of which is thus indicated, is formed by intramolecular rearrangement or by some other method. Lack of time prevented further investigation of the subject for the present. Further and more exhaustive work along all the lines opened by the experiments tried in this preliminary investigation will be carried out in the Kent Chemical Laboratory.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XIII. METHODS OF ESTIMATION OF SEMICARBAZIDE, SEMIOXAMAZIDE AND OXALYLHYDRAZIDE BY THEIR INTERACTIONS WITH HALOGENS AND HALOGEN OXYACIDS.

BY RASIK LAL DATTA AND JOGENDRA KUMAR CHOUDHURY.

Received February 28, 1916.

In a previous paper[1] one of us has given reactions for the volumetric estimation of semicarbazide, using potassium chlorate, bromate and iodate in the presence of strong hydrochloric acid as oxidizing agents. Since hydrochloric acid decomposes chlorate, bromate and iodate with the evolution of halogens, the reactions described are evidently due to free halogens only. Hence a systematic study of the reactions of semicarbazide with the potassium salt of halogen oxyacids with dilute sulfuric acid was undertaken. Furthermore, it was found that substances which are similar in constitution, as those containing a hydrazine group—$NHNH_2$, also undergo decomposition when subjected to the action of the halogens and halogen oxyacids with the liberation of a constant volume of nitrogen.

When semicarbazide is treated with potassium bromate, iodate or periodate in conjunction with sulfuric acid, a quantity of nitrogen which is always three-fourths of the theoretical is liberated. Bromine water also gives the same amount of nitrogen. Chlorine, which cannot be obtained in suitable concentration, is not suitable for such reactions. Potassium chlorate and sulfuric acid do not cause evolution of nitrogen since semicarbazide hydrochloride is stable in the presence of chloric acid and is not decomposed by it. Hypobromite solutions decompose semicarbazide with quantitative evolution of nitrogen. These reactions could be used for the volumetric estimation of the compound, since a constant quantity of nitrogen is always evolved under different conditions of dilution. Semioxamazide is also decomposed by the halogen oxyacids with the liberation of three-fourths of its nitrogen. With bromine, as also with hypobromite, quantitative liberation of nitrogen is the result. Oxalylhydrazide is decomposed by potassium bromate, iodate or periodate in conjunction with sulfuric acid as also by bromine water and hypobromite with the evolution of nitrogen, carbon diozide and carbon monoxide. The evolu-

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[1] Datta, THIS JOURNAL, 36, 1014 (1914).

tion of nitrogen is quite quantitative under varying conditions. Thiosemicarbazide is decomposed by the above reagents with the evolution of nitrogen, but the results obtained are quite anomalous and could not be used for the volumetric estimation of this substance. Aminoguanidine is decomposed by the reagents with the evolution of nitrogen, but the results obtained are quite varying. In the case of semicarbazide and semioxamazide the portion of nitrogen not evolved remains behind as ammonia, as has been noticed in a previous communication.[1] It was further confirmed as follows: Semicarbazide hydrochloride was treated with silver chlorate to form semicarbazide chlorate in solution. This decomposes with evolution of nitrogen on heating or evaporating, leaving behind pure ammonium chloride. A similar result was also obtained by evaporating a little semicarbazide hydrochloride with excess of bromine water, when ammonium bromide is left behind.

Formation of Semicarbazide Chlorate.—An interesting fact has been found in this connection. If the solution of semicarbazide chlorate prepared by double decomposition, instead of heating on the water bath, be allowed to evaporate in a vacuum desiccator, the chlorate is formed, which as soon as it assumes a solid state, decomposes with explosive violence. Quantities of less than a gram have been found to smash large vacuum desiccators to small pieces. As its isolation in a sufficiently cold atmosphere would entail much danger, it was not attempted.

Formation of Urea from Semicarbazide.—In this connection the isolation of semicarbazide nitrite was attempted by the double decomposition between semicarbazide hydrochloride and silver nitrite. The interaction is attended with effervescence, evidently due to the decomposition of the nitrite. On evaporating the filtrate, a solid was obtained which has been found to be pure urea melting at 132°. The yield of urea is quantitative, as the reaction is not accompanied by any secondary action.

