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ON THE OXALATES OF HYDRAZINE.

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In 1889[1] Curtius made mention of the formation of an oxalate of hydrazine obtainable by heating triazoacetic acid with a saturated, aqueous solution of oxalic acid. The product was described as a substance crystallizing in small, glistening plates, soluble in water. No attempt was apparently made to ascertain whether the substance was a monoxalate or a dioxalate of hydrazine, and no analytical data whatever were published.

The purpose of the present investigation has been the preparation and study of the two oxalates of hydrazine, $(N_2H_4)_2H_2C_2O_4$ and $N_2H_4.H_2C_2O_4$. It has been thought possible, moreover, that the decomposition of these substances, especially in view of a probable ring structure of the dioxalate, might yield some interesting results.

Hydrazine Monoxalate.

Method of Preparation.—An aqueous solution of this substance was prepared by treating 10 cc. of a 73 per cent. solution of hydrazine hydrate, with 9.18 grams of oxalic acid dissolved in a small amount of water. The solution was filtered and after evaporation on the water bath to the point of saturation was allowed to cool, with the result that a large quantity of minute crystals was obtained. The crystals were first drained on filter paper and were then dried to constant weight in a desiccator over calcium chloride.

Method of Analysis.—Weighed samples of the dried crystals were dissolved in water and the solutions were made strongly alkaline with ammonium hydroxide. They were then heated to boiling and an excess of a solution of calcium chloride, containing 25 grams per liter, was added

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[1] Curtius and Jay, *J. prakt Chem.*, **39**, 27–59 (1889).

slowly and with constant stirring. After the precipitates had been allowed to subside, they were filtered and were thoroughly washed with hot water.

In order to avoid the error arising from the possible presence of calcium carbonate in the calcium oxalate thrown down by this method, the precipitates were dissolved in hot, dilute sulphuric acid, and the oxalic acid was determined by titration with a standard solution of potassium permanganate.

The results obtained in four determinations indicate the ratio, mols. N_2H_4 : mols. $H_2C_2O_4$ to be (1) 2 : 1.02; (2) 2 : 1.00; (3) 2 : 0.99; (4) 2 : 0.99. Theory, 2 : 1.00. The average of these results, calculated to a percentage basis, is as follows $H_2C_2O_4$ found, 58.60 per cent.; theory for $(N_2H_4)_2.H_2C_2O_4$, 58.44 per cent.

Three analyses of the monoxalate by the permanganate method described in detail in a subsequent paragraph show the ratio, mols. N_2H_4 : mols. $H_2C_2O_4$ to be (1) 2 : 0.99; (2) 2 : 0.98; (3) 2 : 1.00. Theory, 2 : 1.00. The average of the three results, calculated to percentage of N_2H_4, gave N_2H_4 found, 41.45 per cent. Theory, 41.59 per cent.

Properties.—Hydrazine monoxalate is a white substance that crystallizes from aqueous solution in the form of very fine needles and plates. When the attempt is made to recrystallize the compound, an amorphous substance is frequently obtained in the form of a jelly, which, on evaporation, becomes hard and opaque.

The monoxalate is extremely soluble in water, as shown by the results obtained in the following series of solubility determinations made at 35°. One gram of water at this temperature was found to dissolve (1) 2.003, (2) 1.998, and (3) 2.018 grams, or an average of 2.009 grams of the salt.

Three determinations of the solubility of this compound in absolute alcohol at a temperature of 21.9° showed that it was practically insoluble, or that 1 cc. of alcohol dissolved about 0.0003 gram. The substance is also insoluble in ether. No appreciable residue was left after the evaporation of a small portion of ether that had been shaken with the salt at intervals for several hours. In the case of both alcohol and ether, the liquid was heated to its boiling point in the presence of the salt, and was allowed to come to constant temperature, with frequent shaking, in a thermostat.

No definite melting point is shown by the monoxalate, which in this respect is similar to many other hydrazine compounds. At a temperature of 130° (±2°) it begins to decompose, although even at lower temperatures some indication of incipient fusion is obtained. Above this temperature the compound is eventually transformed into a clear liquid, whether the substance be heated in an open or in a closed capillary tube.

