 minutes in Expt. 4 and 100 minutes in Expt. 5. For these five experiments in Series B the values of R were 1.185, 1.19, 1.19, 1.19 and 1.18,¹³ respectively, showing that the reaction is complete in less than three minutes. Judging from the rate at which manganic acetate is decolorized upon coming in contact with the hydrazine, the reaction may be said to be instantaneous.

The order of mixing seems to have no noticeable effect upon the reaction, as can be seen by comparing Expts. 1 and 2 with 3 and 4 in Series A. This

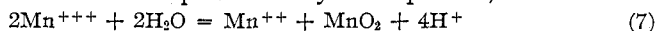
¹³ The inaccuracy is about 1% in this part of the investigation.

fact is brought out more strikingly in Expts. 4 and 5 of Series B to be described below.

That the reaction does not depend upon the amount of oxidizing agent present in excess of that needed is shown by Expts. 1, 2 and 6 of Series B, where the excess of Mn^{+++} was approximately 16%, 54% and 100%, respectively, and R was 1.185, 1.19 and 1.20.

Conversely, to determine the effect of an excess of hydrazine upon the course of the reaction was not easy by direct analytical methods, since the determination of hydrazine in the presence of manganous salts, acetic acid as well as the organic compounds present in small amounts as "impurities" had not been worked out. We therefore had recourse to the following expedient. When an amount of manganic solution, more than sufficient to oxidize a given amount of hydrazine solution, is added to the hydrazine drop by drop while the solution is vigorously stirred, the time of addition being very long, it is evident that during all of the experiment except the last stage, we have a reaction in which the reducing agent is present in large excess. If, therefore, the course of the reaction depends in any way upon the excess of hydrazine present during the reaction, such an experiment will show the effect. Expts. 4 and 5 of Series B are of this type. In the former, the total time of addition was 105 minutes and the manganic salt was added to the hydrazine; in the latter the order was the reverse and the time was 100 minutes. The values of R are 1.19 and 1.18, respectively, the agreement being perfectly satisfactory in spite of the fact that errors due to atmospheric oxidation of the manganous salt, to the better drainage of the pipet of the second reagent, etc., are in this procedure exaggerated. These two experiments are perhaps the most conclusive that the reaction is independent of the order of mixing, the time allowed for the interaction and the excess of either reagent.

Having studied the reaction and found that, independent of experimental conditions within wide limits, it occurs so that one molecule of hydrazine is eliminated by a little over one molecule of manganic salt, we attempted next to determine the reason for this small and to a certain extent variable deviation from unity. The most natural assumption was that the manganic solution contained small and variable amounts of one or more oxides of manganese in the ionically dissolved or colloiddally dispersed state, possibly in equilibrium with the manganic salt. One such hydrolysis reaction could be represented by the equation,



Oxides of manganese, like oxygen compounds in general, might react with hydrazine differently from manganic salts and probably according to Equation 1 to a large extent. This has been reported by Purgotti¹⁴ and confirmed by us.¹⁰

¹⁴ Purgotti, *Gazz. chim. ital.*, **26**, II, 559 (1896).

The following experiments performed to test this assumption were partly confirmatory. In experiments not given in the table colloidal manganese dioxide was added to the manganic solution with a pipet. It was prepared either by interaction of hydrogen peroxide and potassium permanganate and was free from both reagents, or according to the method of Cuy¹⁵ from ammonia and permanganate. Upon reaction with hydrazine it was found that the deviation from Reaction 6, which was about 35% in that series, increased to over 100%, showing that if oxides of manganese were actually present in our manganic solution the deviation from unity would be in the direction observed.

Decreasing the acidity ought (if the hydrolysis reaction is reversible) to increase the amount of oxide and *vice versa*. In Expts. 9 and 10 of Series D, where additional glacial acetic acid was introduced, there is a pronounced decrease in the deviation, as expected, corresponding to a decrease in the amount of oxide. Conversely, in Expts. 11 and 12 of the same series, alkali was added, in the latter case leaving the solution still acid, in the former making it actually alkaline (and in addition in this case it was heated). As we should expect the deviation is increased, and more so in the former case than in the latter.

Heating, which is known to favor hydrolysis and was found to favor the formation of a dark precipitate (presumably manganese dioxide), ought to increase the deviation. In Expts. 3 and 4 of Series E the manganic solution was heated to just below boiling, and in 5 and 6 it was boiled for four minutes before it was allowed to interact with hydrazine. Correspondingly the former experiments give a small increase in the deviation and the latter a very large one. In Expt. 11 of Series D, already mentioned above, the combined effect of moderate heating and increasing the alkalinity is seen.

