From these results it may be seen that in most cases the presence of potassium is shown at once, while even at a dilution of 2 or 3 parts per million the precipitate will form within a minute or two. The extreme sensitiveness attained is 2 parts per million, a delicate enough test for all ordinary purposes.

It is essential that no ammonium salts be present, since they are readily precipitated by this method. Table II illustrates their behavior:

TABLE II.

Mg. NH_3.	Parts per million.	Precipitate perceptible.
0.50	100	At once
0.25	50	"
0.10	20	faintly at once
0.05	10	shortly
0.025	5	never

The extreme sensitiveness attainable in this case was found to be about 10 parts per million, or one-fifth that of potassium.

Bray states that a moderate amount of the alkaline earth elements or lithium does not interfere with the test (as conducted without alcohol), and my own results have shown that save for ammonium there is no metallic salt which interferes in any way with the precipitation so conducted. By reason of these advantages any solution may be tested directly for potassium without removing anything save ammonium. Due care must be taken in case the solution is alkaline to make it slightly acid with acetic acid. If a free acid other than acetic be present in the solution it should be neutralized by means of sodium hydroxide and then made slightly acid with acetic acid.

Summarized, the procedure is as follows: Place 5 cc. of the potassium solution in a tall beaker of 50 cc. or 100 cc. size, set on a mirror beside it 5 cc. of pure water in a similar beaker, and add to each 2.5 cc. of sodium cobaltinitrite reagent and 5 cc. of 95 per cent. alcohol. If upon looking down through the solutions into the mirror an equally sharp image of the observer can be seen in each beaker there is no potassium present; if the test solution shows a dimmer image than the blank, potassium is present amounting to two or more parts per million. The only precautions necessary are to avoid making the test in an atmosphere dense with ammoniacal fumes, to be certain of the absence of ammonium from the solution, and to be certain that the solution is neutral or slightly acid with acetic acid.

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THE OXIDATION OF HYDRAZOIC ACID.

BY HAROLD EATON RIEGGER.

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It has been shown[1] in this laboratory that hydrazoic acid may be

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[1] Browne, THIS JOURNAL, 27, 551–5 (1905); Browne and Shetterly, *Ibid.*, 29, 1305–12 (1907); 30, 53–63 (1908); 31, 221–37 (1909); 31, 783–99 (1909).

formed in varying amounts by the oxidation of hydrazine in acid solution with a number of different oxidizing agents. In contrasting the comparatively low yields of the acid obtained by oxidation methods with the high yields secured by condensation of ethyl nitrite with hydrazine hydrate, Thiele[1] states that small yields only are obtained in the former experiments "offenbar wegen der leichten Oxydierbarkeit der Säure."

It has already been urged[2] that the variation in the amounts of ammonia formed during the oxidation of hydrazine under different conditions points to some other explanation for the lowness of the yields of hydrazoic acid than the assumption of the easy oxidizability of that compound. The most reasonable hypothesis, all things considered, seems to be the assumption of the formation of intermediate products which decompose in different ways.[3]

The present investigation was undertaken with a view to ascertaining the extent to which hydrazoic acid undergoes oxidation by certain typical substances under conditions similar to those prevailing in the experiments on the oxidation of hydrazine. In the present paper are recorded the results of a series of observations upon the behavior of hydrazoic acid in aqueous solution toward hydrogen peroxide, potassium chlorate, potassium iodate, potassium persulfate, potassium permanganate, manganese dioxide, and ferric oxide, respectively.

Materials Used.—The hydrazoic acid used in the experiments was prepared by distillation of 96 per cent. sodium trinitride (obtained from F. Raschig, Ludwigshafen) with dilute sulfuric acid, and contained 1.654 grams of hydrazoic acid per liter.

In order to facilitate comparison with the work upon the oxidation of hydrazine, the solution of hydrazoic acid used was of such strength as to contain one molecule for every two molecules of hydrazine sulfate contained in the 1 per cent. solution of that substance ordinarily employed. The solution was standardized either by the method of Dennis and Isham[4] or by a method that consists in precipitating with a slight excess of dilute silver nitrate solution, and in weighing in a Gooch crucible the resulting silver trinitride after it has been washed free from silver nitrate by means of cold water, and dried to constant weight in a vacuum desiccator over sulfuric acid.

The hydrogen peroxide solution was standardized by means of the potassium permanganate solution used in another part of the work, the latter solution having been standardized with the aid of ammonium

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[1] *Ber.*, 41, 2681 (1908).

[2] THIS JOURNAL, 31, 796 (1909).