When this liquid is allowed to cool it solidifies, yielding a product that melts at 150° (±2°).

Decomposition.—The decomposition of hydrazine monoxalate was studied under four different sets of conditions, as follows: (1) On a platinum plate in the open air; (2) in an open glass tube; (3) in an atmosphere of hydrogen; (4) *in vacuo*, with a view to the analysis of the evolved gases.

(1) When crystals of the monoxalate were heated on a platinum plate in the open air they fused and boiled, assuming a yellow color. This color gradually deepened to a brown and finally to a black, as the charring of the substance progressed. Throughout the decomposition there was a visible evolution of fumes. Whenever the rate of heating was sufficiently rapid the substance took fire and burned with a blue flame of carbon monoxide.

(2) This experiment was performed in order that the fumes noted in Exp. 1 might be partially condensed and examined. A portion of the substance which had been dried to constant weight at a temperature of 100–5° was gradually decomposed, by heating, in an open glass tube. Essentially the same phenomena were observed to take place in the same sequence as in Exp. 1. The vapor which escaped from the tube, as well as that which condensed on the walls, gave a distinct alkaline reaction to red litmus and emitted the odor of hydrazine hydrate. Later in the decomposition the odor of a cyanide was detected, and before the presence of that substance was suspected, symptoms of cyanide poisoning were experienced.

(3) A third experiment was designed with a view to the collection of decomposition products absorbed in acid or in alkaline solution. The decomposition was effected in an apparatus consisting of a glass distilling flask, provided, in lieu of a stopper, with a glass tube sealed in the neck, and extending perpendicularly nearly to the bottom. The side arm of the flask was fused to a Muencke gas wash bottle, containing dilute sulphuric acid. A similar bottle connected to the first and contained carbon-dioxide-free potassium hydroxide.

A stream of hydrogen, purified with the aid of alkaline permanganate, soda lime, and concentrated sulphuric acid, was employed in sweeping the uncondensed products of decomposition into the gas wash bottles.

About one gram of the oxalate was placed in the flask and the air in the entire apparatus was displaced by hydrogen. The compound was then slowly heated to decomposition. At the end of the experiment a small amount of carbon remained in the flask.

An appreciable amount of ammonia and a small quantity of hydrazine were found in the first wash bottle. The alkaline solution in the second bottle was found to contain a small amount of carbonic acid and a considerable quantity of hydrocyanic acid, as shown by both the Prussian blue and the sulphocyanate tests.

During the early stages of the decomposition a liquid condensed on the walls of the neck and side arm of the flask. In Exp. 2 this liquid was shown to be in part, at least, hydrazine hydrate. Two drops of the condensate were subjected to analysis for hydrazine by the method of Rimini.[1] The results obtained when calculated to hydrazine hydrate gave a concentration of 9 per cent. It is probable, however, that the liquid contained in solution compounds of hydrazine other than the hydrate.

The most conspicuous of the substances produced by the destructive distillation of the monoxalate was a white crystalline sublimate deposited on the cooler parts of the flask and of the decomposing substance itself. When a drop of the aqueous solution of this sublimate was evaporated under the microscope, glistening needle-shaped crystals separated out. These crystals were found to contain no carbonic, hydrocyanic, or oxalic acid, and were shown to be capable of reducing acidified potassium iodate in the cold. When the solution from which the hydrazine had been removed by oxidation was subjected to the microchemical test for ammonia with chloroplatinic acid, negative results were obtained. When heated on a platinum plate the substance decomposed, leaving a residue of carbon, thus indicating the presence of organic matter.

(4) The decomposition was effected under such conditions that all gaseous products unabsorbable by sulphuric acid or potassium hydroxide could be collected for analysis, uncontaminated by air. The apparatus employed in this experiment was constructed as follows:

To the capillary tip of a Hempel gas burette was joined, by means of a short section of rubber tubing, a Y-tube, one arm of which was closed by a piece of narrow-bore rubber tubing provided with a screw clamp and a tightly fitting glass plug. To the other arm was sealed a glass stop-cock. A section of glass tubing, 0.5 cm. internal diameter and 19 cm. long, designed as the container for the substance which was to undergo decomposition, was closed at one end and was sealed to the tube bearing the glass stop-cock. It was then bent so as to extend horizontally outward and in a plane perpendicular to that occupied by the glass Y. It was necessary, of course, in each case to place the compound which was being studied in the tube designed as its receptacle before the fused joint was effected. The burette was filled with mercury. By alternate raising and lowering the level tube of the burette and by suitable manipulation of the valves of the Y-tube, the pressure in the tube containing the sample was reduced to less than 1 mm.

