These also show that the calculated values agree tolerably well with the observed.

3. The effect of temperature on the constant k', have been calculated from Geitel's experiment at 25° and 40°. According to this,

$$k' = 0.00253 \quad \text{at} \quad 40^{\circ}\,{}^{1}$$
$$= 0.000936 \quad \text{at} \quad 25^{\circ}$$

Consequently, the temperature coefficient becomes 1.94; that is, the velocity of reaction is almost doubled for every successive 10° elevation of temperature.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE PREPARATION OF TRIMETHYL ARSINE AND TRIMETHYL ARSINE SELENIDE.[2]

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Received April 15, 1920.

Trimethyl Arsine.

Trimethyl arsine, $(CH_3)_3As$, has not previously been isolated in a pure condition. Its preparation seems to have been mentioned first by Cahours and Hofmann,[4] who state that it can be obtained by the action of potassium hydroxide on the double salt resulting from the interaction of arsenic trichloride and zinc methyl. In 1859 Cahours[5] claims to have prepared the compound by the dry distillation of the double salt of tetramethyl arsonium iodide and zinc iodide with potassium hydroxide. He described this arsine as a colorless liquid boiling under 100°. In a later publication[6] the author again mentions this preparation and subsequently[7] states that the pure compound boils at about 70°.

Hibbert, in 1906,[8] seems to have produced the compound by the action of arsenic tribromide on magnesium methyl iodide. He did not isolate the free arsine.

The authors have tried variations of 2 methods for the preparation of this substance: (1) the action of arsenic trichloride or bromide on magnesium methyl iodide and (2) the action of arsenic trichloride on zinc methyl. The latter method seems to be preferable.

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[1] The magnitude of the constant obtained from Geitel's results seems to be excessive, compared with that of my own results.

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] The authors wish to express their appreciation for the generosity shown by Dr. E. Emmet Reid in whose laboratory the work was done.

[4] Cahours and Hofmann, *Compt. rend.*, 41, 831. *Abst. Jahr.*, **1855**, 538.

[5] Cahours, *Ann.*, **112**, 228 (1859).

[6] Cahours, *ibid.*, **122**, 197 (1862).

[7] Cahours, *ibid.*, 337.

[8] Hibbert, *Ber.*, **39**, 160 (1906).

The Action of Arsenic Trichloride on Magnesium Methyl Iodide.—The Grignard reagent was made from 12.2 g. of magnesium, 71 g. of methyl iodide and 125 cc. of ether. The distilling flask containing the reagents was fitted with a dropping funnel and a mechanical stirrer, and attached to a condenser and a receiver. It was immersed in a freezing bath of ice and salt, and 30 g. of arsenic trichloride was added slowly through the dropping funnel. A violent reaction took place, liberating much heat, and yellowish brown crystals gradually formed until at the end of the reaction the contents of the flask consisted of almost one solid mass. When all the chloride had been added, the ether was distilled off over a water bath. The uncondensed vapor passing through the receiver possessed a powerful odor resembling arsine rather than the trimethyl arsine. On redistilling the ether, 2 g. of a liquid was obtained boiling between 45° and 55°. The solid residue in the reaction flask was mixed with sufficient solid potassium hydroxide to unite with all the chlorine and iodine compounds produced in the process, and then subjected to dry distillation. There was obtained a small quantity of liquid which added to that from the ether distillate gave a total yield of approximately 5 g. On redistillation most of this passed over between 50° and 60°. It gave a very heavy precipitate with bromine, and was probably rich in trimethyl arsine, though at that time, following the indications in the literature, we thought that trimethyl arsine boiled materially higher.

While it is felt that the experiment is not wholly conclusive, it seems certain that at least one other volatile compound in addition to trimethyl arsine, having a stronger and more penetrating odor, was produced. This is in line with the results obtained by Auger and Billy,[1] who found that arsenic trichloride produced with magnesium ethyl iodide, primary and secondary derivatives as well as a tertiary.

The Action of Arsenic Tribromide on Magnesium Methyl Iodide.—Fifty g. of arsenic tribromide dissolved in ether was added to a Grignard reagent prepared from 12.3 g. of magnesium and 71 g. of methyl iodide. The reaction was less vigorous than in the case of the arsenic trichloride, and the solid material which formed dissolved on stirring. At the completion of the reaction the contents of the flask consisted of 2 layers, an upper greenish colored ether layer and a lower yellowish brown layer. The product was distilled over a water bath until no more material condensed. Here, as in the experiment with the trichloride, the odor indicated that lower alkylation products than the trimethyl derivative were produced. The distillate, however, contained considerable trimethyl arsine as indicated by the amount of the precipitate obtained by treating a portion of it with bromine.