Estimation of Semicarbazide.—Semicarbazide interacts with potassium bromate, iodate or periodate in the presence of sulfuric acid with evolution of three-fourths of the total nitrogen. With bromine water the same decomposition takes place. With chlorine water, however, the proper concentration could not be secured and hence this could not be used as a reagent for effecting the volumetric estimation of semicarbazide. Potassium chlorate and perchlorate do not decompose semicarbazide and hence they could not be used for the estimation of this compound.

The details for carrying out the experiments are as follows: A known weight of semicarbazide hydrochloride is dissolved in a known volume of water in a graduated test tube. One or two cc. of this solution is taken out in a pipet and poured down a Crum's nitrometer filled with mercury and then washed down with a little dilute sulfuric acid. Next, the finely

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[1] *Loc. cit.*

powdered oxidizing agent, in excess to what is required for complete decomposition, is washed down with dilute sulfuric acd. As soon as the oxidizing agent is introduced there is a brisk evolution of gas which collects in the nitrometer. After a while the nitrometer is thoroughly shaken to ensure that the reacton is complete, when the solution becomes clear and does not effervesce. The gas which collects consists of a mixture of nitrogen and carbon dioxide. To remove the latter gas, the resulting mixture is washed thoroughly with water and then with caustic alkali when all the carbon dioxide is absorbed. The apparatus containing the gas is then removed to a cylinder full of water where the volume of the gas is read.

The results of the experiments with different reagents at varied concentrations are given below.

I.—WITH POTASSIUM IODATE AND SULFURIC ACID.

	Strength of the acid.	Strength of sol.	Vol. of sol. taken.	Vol. of N_2.	Mean vol. of N_2 per cc.	Percentage of N_2 (theory for $^3/_4$ = 28.26%).
1	10%	0.2039 g. in 15 cc.	1 cc.	3.55	3.55	27.88
			2 cc.	7.0		
			1 cc.	3.6		
2	10%	0.1633 g. in 15 cc.	1 cc.	2.9	2.85	28.14
			2 cc.	5.6		
3	20%	0.2982 g. in 16 cc.	1 cc.	4.85	4.85	28.12
			1 cc.	4.88		
			1 cc.	4.82		
			1 cc.	4.85		
4	20%	0.1807 g. in 25 cc.	1 cc.	2.0	1.90	28.46
			2 cc.	3.78		
			2 cc.	3.70		
5	20%	0.1114 g. in 30 cc.	2 cc.	2.05	1.007	28.55
			2 cc.	2.0		
			2 cc.	2.0		

II.—WITH BROMINE WATER.

Found: 27.89; 27.99; 28.19; 28.21

III.—WITH POTASSIUM BROMATE AND SULFURIC ACID.

Found: 28.1; 28.34; 28.47; 28.5; 27.95

IV.—WITH PERIODATE AND SULFURIC ACID.

Found: 28.04; 28.57; 28.35

Semioxamazide.—Semioxamazide has a hydrazine group linked to a carbonyl group, as in the case of semicarbazide. It was therefore expected that it would decompose like semicarbazide and this has been found to be the case.

Semioxamazide is decomposed by potassium bromate, iodate or periodate in conjunction with sulfuric acid with evolution of three-fourths of the total nitrogen. With bromine water, however, quantitative liberation of nitrogen is the result. With hypobromite, the whole amount of nitrogen is evolved. Potassium chlorate and dilute sulfuric acid do not decompose this substance.

The experimental procedure is practically the same as in the case of semicarbazide. Semioxamazide, however, is but sparingly soluble in water, hence a solution of it is prepared in dilute sulfuric acid which has no action on it. As the gas obtained contains carbon dioxide, it is always washed with a solution of caustic potash. The conditions of experiments are varied a good deal as with semicarbazide, *viz.*, using sulfuric acid of different dilution, as also varying strength of semicarbazide solution or using varying excesses of the oxidizing agent. But in all cases the evolution of gas is quite constant. With bromine water the gas does not evolve as soon as it comes in contact with the solution. On shaking, however, nitrogen begins to collect rapidly. The results of experiments are given below.