A sample of the hydrazine monoxalate weighing 0.2128 gram yielded about 35 cc. of gas when decomposed in the apparatus just described.

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[1] Rimini, *Gaz. chim. ital.*, **29**, I, 265–9 (1899); *Chem. Zentr.*, **1899**, II, 455.

Of this gas, a volume of 25.8 cc. was passed successively into Hempel pipettes containing potassium hydroxide, alkaline pyrogallol, and ammoniacal cuprous chloride. The contraction observed in the first case was 3.0 cc., corresponding to 11.6 per cent. of gases absorbable in potassium hydroxide. Only a trace of oxygen was found. The contraction noted after treatment with ammoniacal cuprous chloride was 4.5 cc., corresponding to 17.4 per cent. of carbon monoxide.

The residue, 18.3 cc. in volume, was non-inflammable, and was therefore taken as nitrogen; this volume represented 70.9 per cent. of the whole.

A summary of the results of the above experiments shows that the monoxalate of hydrazine is quite unstable at moderately high temperatures and on decomposing yields water, ammonia, hydrocyanic acid, probably in combination, hydrazine, carbon dioxide, carbon monoxide free nitrogen and carbon. An unidentified and more complex compound of hydrazine is found and appears as a white, crystalline sublimate. This compound is being subjected to further investigation.

Hydrazine Dioxalate.

Method of Preparation.—The dioxalate of hydrazine was prepared by adding, drop by drop, to a hot, concentrated solution of oxalic acid, containing 11.02 grams $H_2C_2O_4.2H_2O$, 6.0 cc. of a 73 per cent. solution of hydrazine hydrate containing 4.4 grams $N_2H_4.H_2O$. Before the last of the hydrate had been added to the solution of the acid, brilliant crystalline flakes began to appear. The solution was heated, with stirring, until these had redissolved. Then, on cooling, a large mass of beautiful, glistening crystals was obtained. These were filtered by suction, were washed rapidly in cold, distilled water, also with the aid of suction, and were then dried in the open air.

Analysis.—Three samples of this compound, previously dried in an air bath for one-half hour at a temperature of 100–8°, were analyzed for oxalic acid by the calcium chloride precipitation method, outlined above under the analysis of the monoxalate.

The result obtained in three determinations showed the ratio between the molecules of hydrazine and oxalic acid to be (1) 1 : 1.00; (2) 1: 1.01; (3) 1 : 0.98; theory, 1 : 1. When calculated to a percentage basis the average of these results is: $H_2C_2O_4$ found, 73.63 per cent.; theory, calculated for $N_2H_4.H_2C_2O_4$, 73.60 per cent.

The principal methods so far proposed for the determination of the hydrazine radical in compounds of that substance involve reactions in which that radical undergoes oxidation. Rimini[1] prescribed the use of potassium iodate in acid solution, adding a measured excess of the iodate and titrating the excess with thiosulphate, after reduction with potas-

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[1] Rimini, *Loc. cit.*

sium iodide. Petersen[1] employed potassium permanganate in acid solution, as did also Roberto and Roncali,[2] while Sebanejeff[3] used the same oxidizing agent in alkaline solution. He determined the hydrazine radical in an inorganic salt by adding an excess of that reagent and titrating back with arsenious acid.