It was decided to convert this crude product into the selenide and use

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[1] Auger and Billy, *Compt. rend.*, 139, 597 (1904).

the more certain zinc methyl method for the preparation of the pure trimethyl arsine. This was done by boiling up the ether solution with finely powdered selenium as described under the preparation of the selenide. Somewhat more than 10 g. of the trimethyl arsine selenide was obtained. This does not represent nearly all of the arsine formed, as there was considerable loss through oxidation and volatilization.

Preparation of Trimethyl Arsine by the Action of Arsenic Trichloride on Zinc Methyl.—The set up of the apparatus was as follows. A dropping funnel was inserted in a distilling flask containing a weighed amount of the zinc methyl. The side arm was connected to a second distilling flask and to the side arm of the latter was attached a U-tube containing enough arsenic trichloride to form a seal. The U-tube was connected to a large bottle through which carbon dioxide was continually passing. Fifty cc. of dry ether was added to the 45 g. of crude zinc methyl through the dropping funnel and the flask thoroughly cooled in an ice pack. Fifty g. of arsenic trichloride diluted with 50 cc. of ether was then slowly dropped into the flask with occasional shaking. Considerable heat was evolved in the reaction. At its completion the ether was poured off and the white solid formed dissolved in water and an excess of a strong alkali solution added. The mixture was then distilled on the water bath until no more condensation took place.

There was obtained about 20 cc. of liquid which boiled on redistillation between 38° and 51°. This was subjected to several fractional distillations. The larger portion of the product gradually worked into the fractions boiling below 38° and one boiling between 50° and 53°. From the latter there was finally obtained about 5 g. of a clear, colorless, highly refractive liquid with a sickening, garlicky odor, boiling between 50.7° and 51.7° at 747.5 mm. pressure.

It would seem from these results that ether and trimethyl arsine form a mixture which is fairly troublesome to separate by fractional distillation. Experiments were then run using xylene as a diluent. This gave very satisfactory results.

The process was carried out as in the foregoing except that xylene was used as a diluent. Thirty g. of zinc methyl and proportional molecular quantities of the other materials were used. On redistilling the crude distillate there was obtained 17.4 g. of a liquid boiling between 50° and 53°. This, on fractionation, gave the pure trimethyl arsine boiling at 51.9° to 52° at 736 mm. pressure.

The specific gravity was determined to be 1.124 at 22°.

The product was subjected to an indirect analysis by converting a sample of the constant boiling liquid into the selenide and determining its selenium content as described under the preparation of the compound.

Trimethyl Arsine Selenide.

Trimethyl arsine selenide, $(CH_3)_3AsSe$, does not appear to have been prepared previously, though the possibility of its formation is a natural inference on account of the similarity between trimethyl arsine and trimethyl phosphine which has been shown to form a selenide.

Five g. of very finely powdered selenium was added to the ether solution obtained in the preparation of trimethyl arsine by the Grignard method using arsenic tribromide. Small prism-like crystals began forming at once, and on standing a mass of crystals was obtained. The ether solution was cooled in ice and the ether poured off. The crystals were taken up with a few cc. of hot alcohol, filtered and then crystallized by cooling in an ice-salt mixture. Instead of the prism-like structure which the crystals had in an ether solution they now came down as long thin needles. The substance is markedly unstable in the presence of air, giving off an odor similar to that of trimethyl arsine, and quickly forming a brick-red deposit on the surface of the crystal. This reddish substance is somewhat soluble in alcohol and carbon disulfide and is likely amorphous selenium. The crystals, however, seem to be fairly stable when covered with alcohol or ether or when dissolved in water, especially if kept in the dark. When standing in the light, even when covered with alcohol, they gradually become red. On heating they begin to decompose appreciably at 100°, evolving condensible vapors believed to be trimethyl arsine and finally leaving a black residue of selenium.

Some dexterity was required in getting a colorless sample weighed for analysis. A concentrated solution of the substance in ether was carefully transferred to a weighing bottle through which hydrogen was being passed and which had been previously weighed full of hydrogen. The bottle was then stoppered with a cork which had been given a slight impregnation with wax and which was fitted with an inlet and an outlet tube. After cooling the bottle, the ether was poured off from the crystals which had formed, while at the same time hydrogen was passed into the flask. It was then dried to constant weight at room temperatures in a current of hydrogen, the crystals quickly dissolved in water and the selenium precipitated with standard silver nitrate solution. After standing overnight, the amount of silver selenide was determined gravimetrically and the excess of silver nitrate estimated volumetrically by the thiocyanate method.

Calc. for $C_3H_9As.Se$: Se, 39.76. Found: gravimetrically, Se, 40.00, 39.85. Found: volumetrically, Se, 39.48, 39.69.

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