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THE OXIDATION OF HYDRAZINE. VI. REACTION BETWEEN MERCURIC OXIDE AND HYDRAZINE HYDRATE IN ALCOHOLIC SOLUTION.[1]

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Curtius and Jay[2] have noted that hydrazine hydrate explodes when dropped upon mercuric oxide. By the action of yellow mercuric oxide upon the unsymmetrical secondary hydrazines, numerous tetrazones have been prepared.[3] The behavior of hydrazine sulfate toward red and toward yellow mercuric oxide both in acid and in alkaline solution has been studied in this laboratory.[4] When heated with either red or yellow mercuric oxide, the hydrazine was found to undergo complete oxidation, without the formation of either ammonia or hydronitric acid. When yellow mercuric oxide was added a little at a time, however, to a slightly alkaline solution of hydrazine sulfate held at a temperature of 0°, appreciable amounts of both hydronitric acid and ammonia were formed.

The present work was undertaken with a view to ascertaining whether the behavior of hydrazine hydrate in alcoholic solution is analogous with the behavior of hydrazine in aqueous solution, or with the behavior of the unsymmetrical secondary hydrazines in non-aqueous solution; and also

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[1] For the earlier articles of this series see Browne and Shetterly, THIS JOURNAL, **29**, 1305–12 (1907); **30**, 53–63 (1908); **31**, 221–37 (1909); **31**, 783–99 (1909); also Hale and Redfield, THIS JOURNAL, **33**, 1353–62 (1911).

[2] *J. prakt. Chem.*, [2] **39**, 27–58 (1889), page 43.

[3] See for example E. Fischer, *Ann.*, **190**, 67–183 (1878) page 166; **199**, 281–332 (1879), page 319; Renouf, *Ber.*, **13**, 2169–2174 (1880); Michaelis, *Ann.*, **252**, 266–317 (1889); Franchimont and Van Erp, *Rec. trav. chim.*, 14, 317–26 (1895).

[4] THIS JOURNAL, **31**, 789 (1909).

whether the nitrogen of the hydrazine is liberated quantitatively by the action of mercuric oxide, or is held back in part as ammonia, hydrazoic acid, or some other compound of nitrogen and hydrogen.

The experiments to be recorded in the present paper will be considered under two headings: (1) Gasometric study of the reaction between yellow mercuric oxide and hydrazine hydrate in ethyl alcohol, and (2) study of certain by-products of the foregoing reaction.

Gasometric Study of the Reaction between Yellow Mercuric Oxide and Hydrazine Hydrate in Ethyl Alcohol.

Materials Used.—The hydrazine hydrate, which was obtained from Raschig, was found by the method of Rimini[1] to contain 93.6 per cent. of $N_2H_4.H_2O$. The yellow mercuric oxide, obtained from the J. T. Baker Chemical Company, was found by analysis to be of a high degree of purity. It was finely pulverized before using. The ethyl alcohol, after having been boiled with quicklime for 12 hours, was found to be 99.96 per cent. pure. It was then further purified by boiling for 9 hours with solid potassium hydroxide and quicklime and by subsequent distillation. The final product gave no indication of the presence of appreciable amounts of aldehyde, when tested with the fuchsine reagent.

Apparatus Used.—The experiments of this series were carried out in a Hempel nitrometer[2] from which the weighing tube had been removed. The nitrometer was closed at the bottom by means of a one-hole rubber stopper through which connection was made with a level-bulb filled with mercury. This stopper was adequately protected by a considerable depth of mercury from the action of the hydrazine hydrate solution.

Procedure Followed.—Owing to the comparative rapidity with which the dilute alcoholic solutions of hydrazine hydrate were found to oxidize in air, it was found necessary to analyze the solutions immediately before or after each experiment. The manipulation of the nitrometer was as follows: Into the clean, dry nitrometer cylinder was introduced a weighed amount of yellow mercuric oxide 50 per cent. in excess of the quantity theoretically needed to oxidize the hydrazine in the solution used. The rubber stopper was then inserted in the bottom of the nitrometer, and was securely fastened with a clamp. Mercury was run in from the level-bulb until the side arm was covered. After 5 cc. of alcohol had been introduced through the side arm, with the precaution to prevent the lodgment of mercuric oxide in that part of the apparatus, the nitrometer was filled with mercury, and all air bubbles were carefully driven out.