These methods do not lend themselves readily to the analysis of the oxalates of hydrazine on account of the peculiar fact that both the basic and the acid radicals in this compound are strong reducing agents and both react with the oxidizing substances prescribed. This consideration debars the use of the methods of Rimini, of Petersen and of Roberto and Roncali. The use of permanganate in alkaline solution as outlined by Sebanejeff might be employed with modification, as permanganate is not reduced by oxalic acid in alkaline solution, but this procedure would involve a tedious titration with arsenious acid. To acidify the solution for this titration would result in the immediate reduction of the excess of permanganate by the oxalic acid. In the alkaline solution which is therefore required, a voluminous precipitate of manganese compound forms which must be allowed to settle before any color change can be detected in the solution. Moreover, the presence of oxalic acid might interfere in the titration by reducing the arsenic acid[4] then formed, though it is doubtful whether this reduction could occur in an alkaline solution.[5]

These considerations made it necessary to devise a method of analysis which would take into account the reducing action of both radicals of the oxalates and which would therefore permit the simultaneous determination of both hydrazine and oxalic acid. The method of Rimini, which is the most satisfactory for the determination of hydrazine, could not be adapted to this purpose, for while potassium iodate oxidizes oxalic acid, the reaction is too slow,[6] even in hot acid solution, to admit of titration. Potassium permanganate, it has been shown by Browne and Shetterly in their studies on the oxidation of hydrazine,[7] does not oxidize hydrazine in acid solution quantitatively to nitrogen and water, but yields varying amounts of hydronitric acid and ammonia. Methods based on the use of this reagent in acid solution are therefore unreliable. Likewise, in alkaline solution, if the permanganate be added slowly, small amounts of these products are formed. On the contrary, if an ex-

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[1] Petersen, *Atti. accad. Lincei,* [5] 15, II, 320–5 (1906); *Chem. Zentr.,* 1906, II, 1662.

[2] Roberto and Roncali, *Industria chimica,* 6, 178 (1904); *Chem. Zentr.,* 1904, II, 616

[3] Sebanejeff, *Z. anorg. Chem.,* 20, 21–9 (1889).

[4] Prescott and Johnson, "Qualitative Chem. Analysis," 5th Ed., p. 257.

[5] Naylor and Braithwaite, *Pharm. J. and Trans.,* 13, [3] 464 (1883).

[6] Guiard, *J. Chem. Soc.,* 36, 593 (1879).

[7] Browne and Shetterly, THIS JOURNAL, 31, 221 (1909).

cess of the permanganate is added at once in alkaline solution, the amounts of hydronitric acid and ammonia formed are negligible.[1]

In the light of these facts a method of analysis was devised in which the hydrazine was oxidized by permanganate in alkaline solution, and the oxalic acid by more permanganate in the same solution after acidification.

Essentially the following procedure was adopted: The sample to be analyzed was dissolved in water in an Erlenmeyer flask and was treated with 10 cc. of a 4 *N* solution of sodium hydroxide. An amount of standard permanganate solution sufficient to oxidize the hydrazine completely, but not enough to oxidize all of the oxalic acid, was then added and the solution was acidified by adding 5 cc. of concentrated sulphuric acid. After the solution had been warmed until the oxides of manganese had gone into the solution, a clear, colorless liquid remained. Potassium permanganate was then added, drop by drop, until the faintest possible permanent coloration was produced.

The permanganate solution employed in the analysis was standardized first against a standard solution of oxalic acid and then against a solution containing accurately known amounts of both hydrazine sulphate and oxalic acid. The procedure followed in this standardization was identical with that adopted in the analysis. By subtracting from the total volume of permanganate solution used the volume required for the complete oxidation of the oxalic acid, the volume consumed by the hydrazine present was ascertained. From these results may be calculated the value of the permanganate solution in terms either of the monoxalate or of the dioxalate. One cc. of permanganate solution employed was found to correspond to 0.00213 gram of $N_2H_4.H_2C_2O_4$.

The results of the analysis are recorded in Table I:

TABLE I.

No. of experiment.	Weight of $N_2H_4.H_2C_2O_4$.	$KMnO_4$ solution used. Calculated. cc.	Found. cc.	Weight of $N_2H_4.H_2C_2O_4$ found.	Per cent. $N_2H_4.H_2C_2O_4$ found.
1	0.0530	24.8	24.8	0.0530	100.0
2	0.0446	20.9	20.8	0.0443	99.3
3	0.0449	21.0	21.2	0.0451	100.4
4	0.0461	21.6	21.6	0.0461	100.0
5	0.0561	26.3	26.5	0.0564	100.5
6	0.0503	23.6	23.5	0.0501	99.6
7	0.0576	27.0	27.0	0.0576	100.0

Properties.—The dioxalate of hydrazine crystallizes in glistening needles, without water of crystallization.