Attention may now again be called to the fact that the deviations on different days were slightly different. This may be largely due to the fact that, in order to dissolve the acetate rapidly, gentle heating was resorted to. It is therefore probable that small amounts of oxide were formed to a different extent in different preparations, causing the small and variable deviations. This explanation involves the assumption that the reverse of the hydrolysis reaction (Equation 7 for example) takes place slowly. In support of this it may be noted that the precipitate formed by heating the manganic solution did not redissolve when the mixture was cooled and allowed to stand for some time.

Additional evidence that the particular hydrolysis reaction represented by Equation 7 does not take place rapidly in the reverse direction is furnished by the experiments on the effect of adding manganous salt, Series C; and Series D, Nos. 1-8. Instead of the expected lowering of the de-

¹⁵ Cuy, *J. Phys. Chem.*, **25**, 415 (1921).

viation of R from unity, which would correspond to a displacement of equilibrium, manganous sulfate seems to have no effect, and the acetate a small effect in the opposite direction.

Definite evidence of a rapid equilibrium reaction of the type of Equation 7 is thus lacking, but the theory of the presence of an oxide of manganese higher than MnO seems to furnish a satisfactory explanation of the deviations of R from unity in our experiments on the manganic-hydrazine reaction. Other factors are possible, of course. For example, there may have been present in small amount an organic reducing agent introduced with or formed from the acetates or acetic acid. No work has been done along this line.

It can therefore be stated, regardless of any theory, that the manganic-hydrazine reaction in acid solution shows only small deviations from the ratio $R = 1$ required by Equation 6; that this deviation can under certain conditions be decreased; and that from the increase of the deviation under other conditions, it is probable that, if certain possible sources of error were eliminated, the ratio would be exactly one.

As a further check on this reaction, the amounts of nitrogen and am-

TABLE III

SIMULTANEOUS DETERMINATION OF OXIDIZING AGENT USED UP AND OF AMMONIA AND NITROGEN FORMED IN THE REACTION BETWEEN MANGANIC AND HYDRAZINE SALTS IN ACETIC ACID SOLUTION

Volume in cc.	} of N_2H_4	= 47.12	Volume in cc.	} of Br_2	= 70.19
Molal concn.		= 0.09054	Normality		= 0.07975
Millimoles		= 4.267	Milli-equivalents		= 5.598
Volume in cc.	} of Mn^{+++}	= 28.86	Normality of thio.		= 0.1117
Normality		= 0.1809			
Millimoles		= 5.212			

1. Expt.....	1	2	3		
2. Volume of N_2 liberated.....	49.6	51.5	51.2		
3. Millimoles of N_2 liberated.....	2.214	2.300	2.287		
4. Volume of thio. (for Mn^{+++} excess in $\frac{1}{5}$ solution).....	} 0.72	} 0.75	} 0.80		
				.73	.73
5. Milli-equivalents of thio. (for Mn^{+++} excess).....	.405	.414	.436		
6. Millimoles of Mn^{+++} used up.....	4.807	4.798	4.776		
7. Volume of thio. (for $Br_2 + Mn^{+++}$)....	28.66	28.72	28.67		
8. Volume of thio. (for Br_2 excess alone)...	27.94	27.98	27.89		
9. Milli-equivalents of thio. (for Br_2 excess alone).....	3.121	3.125	3.115		
10. Milli-equivalents of Br_2 used up.....	2.477	2.473	2.483		
11. Millimoles of NH_3 formed.....			Av.		
12. Moles of manganic	} per mole of hydrazine	1.126	1.124	1.119	1.12 (=R)
13. Moles of nitrogen		0.519	0.539	0.536	0.53
14. Moles of ammonia		.968	.967	.970	.97

monia formed, as well as the value of R, were determined in triplicate experiments.

The procedure was as follows: 47.12 cc. of 0.0905 *M* hydrazine sulfate was mixed in a Lunge nitrometer with 28.86 cc. of 0.1809 *M* manganic acetate in glacial acetic acid. The amount of nitrogen evolved is given in cubic centimeters, and in millimoles, in Lines 2 and 3 of Table III. The nitrometer was of the type giving directly the volume corrected for pressure, temperature and water vapor.

The solution was then carefully diluted to 100 cc. To two 20cc. samples potassium iodide was added and the excess of manganic salt determined with 0.1117 *N* thiosulfate solution as before. The results in cubic centimeters and milli-equivalents of thiosulfate, and in millimoles of Mn^{+++} used up, are given in Lines 4, 5 and 6, respectively.