[3] For complete presentation of this hypothesis, see THIS JOURNAL, 31, 783–99 (1909), page 791 *et seq.*

[4] THIS JOURNAL, 29, 18–31 (1907), page 26.

ferrous sulfate. The solutions of potassium chlorate, potassium iodate, and potassium persulfate were prepared by dissolving carefully weighed amounts of the ordinarily pure compounds. The remaining oxidizing agents, manganese dioxide and ferric oxide, were used in the solid form

General Procedure.—The oxidation experiments were conducted in an ordinary distillation apparatus. This consisted of a 500 cc. round-bottom flask provided with a two-hole rubber stopper carrying a 100 cc. dropping funnel and a Reitmeier bulb through which connection was established with a condenser. The receiver consisted of two 250 cc. Erlenmeyer flasks connected in series with the condenser, and so arranged that the delivery tube in each flask was immersed beneath the surface of the liquid in the flask.

In the experiments in which the oxidizing agent was used in the form of a solid, a known weight was first introduced into the distilling flask, and such a volume of the standard hydrazoic acid, that the molecular ratio of the acid to the oxidizing agent corresponded with the expression $2HN_3 : O$, was then added. In case the oxidizing agent was in the form of a solution, the hydrazoic acid was first introduced, then the oxidizing agent, the ratio of the hydrazoic acid to the oxygen being the same as before, except in the case of potassium permanganate.

In case it was decided to carry on the oxidation in the presence of sulfuric acid, that reagent was next added, having first been diluted so as to bring the total volume of the liquid in the distilling flask up to 200 cc. Otherwise, water alone was added to bring the liquid up to this volume.

The first receiving flask contained a known volume of standard sodium hydroxide, sufficient to neutralize all of the hydrazoic acid employed in the experiment. The second receiving flask contained a small measured amount of the standard alkali, and was used merely as a guard, to insure complete absorption of all hydrazoic acid.

After the reacting mixture had been permitted to stand at room temperature for about half an hour, during which period the flask was occasionally shaken, heat was gently applied until the temperature of the solution was raised to the boiling point. It was assumed that all hydrazoic acid that had escaped oxidation had been expelled from the reacting mixture after one-third[1] of the liquid had been distilled from the flask.

The contents of the receiving flasks were then mixed together and the percentage of hydrazoic acid was determined by back-titration with standard sulfuric acid, with phenolphthalein as indicator. The neutral residual solution was then in each case treated with a slight excess of dilute

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[1] West, *J. Chem. Soc.*, 77, 705 (1900).

silver nitrate solution and the resulting silver trinitride was weighed in the manner described in a preceding paragraph. The amount of unoxidized hydrazoic acid was therefore determined both volumetrically and gravimetrically.

From the foregoing it will be observed that the treatment to which the hydrazoic acid has been subjected during the present research is closely similar to that undergone by the acid in the experiments on the oxidation of hydrazine performed in this laboratory.[1]

Behavior of Hydrazoic Acid toward Hydrogen Peroxide Solution.—The hydrogen peroxide used in these experiments was the ordinary 3 per cent. Mallinckrodt product. In each experiment a volume of this solution containing 0.06535 gram of the peroxide was brought into contact with 100 cc. of the solution of hydrazoic acid. The results of the experiments are summarized in Table I.

TABLE I.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams.	
			By volumetric method.	By gravimetric method.
1	0	0.5758	0.1648	0.1653
2	5	0.5759	0.1648	0.1653
3	5	0.5758	0.1648	0.1653
4	10	0.5757	0.1657	0.1653
5	10	0.5759	0.1657	0.1653
6	25	0.5754	..	0.1652
7	25	0.5755	..	0.1652
8	50	0.5758	0.1655	0.1653
9	50	0.5759	0.1653	0.1653

From these experiments it is apparent that under the prevailing conditions, hydrazoic acid does not undergo appreciable oxidation when treated with hydrogen peroxide.

Behavior of Hydrazoic Acid toward Potassium Chlorate Solution.—The solution of potassium chlorate contained 6.7424 grams of the salt per liter. In each experiment 11.65 cc. of this solution and 100 cc. of the solution of hydrazoic acid were used. In Experiments 10 and 11, the silver trinitride was weighed directly, while in Experiments 12–17, in which sulfuric acid was used, the small amounts of hydrochloric acid which distilled over with the hydrazoic acid that escaped oxidation necessitated the use of the Dennis and Isham method[2] for the determination of hydrazoic acid. The presence of hydrochloric acid in the receiver also rendered the volumetric method useless in these experiments. The results are shown in Table II.

From this series of experiments it is evident that hydrazoic acid undergoes oxidation to some extent when treated with potassium chlorate in

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[1] Browne and Shetterly, *Loc. cit.*

[2] *Loc. cit.*

neutral solution, and that in the presence of sulfuric acid the amount of oxidation increases slightly with increase in the concentration of the acid.