As compared with the monoxalate, the dioxalate of hydrazine is only sparingly soluble in water. The following procedure was followed in the

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

solubility determinations: An aqueous solution of the salt, saturated at higher temperatures, was allowed to cool in a thermostat with frequent shakings. When equilibrium had been reached, portions of the clear solution were removed, were weighed and were then evaporated to constant weight in an air bath at 100–5°. One gram of water at a temperature of 22.5° was found by this method to dissolve (1) 0.0213, (2) 0.0207, (3) 0.0200 gram, or an average of 0.0206 gram hydrazine dioxalate. A second series of determinations was made with the single variation in the procedure that the desiccation to constant weight was effected *in vacuo* over sulphuric acid at room temperature. One gram of water at a temperature of 22.5° in this series of determinations was found to dissolve (1) 0.0214, (2) 0.0202, (3) 0.0189 gram, or an average of 0.0202 gram of the salt.

In boiling water the dioxalate is very readily soluble. In the matter of their relative solubilities in water, the two oxalates resemble the two sulphates. Solubility determinations of the dioxalate in alcohol and ether showed this salt to be quite insoluble in those liquids.

Like the monoxalate of hydrazine, the dioxalate fails to show a definite melting point. The attempts to determine the melting point of this compound resulted quite differently, depending on whether the substance was contained in an open or in a sealed capillary tube. In the former case there was no change in the appearance of the crystals until a temperature of about 200° was reached, whereupon they assumed a slight yellow tint which became quite marked at 230°.

Further heating merely led to a deepening of this coloration. In a sealed tube, however, at a temperature of 170–3°, the crystals showed evidences of incipient fusion and, on being further heated, slightly decomposed with an evolution of gas; at 200° they were completely fused. The resulting liquid, however, did not solidify on cooling at room temperature.

Crystallization of Hydrazine Dioxalate.—Professor A. C. Gill, of the Department of Geology, Cornell University, has had the very great kindness to determine the crystallographic structure of the dioxalate.

The clear, colorless crystals are monoclinic, usually in the form of rhomboidal tablets, more rarely in long columnar or acicular shape. In the tabular crystals the clinopinacoid is the large face, bounded by two sets of narrow faces, one set in the zone 010 to 100, and the other set in the zone 010 to 001. These faces are so narrow and imperfect, and in some cases so disturbed by twinning (on the orthopinacoid), that no satisfactory measurements could be made. The best set of these was:

010–110 = 53° 25′
110–210 = 16° 18′
210–100 = 20° 20′

The angle β is about 63° 20′. There is a very perfect basal cleavage. Optically the substance is biaxial with a small optical angle (about 20°) and the acute negative bisectrix lies in the clinopinacoid about 34° from the vertical axis in the obtuse angle β. Since this is only 7.5° inclined from normal to the base, the basal cleavage laths show excellent optical figures. They also show parallel extinction. The plane of the optical axes is normal to the plane of symmetry, and the dispersion is not strong. The strength of the double refraction is about 0.090, and a rough determination of γ for yellow light in the spectrum of an incandescent lamp gave 1.631.

Decomposition.—The decomposition of the dioxalate of hydrazine was studied under five different sets of conditions, the first to fourth, inclusive, being similar, respectively, to those under which the corresponding experiments with the monoxalate were conducted, as described above. The fifth decomposition was carried out in a sealed tube in a bomb furnace.

(1) The results obtained on heating the dioxalate on a platinum plate were the same as those reported above for the similar decomposition of the monoxalate.

(2) A portion of the dried salt, when decomposed by heat in a test tube, evolved vapors which condensed on the walls of the tube, and, while at first giving a distinct acid reaction, they later became alkaline in their behavior toward litmus. The odor emitted was at first that of a cyanide, but later became pronouncedly ammoniacal.

(3) The apparatus used and the procedure followed in this experiment have already been described.