Twenty-five cc. of an accurately standardized solution of hydrazine hydrate in ethyl alcohol containing from 3.28–4.57 grams $N_2H_4.H_2O$ per liter were then slowly introduced from a buret into the side arm, and the

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[1] See the preceding article of this series, THIS JOURNAL, 33, 1353–62 (1911).

[2] Hempel-Dennis, "Methods of Gas Analysis," 1902, page 387.

nitrometer was carefully shaken until the evolution of gas was complete. The evolved gas was drawn out into a water-jacketed Hempel gas buret containing mercury, above which was a small quantity of water, which served to saturate the gas with water vapor. The gas was freed from alcohol vapor by shaking in a Hempel pipet with 30 cc. of water that had been previously saturated with nitrogen, and from oxygen by shaking with alkaline pyrogallol. The volume of oxygen found varied in the experiments from 0.2–0.8 cc. The residual volume of gas was in each case measured as nitrogen, no correction being made for the volume of nitrogen that may have been dissolved in the solutions used.

The results of nine experiments are recorded in Table I.

Table I.

Number of experiment.	Nitrogen found (0°, 760 mm.). Cc.	Nitrogen theory. Cc.	Deficit in nitrogen. Cc.	Percentage deficit.
1..........	35.26	36.73	1.47	4.0
2..........	33.9	36.73	2.83	7.7
3..........	34.4	36.73	2.33	6.3
4..........	50.1	51.2	1.1	2.1
5	50.1	51.2	1.1	2.1
6..........	39.95	41.25	1.3	3.2
7..........	40.45	41.25	0.8	1.9
8..........	49.78	49.84	0.06	0.12
9..........	48.84	49.80	0.96	1.9

These results indicate that there is usually a small but appreciable deficit in the amount of gaseous nitrogen liberated at room temperature by the action of yellow mercuric oxide upon hydrazine hydrate in dilute alcoholic solution, although the reaction proceeds, under these conditions, substantially in accordance with the equation

$$N_2H_4.H_2O + 2HgO = N_2 + 2Hg + 3H_2O.$$

The residual solutions in the nitrometer were washed out with alcohol, were filtered, and were tested for hydrazine, for ammonia, and for hydronitric acid, in each case with negative results. Some other hypothesis than that of the formation of ammonia and hydronitric acid must therefore be formulated to account for the deficit in nitrogen gas.

Study of Certain By-products of the Reaction between Yellow Mercuric Oxide and Hydrazine Hydrate in Ethyl Alcohol.

The first step toward the identification of the by-products of the reaction consisted in working the reaction upon a larger scale and under conditions somewhat different from those prevailing in the nitrometer experiments.

Seventy grams of 97.6 per cent. hydrazine hydrate were dissolved in 1600 cc. of pure ethyl alcohol. The solution was constantly stirred, and was kept at a temperature of from —10° to —16° by means of a freezing mixture. Yellow mercuric oxide was slowly added, until, during the course of 15 hours, 425 grams had been introduced. Nitrogen gas was continuously evolved until about 400 grams of the mercuric oxide had been added. The odor of ammonia was distinctly recognized throughout the oxidation, as well as a peculiar odor resembling that of dilute witch-hazel. The mercury and the unreduced mercuric oxide were filtered off, and a 10 cc. portion of the filtrate was treated with 2 cc. of a 10 per cent. solution of concentrated sulfuric acid in ethyl alcohol, with the result that a small amount of a white crystallin precipitate was obtained. After it had been filtered off, washed with absolute alcohol, and air-dried, this precipitate was examined microchemically with the result that it was found to contain no ammonium sulfate, and that it in all probability consisted chiefly of hydrazine sulfate, or of some substance of very similar crystallin form. The alcoholic solution, before treatment with sulfuric acid, was of course incapable of reducing mercuric oxide, and was also found unable to reduce Fehling's solution, or even potassium iodate. The crystals, on the other hand, readily reduced these substances.