TABLE II.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3. Gram.	Unoxidized HN_3 in grams. By volumetric method.	Unoxidized HN_3 in grams. By gravimetric method.
10	0	0.5561	0.1595	0.1597
11	0	0.5562	0.1595	0.1598
12	5	0.5469	..	0.1570
13	5	0.5449	..	0.1564
14	10	0.5435	..	0.1560
15	10	0.5438	..	0.1561
16	25	0.5422	..	0.1557
17	25	0.5414	..	0.1554

Behavior of Hydrazoic Acid toward Potassium Iodate Solution.—The solution of potassium iodate contained 12.12 grams of the salt per liter. In each experiment 11.3 cc. of the oxidizing agent and 100 cc. of the hydrazoic acid were used. In Experiments 20, 21, 22, and 23, small amounts of iodine distilled over into the receiver. This necessitated the use of the Dennis and Isham method for determination of the hydrazoic acid. In order to ascertain whether or not the liberation of iodine, which must have resulted from the decomposition of a part of the potassium iodate, was attributable to hydrazoic acid, two blank experiments were performed, in each of which 100 cc. of distilled water were substituted for the hydrazoic acid solution. In the first of these experiments, in which 10 cc. of concentrated sulfuric acid were used, a quantity corresponding to 0.0063 gram of silver iodide was liberated. In the second, in which 25 cc. of sulfuric acid were used, a yield of 0.0077 gram of silver iodide was obtained. In the first case 4.18 per cent., and in the second case 5.12 per cent. of the total amount of iodine in the potassium iodate used were set free. These results confirm the conclusion to be drawn from the data given in Table III, to the effect that hydrazoic acid does not undergo appreciable oxidation when treated with potassium iodate under the specified conditions.

TABLE III.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	Unoxidized HN_3 in grams. By gravimetric method.
18	0	0.5755	0.1653	0.1652
19	0	0.5753	0.1649	0.1652
20	10	..	0.1654	..
21	10	0.5748	0.1651	0.1650
22	25	..	0.1653	..
23	25	0.5752	0.1650	0.1652

Behavior of Hydrazoic Acid toward Potassium Persulfate Solution.—A solution containing 11.4852 grams of potassium persulfate per liter was used. In each experiment 45.22 cc. of this solution were brought into contact with 100 cc. of the hydrazoic acid solution. In the first two experiments, in which no sulfuric acid was used, the weight of silver trinitride was respectively 0.4790 and 0.4730 gram. The amount of unoxidized hydrazoic acid as determined by the volumetric method was found to be 0.1362 and 0.1358 gram, and by the gravimetric method 0.1375 and 0.1358 gram respectively. It is thus apparent that in the absence of sulfuric acid, hydrazoic acid is oxidized to a considerable extent by potassium persulfate. In the experiments performed in the presence of sulfuric acid it was invariably found that sulfur dioxide was liberated. This interfered greatly with the determination of the hydrazoic acid. The attempt was made to remove the sulfur dioxide quantitatively by oxidation with hydrogen peroxide solution, but the method was not found to be satisfactory. The extent to which oxidation of the hydrazoic acid took place in the experiments in which sulfuric acid was used was therefore not determined, although it is likely that oxidation was more nearly complete in the presence of sulfuric acid than in its absence.

Behavior of Hydrazoic Acid toward Potassium Permanganate Solution.—It has already been shown in this laboratory[1] that hydrazoic acid is oxidized by potassium permanganate in the presence of sulfuric acid, either in accordance with the equation

$$2KMnO_4 + 6HN_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 6H_2O + 9N_2 + O_2$$

or, in case the permanganate is present in excess, with the equation

$$4KMnO_4 + 2H_2SO_4 + 8HN_3 = 2K_2SO_4 + 4MnO_2 + 6H_2O + 12N_2 + O_2.$$

In the experiments performed during the present investigation, a solution of potassium permanganate containing 10.604 grams per liter was employed. Of this solution, 19.09 cc. were in each case brought into contact with 100 cc. of the hydrazoic acid solution. The results are recorded in Table IV.

TABLE IV.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams.	
			By volumetric method.	By gravimetric method.
24	0	0.1665	0.0494	0.0478
25	0	0.1915	0.0513	0.0550
26	5	0.0113	0.0033	0.0032
27	5	0.0111	0.0033	0.0032
28	10	0.0099	0.0033	0.0028
29	10	0.0102	0.0033	0.0029
30	25	0.0755	0.0230	0.0217
31	25	0.0759	0.0226	0.0218
32	50	0.1261	0.0373	0.0362
33	50	0.1264	0.0393	0.0363

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[1] Dennis and Browne, THIS JOURNAL, **26**, 577–612 (1904), page 605.