The decomposition of the dioxalate took place in two distinct stages—first, the breaking down of the white crystals of the salt, accompanied by vigorous boiling and the appearance of an amorphous, yellow mass in their place; and second, the distillation of the yellow mass, with evolution of white fumes, and the formation of a black carbonaceous residue. During the first stages water vapor condensed in comparatively large amounts and evaporated again during the second stage. With the evaporation of the aqueous condensate the white fumes which were evolved condensed as a white coating on the walls of the cooler parts of the apparatus. At the same time a tar-like deposit appeared in those regions where the heat was more intense.

A qualitative examination was made of the (*a*) gaseous, (*b*) liquid, and (*c*) sublimated products of the decomposition, with the following results: (*a*) On the analysis of the acid and alkaline solutions respectively for the detection of those gaseous products liable to be retained by them, there was shown the presence of ammonia in the former, and of cyanides and carbonates in the latter solution. Tests applied to the acid solution for hydrazine with Fehling's solution yielded negative results. (*b*) The liquid condensate showed a slight alkaline reaction toward litmus and responded feebly to tests with iodate for hydrazine. On evaporation a slight residue was obtained which was identical with the white sublimate described below. Acidification caused effervescence. (*c*) The white sublimate was removed from the side arm of the distilling flask, partly in solution and partly in suspension in a small amount of water; in this solvent it was not very soluble. On the evaporation of a few drops of the aqueous solution there separated out what, through the microscope, appeared to be small, amorphous particles. It was more soluble in hot water than in cold, and it also dissolved readily in dilute sulphuric acid. The solution in acid was not accompanied by any effervescence, which fact showed the absence of carbonates. Negative results were obtained from tests for cyanides and also for hydrazine by the iodate method. Ammonia was freely evolved when sodium hydroxide was added to the warm aqueous solution of the compound. When heated on the platinum plate, the substance decomposed and left a deposit of carbon, thus showing the presence of organic matter.

(4) This experiment was designed to parallel as closely as possible the corresponding experiment on the decomposition of the monoxalate.

A sample of dried crystals, 0.5030 gram in weight, gave rise on decomposition to a total volume of gas of about 127 cc., of which 116.8 cc. were analyzed. When this volume of the gas was subjected to the action of the different absorbents there was a contraction in potassium hydroxide solution of 68.9 cc., corresponding to 59.1 per cent. of carbon dioxide and hydrocyanic acid or cyanogen; in alkaline pyrogallol, a slight contraction representing a trace of oxygen; and in ammoniacal cuprous chloride, a decrease in volume of 19.8 cc., corresponding to 17.0 per cent. of carbon monoxide. The residue, which occupied a volume of 27.5 cc., equal to 23.5 per cent. of the total volume, was assumed to be nitrogen.

(5) It was noticed in the melting point determination of the dioxalate that, when a sealed capillary tube was used, at a temperature of 200°, a liquid was formed which did not solidify on cooling. In order to study this decomposition more thoroughly the following procedure was adopted.

A small sample of the pure, dry dioxalate was sealed in a section of combustion tubing, from which the air had been exhausted by means of a mercury pump, and was heated in a bomb furnace for about one-half hour at a temperature varying from 200° to 210°. A certain volume of xylene was enclosed with the tube in the bomb so that the internal pressure exerted by the gases evolved during the decomposition might be equalized in part by the external pressure developed by the vapor of the xylene. When the tube was removed from the bomb the substance which it contained was found to be a clear, sirupy liquid.

On examination, the liquid as well as the vapor showed marked alkalinity toward red litmus. By means of suitable tests, cyanides were found to be absent; in Fehling's solution very small amounts of the liquid were sufficient to produce a decided reduction.

This liquid was allowed to stand for several days in a tube closed only with a cork whereupon a white crystalline solid separated out. The crystals were washed thoroughly with absolute alcohol, in which they showed only slight solubility. The alcohol precipitated more crystals from the mother liquid. The crystalline substance was dissolved in water from which, on evaporation, it separated readily in glistening needles. It was found to reduce acidified potassium iodate and contained no carbonic or hydrocyanic acid. The addition of a few drops of calcium chloride solution to the aqueous, ammoniacal solution of the substance resulted in no precipitation whatever. The subsequent tests, made microchemically, with the same reagents but in a much more concentrated solution, resulted in a decided precipitation, appearing to indicate the presence of an oxalate. A quantitative determination of oxalic acid in a weighed sample was then attempted with the surprising result that when the supposed precipitate of calcium oxalate was being washed on the filter with hot water, it completely dissolved.