A larger quantity of the crystallin substance was prepared by slowly adding, to 800 cc. of the solution, 10 cc. of an alcoholic solution of sulfuric acid containing 25 grams of the acid per liter. A rather heavy white precipitate appeared first, and settled rapidly, while a finer precipitate remained in suspension. An attempt was made to separate the two precipitates by first filtering off the finer one through one paper and throwing the apparently heavier one upon another. Qualitative tests later showed, however, that the two precipitates were in all probability identical. After it had been washed with alcohol, and dried in a desiccator over solid potassium hydroxide, the substance was subjected to analysis in the special apparatus described in an earlier article.[1] The procedure consisted essentially in oxidizing the sample with a measured excess of potassium iodate, and measuring the volume of nitrogen liberated. The unused potassium iodate was then determined in the usual way. In the present instance the value of this method of effecting the simultaneous nitrometric and oxidimetric determinations lies in the fact that it affords a direct means of establishing the ratio of oxidizable hydrogen to nitrogen in the compound, and thus of distinguishing between hydrazine on the one hand, and some other oxidizable compound of nitrogen and hydrogen, or a mixture of such a compound with hydrazine, on the other.

The results of the analysis of three samples of the crystallin compound are given in Table II.

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[1] THIS JOURNAL, 33, 1353–62 (1911).

TABLE II.

Number of experiment.	Weight of sample. Gram.	Hydrogen found.		Nitrogen found.		Atomic ratio. H:N.
		Gram.	Per cent.	Gram.	Per cent.	
1.....	0.1171	0.00253	2.16	0.0180	15.37	4 : 2.04
2.....	0.1152	0.00253	2.20	0.0177	15.37	4 : 2.01
3.....	0.0933	0.00277	2.97	0.0180	19.29	4 : 2.04

In all three experiments the results in the last column indicate that the substance oxidized was hydrazine, rather than a new compound of hydrogen and nitrogen, or a mixture of such a compound with hydrazine. Tests for ammonia and hydronitric acid were made in the residual solutions, but negative results only were obtained. It will be seen, however, by inspection of the table, that the samples analyzed cannot be considered to consist entirely of hydrazine sulfate. The first two samples, which were prepared a short time before the analysis by the method outlined above, may be considered to contain, respectively, 69.8 per cent., and 70.9 per cent. of hydrazine sulfate. The third sample, which had been prepared by Dr. J. W. Turrentine during the preceding year by a similar method, and which had been stored in the meantime over solid potassium hydroxide, was found to contain 95.8 per cent. of hydrazine sulfate. The nature of the substance or substances mixed with the hydrazine sulfate has not yet been determined.

The most plausible explanation of the formation of hydrazine sulfate by treating with sulfuric acid an alcoholic solution from which all hydrazine had apparently been removed, is furnished by the recent work of Curtius and Zinkeisen.[1] These investigators found that hydrazine hydrate reacts very readily with acetaldehyde in accordance with its usual behavior toward aldehydes, with the formation of ethylidene azine. The reaction may be expressed by the equation

$$2CH_3CHO + N_2H_4 = CH_3.CH : N.N : CH.CH_3 + 2H_2O.$$

This compound, which boils at 95-96° under atmospheric pressure, was found to be fairly stable toward alkalies, but to decompose at once in acid solution, yielding acetaldehyde and the hydrazine salt of the acid used.

It cannot be stated with certainty at the present writing, whether the small amounts of acetaldehyde contained in the ethyl alcohol used as solvent are sufficient to account for the formation of the ethylidene azine, or whether, under certain conditions in the presence of hydrazine, ethyl alcohol may be oxidized by mercuric oxide to acetaldehyde. The former seems to be the more satisfactory explanation, especially in view of the fact that the alcohol used in this series of experiments was not quite so carefully purified from all but the last traces of aldehyde as was that used

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[1] *J. prakt. Chem.*, [2] **58**, 310-32 (1898), page 325.

in the gasometric work or in the work to be described below. Even in the gasometric work, however, it was found that certain of the residual solutions gave a faint white precipitate when treated with sulfuric acid. Attempts to isolate the ethylidene azine from the residual solution by fractional distillation were unsuccessful because of the small quantity of the substance present, and because of its admixture with other substances to be mentioned later.

