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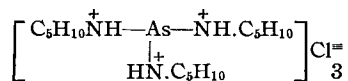
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ARSENIOUS CHLORIDE AND 1,4-DIOXANE.*

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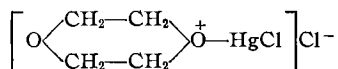
It has been shown in previous reports that arsenious chloride reacts with amines to form substituted ammonium halides, in which one, two or three of the chlorines were replaced by amine groups, the halogens being ionized in the resulting complex (1,9). Thus for example piperidine and arsenious chloride form the compound $(C_5H_{10}N.HCl)_3As$ which may be written structurally as:

* Scientific Section, A. Ph. A., Madison meeting, 1933.



It is known that many oxygen compounds will form oxonium salts with acids and there is therefore a possibility that a compound in which the oxygen is relatively basic might combine with arsenous chloride to form a substituted oxonium halide similar to the ammonium halides formed between amines and arsenous chloride. Bayer and Villiger (2) have pointed out that the same factors that influence the basicity of nitrogen do the same with oxygen. Thus alkyl groups increase the basicity, phenyl groups decrease it. They showed also that oxygen in such compounds as cineol and dimethyl pyrone is strongly basic. Collie and Tickle (3) showed that dimethyl pyrone and diacetylacetone formed oxonium salts with a number of acids.

Dioxane having become readily available in a fairly pure state, it seemed desirable to study its additive capacity toward AsCl_3 . Paterno and Spallino (4) have shown that this substance combines with mercuric chloride to give a compound of the formula $(\text{C}_4\text{H}_8\text{O}_2)\cdot\text{HgCl}_2$. If this is regarded as an oxonium salt it will possess the structure



1,4-Dioxane also forms a sulphate $(\text{C}_4\text{H}_8\text{O}_2)_2\text{H}_2\text{SO}_4$, which may also be regarded as an oxonium salt.

Experimental.—Commercial 1,4-dioxane was dried for one week over metallic sodium and distilled, the fraction boiling 101–102° being taken. 26.4 Gm. ($\frac{3}{10}$ mole) were placed in a flask cooled with ice, and equipped with a mechanical stirrer, and 9.06 Gm. ($\frac{1}{20}$ mole) of arsenous chloride added dropwise. At first there was no sign of a reaction, then a heavy white precipitate formed. When all the arsenous chloride had been added the mixture was warmed. The precipitate dissolved on slight warming but crystallized out on cooling. The crystals were filtered off, and a second crop obtained by evaporating the solvent. Yield of crystalline substance—6 Gm. The crystalline product was soluble in ethyl-alcohol, ethyl ether, acetone and benzene, insoluble in cold heptane, soluble in warm heptane. With water a precipitate of arsenous oxide was formed. Melting point, 62° C. It possessed a strong odor of arsenous chloride, appeared to be deliquescent and left an oily spot on paper.

Chlorine analysis according to Stepanow (5) yielded 33.66% and 33.86%.

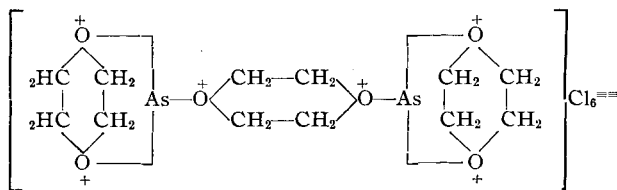
Arsenic analysis according to Morgan and Walton (6) yielded 23.84% and 23.69%.

These results would correspond to the formula $(\text{C}_4\text{H}_8\text{O}_2)_2\cdot 2\text{AsCl}_3$ with a chlorine content of 33.67% and an arsenic content of 23.93%.

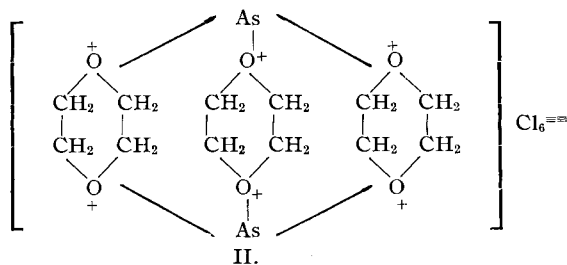
However, the substance appeared to be quite hygroscopic and it is possible that it may be a hydrate. Thus for the formula $(\text{C}_4\text{H}_8\text{O}_2)\cdot\text{AsCl}_3\cdot 2\text{H}_2\text{O}$, the theoretical value for chlorine is 34.55% and for arsenic 24.55%. The reaction was run a second time, taking precautions that all moisture was excluded, and the crystals dried for two days over P_2O_5 in a vacuum. The sample for analysis was transferred from the desiccator to a tared weighing bottle filled with absolute alcohol. In this way the absorption of moisture from the air was prevented during the weighing process. Chlorine found, 33.57%. It is thus apparent that the substance is not a hydrate but corresponds to the formula $(\text{C}_4\text{H}_8\text{O}_2)_2\cdot 2\text{AsCl}_3$.

The molecular weight was determined in benzene by depression of the freezing point. Molecular weight found, 157; theoretical for $(\text{C}_4\text{H}_8\text{O}_2)_2\cdot 2\text{AsCl}_3$, 626.6. It is apparently highly dissociated in benzene solution. Unless it ionizes to give three chlorine ions and a positive ion

($157 \times 4 = 628$) which seems unlikely the substance cannot be completely dissociated in benzene. It would seem most probable that it dissociates into its component molecules $3C_4H_8O_2$ and $2AsCl_3$, which should give a molecular weight of 125 if completely dissociated. According to the Nernst-Thompson rule the dielectric constant of the solvent greatly influences the dissociation of the solute; hence, if this substance is dissolved in a solvent of higher dielectric constant there should be greater dissociation and hence a smaller molecular weight. Acetone was chosen as a solvent. (Dielectric constant for acetone 21.4, for benzene 2.82 (7).) Molecular weight was determined by elevation of the boiling point using the McCoy apparatus (8). Molecular weight found, 148.4. It would thus appear that the substance is highly dissociated, more so in acetone than in benzene. If it is an oxonium halide two structures are possible.



I.



II.

I is the more probable as it contains five-membered rings as compared to ten-membered in II. In support of the oxonium structure, the substance dissolved in absolute alcohol precipitates silver chloride with alcoholic silver nitrate solution, while arsenous chloride in absolute alcohol gives no precipitate with alcoholic silver nitrate. This indicates that even in a solvent possessing such high dissociating powers as ethyl alcohol, chlorine is present as chloride ion.

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