I.—WITH POTASSIUM PERIODATE AND SULFURIC ACID.
Found: 30.51; 30.25; 30.45; 30.65. Theory $(^3/_4)$ 30.6

II.—WITH POTASSIUM IODATE AND SULFURIC ACID.
Found: 30.57; 30.37; 30.67; 30.47

III.—WITH POTASSIUM BROMATE AND SULFURIC ACID.
Found: 30.75; 30.44; 30.39; 30.71

IV.—WITH BROMINE WATER.
Found: 40.69; 40.52; 40.47; 40.67. Theory (total), 40.8

V.—WITH SODIUM HYPOBROMITE.
Found: 40.59; 40.67; 40.82

Oxalylhydrazide.—Oxalylhydrazide decomposes in the presence of oxidizing agents giving one molecule of carbon dioxide, one molecule of carbon monoxide and two of nitrogen according to the equation

$$(CO.NH.NH_2)_2 + 2O_2 = CO_2 + CO_2 + 3H_2O + 2N_2.$$

After the absorption of carbon dioxide by alkali and carbon monoxide by ammoniacal cuprous chloride, it has been found that the volume of nitrogen is quite constant and hence the reactions can be used as a method for the volumetric estimation of the compound. As the substance is not soluble in the ordinary solvents, use was made of the slight solubility of the substance in water acidulated with a little sulfuric.

The results of experiments are given below.

I.—WITH POTASSIUM IODATE AND SULFURIC ACID.
Found: 47.65; 47.36; 48.59. Theory (total), 47.45

II.—WITH POTASSIUM PERIODATE AND SULFURIC ACID.
Found: 47.21; 47.31; 47.66

III.—WITH POTASSIUM BROMATE AND SULFURIC ACID.
Found: 47.51; 47.39; 47.88

IV.—WITH BROMINE WATER.
Found: 47.15; 47.59; 47.51

V.—WITH SODIUM HYPOBROMITE.
Found: 47.22; 47.83; 47.66

Investigations on similar lines are being continued.

CALCUTTA, INDIA.

[FROM THE RESEARCH LABORATORY OF PARKE, DAVIS & COMPANY.]

STUDIES ON DERIVATIVES OF TRIHALOGENTERTIARY-BUTYL-ALCOHOLS.

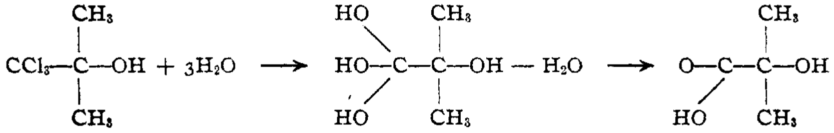
I. THE ACETIC ESTER OF TRIBROMOTERTIARY-BUTYL-ALCOHOL OR BROMETONE ACETIC ESTER.

BY T. B. ALDRICH AND C. P. BECKWITH.

Received September 27, 1916.

The trichloro- and tribromotertiary-butyl-alcohols are most interesting compounds, both chemically and pharmacologically. The trichloro-compound, "Chloretone,"[1] has pronounced hypnotic, sedative and anesthetic properties, both local and general, and the same may be said of the tribromo-compound, "Brometone,"[2] which is considered to have more marked sedative, but less pronounced hypnotic and anesthetic properties. Both compounds are sparingly soluble in water (chloretone 0.8% and brometone still less), but readily soluble in the organic solvents; both have a camphor-like odor and taste, are readily volatile in the air or with steam, and may be crystallized from dilute alcohol and obtained in the form of beautiful white crystals. Both compounds combine with water more or less firmly and in this respect resemble chloral, although the water is not chemically bound as in the latter substance to form a stable hydrate.

The three halogens attached to one carbon atom impart to these bodies properties different from those of the unsubstituted tertiary alcohols; indeed, as pointed out by Willgerodt,[3] they may be regarded as trihalides of *o*-α-hydroxyisobutyric acid, for they yield α-hydroxyisobutyric acid upon treatment with alkalies under suitable conditions, probably thus:



The trichlorotertiary-butyl-alcohol may be crystallized from warm moderately concentrated nitric acid without material decomposition. With care the tribromo-alcohol may be similarly crystallized, though with considerable decomposition. They are broken down by concentrated sulfuric acid and by moderately dilute caustic alkali solutions(5%). In general, they are chemically rather inert bodies, fairly resistant to anything

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[1] Chloretone and [2]brometone are the commercial names given the trichloro- and tribromotertiary-butyl-alcohols, respectively.

[3] *Ber.*, 15, 2305 (1882).