One of the most conspicuous facts noted in connection with the oxidation experiments was the constant presence of the peculiar witch-hazel odor mentioned above. It was soon ascertained that this odor was not characteristic of ethylidene azine. Alcoholic solutions of this substance, prepared by the method of Curtius and Zinkeisen,[1] possessed an odor distinctly different from that of the substance under investigation. Moreover, the witch-hazel odor still persisted after the residual solutions had been treated with sulfuric acid. When the residual solutions, prior to treatment with sulfuric acid, were subjected to fractional distillation, the odor could readily be detected in nearly all of the fractions, but was strongest in the last fractions. No precipitate was obtained when the fractions were treated with sulfuric acid. The odor was found to persist indefinitly when the alcoholic solution of the substance was kept in a stoppered bottle. When the distillation was interrupted before the last fractions had come over, it was found that the highly concentrated residue in the distilling flask possessed an exceedingly pungent odor, and that on evaporation to dryness it yielded a waxy solid with an odor somewhat resembling that of garlic. In these preliminary experiments neither the quantity nor the purity of the substances obtained was sufficient to warrant the attempt to analyze them.

As the result of numerous blank experiments it was found that the substance possessing the witch-hazel odor was not formed: (1) when yellow mercuric oxide acted upon 93.6 per cent. hydrazine hydrate in the absence of ethyl alcohol; (2) when alcoholic solutions of acetic aldehyde, freshly prepared by distillation of paraldehyde, and of hydrazine hydrate were brought together under various conditions; (3) when ferric oxide or manganese dioxide acted upon hydrazine hydrate in alcoholic solution at room temperature; and (4) when mercuric oxide and alcohol were brought together in absence of hydrazine.

These results seemed to furnish presumptive evidence that all three compounds, mercuric oxide, hydrazine hydrate, and ethyl alcohol, contributed in some way to the formation of the compound possessing the witch-hazel odor. This led to the tentative conclusion that mercury diethyl might be the compound present.

In order to test this conclusion an alcoholic solution of mercury diethyl

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[1] *Loc. cit.*

was prepared by the method of Frankland and Duppa.[1] A rather stiff sodium amalgam was gently warmed with 20 grams of ethyl iodide and 1 gram of ethyl acetate. The reaction was carried out in a round-bottomed flask provided with a reflux condenser. Fifty cc. of absolute alcohol were added to the mass in the flask which, after prolonged shaking, was subjected to fractional distillation. The fractions collected below 78° consisted chiefly of ethyl iodide and ethyl acetate. The fractions above 78° contained varying amounts of mercury diethyl, and possessed an odor which was at once recognized as identical with that of the unknown by-product of the reaction between mercuric oxide and hydrazine hydrate in alcoholic solution. Solutions prepared directly by mixing varying amounts of pure mercury diethyl and alcohol were found to possess the same odor, while the pure substance itself showed the unmistakable, pungent, persistent odor noted in the distillation residues obtained during the fractionation of the alcoholic solutions. A sample of the pure mercury diethyl when exposed for some time to diffused daylight was found to deposit a white, waxy solid, soluble in ether and in hot alcohol, and partially decomposing when heated, to form metallic mercury, a combustible gas, and a black carbonaceous residue. A small sample of this waxy solid, when applied to the flesh, produced after several hours a painful and slow-healing burn. The substance possessed a strong, disagreeable odor, somewhat resembling that of garlic, and identical with that of the waxy solid left after evaporation to dryness of the alcoholic residues mentioned above.

In order to ascertain the conditions most favorable for the formation and isolation of the mercury compound obtained as a by-product in the oxidation of hydrazine hydrate by mercuric oxide in alcoholic solution, a series of experiments was carried out with varying concentrations of the hydrate, and at different temperatures. The resulting solution was filtered in each case, and was distilled in a special form of glass apparatus. It was found that the best yields of the waxy solid were obtained by slowly dropping an approximately 5 per cent. solution of the hydrate upon the mercuric oxide, with constant shaking, the temperature being held at the boiling point of the alcohol. Distillation of alcohol from the filtered solution was in general discontinued when the boiling point had reached 90–95°. The white solid separated out as soon as the solution had cooled or in some cases even while it was still hot. The last fractions of the distillate invariably possessed the odor of mercury diethyl, and if the temperature of the distilling flask was allowed to rize above 95° a certain amount of the white solid was carried over into the distillate.