It is clear from these results that the maximum oxidation occurs when the sulfuric acid is comparatively dilute, and that as the concentration of the acid is increased beyond this point, the amount of oxidation is very appreciably diminished.

Behavior of Hydrazoic Acid toward Manganese Dioxide.—The manganese dioxide used was in the form of pyrolusite. The available oxygen was found by analysis to be 90.5 per cent. of theory. In each experiment 0.1845 gram of the solid oxidizing agent was brought into contact with 100 cc. of the hydrazoic acid solution. The details of the experiments are given in Table V.

TABLE V.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	Unoxidized HN_3 in grams. By gravimetric method.
34	0	0.5743	..	0.1649
35	0	0.5715	0.1636	0.1641
36	1	0.5746	0.1649	0.1649
37	1	0.5701	0.1654	0.1637
38	5	0.5664	0.1623	0.1626
39	5	0.5740	0.1644	0.1648

These experiments indicate that hydrazoic acid is oxidized to a slight but appreciable extent by the action of manganese dioxide under the specified conditions.

Behavior of Hydrazoic Acid toward Ferric Oxide.—The ferric oxide used in these experiments was found by analysis to contain 96.6 per cent. Fe_2O_3. In each case 0.6354 gram of the solid substance was treated with 100 cc. of the hydrazoic acid solution. From the results which are appended in Table VI, it is clear that no appreciable oxidation of hydrazoic acid takes place under the conditions of these experiments.

TABLE VI.

No. of expt.	Conc. H_2SO_4. Cc	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	Unoxidized HN_3 in grams. By gravimetric method.
40	0	0.5759	0.1654	0.1653
41	0	0.5757	0.1651	0.1653
42	10	0.5750	0.1653	0.1651
43	10	0.5756	0.1652	0.1653
44	50	0.5758	..	0.1653
45	50	0.5722	..	0.1643

Discussion of Results.—On the basis of their behavior toward hydrazine sulfate in the presence of dilute sulfuric acid, certain of the more common oxidizing agents have been tentatively classified into three groups:[1] oxidizing agents of the first class comprize those which oxidize hydrazine with formation of considerable amounts of both hydrazoic acid and

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[1] THIS JOURNAL, 31, 783–799 (1909), page 793.

ammonia; those of the second class yield little or no hydrazoic acid but large amounts of ammonia; those of the third class yield little or no hydrazoic acid or ammonia.

If Thiele's idea[1] that the lowness of the yields of hydrazoic acid obtainable from hydrazine by the action of certain oxidizing agents is attributable to the easy oxidizability of hydrazoic acid be correct, it would seem reasonable to suppose (1) that oxidizing agents of the second and third classes should readily oxidize hydrazoic acid, and (2) that oxidizing agents of the first class should oxidize hydrazoic acid either not at all or only with some difficulty.

Of the oxidizing agents employed in the present investigation, those belonging to the first class are hydrogen peroxide, potassium chlorate, and potassium persulfate. While hydrogen peroxide has been shown to have no perceptible oxidizing action upon hydrazoic acid, both potassium chlorate and potassium persulfate have been found to oxidize the acid appreciably. Of the oxidizing agents belonging to the second class, potassium permanganate was found to oxidize the acid vigorously, manganese dioxide but slightly, and ferric oxide not to any appreciable extent. Potassium iodate, which belongs to the third class, does not oxidize hydrazoic acid at all under the conditions prevailing in the experiments. From these facts it is apparent that of the seven oxidizing agents studied, only two, hydrogen peroxide and potassium permanganate, behaved consistently with the explanation offered by Thiele.

Summary.

In the present investigation the action of seven oxidizing agents upon hydrazoic acid in aqueous solution has been studied under conditions duplicating as far as possible those prevailing in the oxidation of hydrazine. It has been shown (1) that potassium permanganate oxidizes hydrazoic acid vigorously, (2) that potassium persulfate oxidizes the acid to a considerable extent, (3) that potassium chlorate and manganese dioxide exert a slight but appreciable oxidizing action, and (4) that ferric oxide, hydrogen peroxide, and potassium iodate do not perceptibly oxidize hydrazoic acid.

From these results the conclusion is drawn that the comparative lowness of the yields of hydrazoic acid obtained by the action of oxidizing agents upon hydrazine is probably not to be explained on the ground that hydrazoic acid is oxidized during these reactions, as suggested by Thiele.

The present investigation was undertaken at the suggestion of Professor A. W. Browne, and carried on under his personal supervision.

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[1] *Loc. cit.*