Then another 20cc. sample was almost neutralized, a phosphate buffer added and the ammonia formed determined by an oxidation method, worked out for this purpose. This method was similar to that of Artmann and Skrabal,¹⁶ and Willard and Cake,¹⁷ and our procedure was such that results accurate to within 0.2% were obtained. 70.19 Cc. of 0.07975 *N* bromine solution was added,¹⁸ and after the completion of the reaction, potassium iodide and acid. The thiosulfate in cubic centimeters needed to remove the iodine liberated by the excess of both bromine and manganic salt is given in Line 7, and that which would have been needed, if Mn^{+++} had not been present, is given in cubic centimeters in Line 8 and milli-equivalents in Line 9. Lines 10 and 11 give the amounts of bromine used up and of ammonia formed, respectively. (In examining the table it must be borne in mind that the data in Lines 4, 7, 8, 9 and 10 refer to one-fifth of the final solution. The factor 5 has been introduced in obtaining the results given in Lines 5, 6 and 11.) Finally, Lines 12, 13 and 14 give the number of moles of manganic salt used up, and of nitrogen and ammonia formed, per mole of hydrazine; the average values for the three experiments are given in the right hand column.

On the basis of Equation 6 one mole of hydrazine should react with one mole of manganic salt to give one mole of ammonia and one-half mole of nitrogen; our experimental values are 1.12, 0.97 and 0.53, respectively. In view of the fact that in our procedure the effect of the errors is cumulative, the results can be considered satisfactory.

Attention may be called to the following two cross checks. An examination of the nitrogen balance shows that one mole of hydrazine yields 2.01, 2.04 and 2.04 (av., 2.03) gram atoms of nitrogen in the form of free

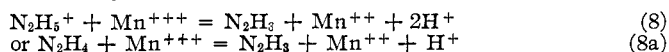
¹⁶ Artmann and Skrabal, *Z. anal. Chem.*, **46**, 5 (1907). See also Rupp and Rössler, *Arch. Pharm.*, **243**, 104 (1905).

¹⁷ Willard and Cake, *THIS JOURNAL*, **42**, 2646 (1920).

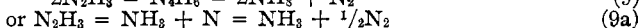
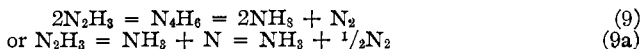
¹⁸ Ref. 1, p. 865.

gas and ammonia, instead of the theoretical two. The difference lies almost within the experimental error. Secondly, if we assume that the deviation from unity in the $Mn^{+++}\cdot N_2H_4$ ratio is due to the oxidation of a small part of the hydrazine to N_2 according to Equation 1, then we should expect the ammonia yield to be correspondingly slightly less than unity and the nitrogen slightly higher than 0.50. Our results, 0.97 and 0.53, are in fair quantitative agreement with this prediction. Thus the value $R = 1.12$ corresponds to 0.04 mole of hydrazine reacting by Equation 1 and 0.96 mole by Equation 6, and the calculated amounts of ammonia and nitrogen are then 0.96 and 0.52, respectively.

The following theory of mechanism was proposed by Cuy early in the investigation. Since the reduction of one mole of Mn^{+++} to Mn^{++} involves only one equivalent, and a bi-molecular reaction is more probable than a reaction of higher order, then the first step of the hydrazine-manganic reaction may be expected to be the formation of N_2H_3 (or $N_2H_4^+$) by the removal of one hydrogen from hydrazine.



N_2H_3 is an "odd molecule" (containing an uneven number of electrons), and either of the following reactions is possible.



The net result will be Reaction 6, provided that Reaction 9 or 9a takes place in preference to the further removal of hydrogen by direct action between Mn^{+++} and N_2H_3 .

The proviso in the preceding sentence implies the condition for quantitative oxidation of hydrazine to nitrogen (Equation 1; $R = 4$), namely, that the removal of the hydrogens of hydrazine in successive steps must take place so rapidly that the accumulation of intermediate products as N_2H_3 or N_2H_2 is prevented. The same result would of course be attained if all the hydrogens were removed in a single step.

Another example of the type of reaction in which R is equal to unity (Equation 6) will be considered in the next paper. These examples render more plausible the suggestion in the preceding paper that the reaction between hydrazine and quadrivalent chromium is of this type.

Summary

In the reaction between hydrazine and permanganate in acid solution, the presence of the manganous salt formed during the reaction is responsible for the fact that the amount of oxidizing agent needed to oxidize one mole of hydrazine is variable and much lower than the expected four equivalents; it may be as low as 1.45 in the presence of the excess of manganous salt.

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, $N_2H_5^+ + Mn^{+++} = NH_4^+ + \frac{1}{2}N_2 + H^+ + Mn^{++}$, 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.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

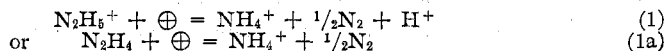
THE OXIDATION OF HYDRAZINE. IV THE INTERACTION OF HYDRAZINE AND FERRIC SALT IN ACID SOLUTION

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



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 $Mn^{+++} \rightarrow Mn^{++}$. The converse is not necessarily true, since the intermediate product, N_2H_3 , 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 Shetterly¹ 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).