It was not found possible, under the conditions of the experiments performed, to effect the isolation of mercury diethyl in sufficiently pure

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[1] *Ann.*, 130, 105–9 (1864).

form for analysis, but qualitative tests strongly indicated that this substance was formed in small amounts during the reaction. Attempts to isolate the white solid, however, which seems to be either a decomposition product or a reaction product of mercury diethyl, were more successful. By extraction of the solid distillation residues with ether a solution was obtained which when cautiously evaporated yielded a white, waxy solid which under the microscope presented the appearance of long curved forks and crosses. This solid, which possessed a characteristic odor somewhat similar to that of garlic, was found to be readily soluble in ether and in hot alcohol, and to be slightly soluble in water. A sample of the substance when heated in a small test tube sublimed to some extent, forming thin, iridescent plates upon the cooler portions of the tube. It also decomposed partially, yielding a small amount of a yellow, oily liquid. When rather strongly heated it decomposed more completely with a slight puff, leaving a black, carbonaceous residue and forming a cloud of white mist, which gradually settled as a deposit of minute globules of mercury. This deposit was dissolved in a few drops of aqua regia, and the presence of mercury was confirmed by means of three of the usual tests for that element.

In a second experiment a sample weighing 0.0455 gram was introduced into a glass tube which was then sealed to one of the arms of a two-way stopcock that had been fused to the capillary of a Hempel gas buret. When heated, the solid showed a tendency to sublime partially, as before, and then began to decompose, yielding first a yellow oil, and finally giving a black residue, metallic mercury, and about 3 cc. of a combustible gas. The presence of mercury, carbon, and hydrogen thus seems to be assured.

Other samples of the compound were treated with aqua regia, which was found unable to effect complete decomposition either in the cold or when heated for 6 hours in a sealed glass tube to temperatures ranging from 280–360°. A weighed sample was sealed into a thin-walled glass tube which was introduced into a combustion tube containing copper oxide, and which was broken after the copper oxide had been heated to redness. It was found that the substance when heated sublimed without apparent decomposition through about 30 cm. of red hot copper oxide.

Decomposition of the substance was finally effected by heating it with concentrated nitric acid in a sealed tube to 100–120° for 2 hours. Considerable difficulty was experienced in attempting to dry the solid for analysis. Owing to its volatility it lost weight rather rapidly on exposure to the air. Unless proper care was taken in applying heat the substance quickly assumed a dirty yellow color. It is probable, therefore, that the substance as prepared for analysis still contained small amounts of the mercury diethyl with which it had been previously associated, and perhaps also traces of water and of alcohol. The carefully purified samples yielded, after the treatment with nitric acid, clear yellow solutions in which the percentage of mercury was determined by the method of Volhard.[1] In one sample 53.2 per cent., and in another 56.2 per cent. of mercury were found.

The substance does not show a definit melting point. At about 160° it seems to undergo partial decomposition, yielding a yellow liquid. The residual solid turns first yellow and then brown on further heating, but gives no indication of melting at temperatures up to 260°. When applied to the flesh the substance behaved in the same way as the white solid obtained from pure mercury diethyl, producing after several hours a painful and slow-healing burn.

The smallness of the yields of the mercury compound obtained under the conditions of the experiments has made further investigation of its properties in connection with the present research seem inadvizable. During the oxidation of 20 grams of the hydrate, for example, only from 0.1-0.2 gram of the compound was obtained.

Summary.

In the present investigation it has been shown that:

(1) Hydrazine hydrate in ethyl alcohol is oxidized by yellow mercuric oxide substantially in accordance with the equation

$$N_2H_4.H_2O + 2HgO = N_2 + 3H_2O + 2Hg.$$

(2) There is usually an appreciable deficit in the percentage of nitrogen evolved, however, which is not as a rule to be explained by the formation of ammonia, or of hydronitric acid, but seems to be attributable, in part at least, to the formation of ethylidene azine.

(3) Qualitative tests indicate the formation of mercury diethyl as a by-product of the reaction, together with a white, solid compound containing carbon, hydrogen, and about 55 per cent. of mercury.

This investigation was undertaken at the suggestion of Professor A. W. Browne, and was carried out under his direction.

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ISOMERIC INORGANIC COMPOUNDS.

BY ADOLPH LAW VOGE.

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Recently it has fallen to my lot to compile an index alphabetically according to condensed formulas of 15,000 inorganic compounds. In doing this many isomerisms and polymerisms were brought to light. I have thought that the new instances might be worth a note in the Journal. They are as follows:

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[1] Treadwell-Hall, ' Analytical Chemistry," Vol. II, first edition, p. 134.