The results of this series of experiments show that the dioxalate, when subjected to destructive distillation in absence of air, breaks down with formation of water, ammonia, hydrocyanic acid, probably combined, carbon dioxide, carbon monoxide, nitrogen and carbon. An unidentified white compound of ammonia appears as a sublimate. The decomposition in a sealed tube leads to the formation of a substance which appears to be a hydrazine compound of a carboniferous acid. This unidentified acid, in concentrated aqueous solution, forms a calcium salt, insoluble in cold water but soluble in hot water.

On comparing the respective products of decomposition of the two oxalates, it is seen that intramolecular oxidation in the case of a dioxalate results in the almost complete destruction of the hydrazine radical, so that only minute amounts of that substance are found among the products, while, in that of the monoxalate, where the amount of acid present is only one-half as great, the oxidation is so incomplete that hydrazine is freely evolved. Also, where an ammonium compound, appearing as a sublimate, is formed from the dioxalate, from the monoxalate is produced a hydrazine compound. Both substances appear to be a salt of an acid containing carbon.

A comparison of the two substances obtained respectively from the destructive distillation of the monoxalate and the heating of the dioxalate in a sealed tube, neither as yet having been subjected to a quantitative analysis, indicate that they are closely related if not identical. This judgment is based on the similarity of their behavior toward certain reagents and when heated in melting-point tubes; neither exhibits a definite melting point, but the one duplicates closely the behavior of the other at like temperatures.

Titration of Hydrazine Dioxalate with Standard Alkali.—Salts of hydrazine, such as the dichloride[1] and the disulphate, show an acid reaction in aqueous solution.

One-half of the acid in the salts behaves as so much free acid[2] and may be titrated with alkalies. In agreement with the other diacid salts, hydrazine dioxalate is likewise acid in its reactions. Consequently attempts were made to titrate its free acid.

In previous titrations methyl orange has been employed, but on account of its lack of sensitiveness to oxalic[3] acid it could not be used in these experiments.

Curtius[4] has shown that the indicators—methyl orange, cochineal, corallin, tropeolin, fluorescein and litmus—give definite end points when used in the titration of hydrazine hydrate with 0.1 N H_2SO_4. He did not show, however, what the condition of the hydrazine at this end point was with respect to its combination with the acid. Cohn states that litmus and corallin are sensitive to oxalic acid. The titration of hydrazine dioxalate with azolitmin and with rosolic acid as indicators fail to give with any degree of sharpness the point of neutralization of that salt. Titrations with standard sulphuric acid with the extremely sensitive indicator, erythrosin, however, of a solution made alkaline by the addition of a definite volume of standard sodium hydroxide, gave results which indicated that the neutral point corresponds to the presence in the solution of only the monoxalate. The reaction may be represented by the following equation:

$$2N_2H_4.H_2C_2O_4 + 2NaOH = (N_2H_4)_2.H_2C_2O_4 + Na_2C_2O_4 + 2H_2O.$$

With phenolphthalein as indicator, the whole of the oxalic acid may be titrated with sodium hydroxide solution. In the case of none of the indicators tried was a sharp end point obtained.

CORNELL UNIVERSITY, September, 1909.

THE EXACT DETERMINATION OF SULPHUR IN SOLUBLE SULPHATES.

BY E. T. ALLEN AND JOHN JOHNSTON.

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It was in the course of an investigation of the sulphides of iron that our attention was first directed to the inaccuracy of the ordinary sulphur

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[1] Curtius and Schulz, *J. prakt. Chem.*, 42, 521 (1890).

[2] Stollé, *Ibid.*, [2] 66, 332–8 (1902).

[3] Cf. Cohn, "Indicators and Test-papers," 2nd Ed., p. 114.

[4] Curtius and Schulz, *loc. cit.*