

Studies on Arsenic Trichloride as a Solvent I. The Existence of Crystalline Solvates

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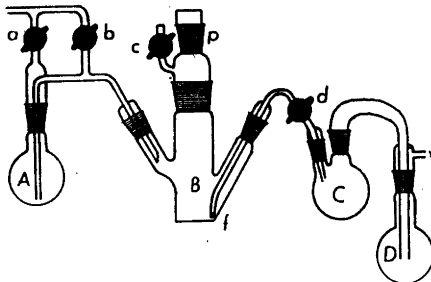


Fig. 1.

The first experimental studies of AsCl_3 as a solvent were carried out by P. Walden¹, who investigated the solubility of some salts. The pioneer work, however, was done by V. Gutmann². His main results can be summarized thus:

1. Extensive knowledge of the solubility and reactions of inorganic compounds in AsCl_3 was obtained.

2. The existence of a number of reactions similar to the acid-base reactions in aqueous solutions was proved.

3. The usefulness of AsCl_3 as a medium for the preparation of complex chlorides was established.

From the point of view of an extended acid-base conception later suggested by Gutmann and Lindqvist³, it seemed interesting to study the reactions in AsCl_3 further than had been done by Gutmann in his broad survey work. This is the aim of the present and some following papers.



Tetramethylammoniumchloride $(\text{CH}_3)_4\text{NCl}$ is one of the salts most soluble in AsCl_3 . Gutmann obtained from its solution a compound $(\text{CH}_3)_4\text{NAsCl}_4$ by evaporation of the excess solvent followed by heating to constant weight *in vacuo* at 40° C. Using conductometric measurements he was also able to show that the compound contained AsCl_4^- ions. Many other similar compounds, tetrachloroarsenites, are described by Gutmann. On the other hand, no solvates of these salts have been prepared analogous to the hydrates of the aqueous system, *i.e.* containing more loosely bound AsCl_3 . Knowledge of the crystal chemistry of crystalline hydrates has been very useful, however, for the understanding of the hydration mechanisms (*cf. e. g.* Tovborg Jensen⁴). We have therefore tried to prepare such a solvate. It is obvious that milder evaporation must be used in this case. We were able to

prepare a salt $(\text{CH}_3)_4\text{NAsCl}_4 \cdot 2\text{AsCl}_3$ by such a careful treatment. It crystallizes in well developed crystals which are unstable in air because they are attacked by water vapour (at a humidity of about 40 % at room temperature). We intend to try to study the structure of this compound by X-ray methods.

Chemicals used: Arsenic trichloride (Schuchardt) was allowed to stand for three days with sodium, and was then removed from the sodium and distilled. The main fraction (95 % of the crude product) has a boiling point of 130.0° C. Tetramethylammonium chloride (Eastman Kodak) was dried for 12 hours at 110° C.

Procedure. The apparatus used is sketched in Fig. 1. In A there was supply of AsCl_3 . The $(\text{CH}_3)_4\text{NCl}$ was transferred to B through P, and a suitable amount of AsCl_3 was then pressed to B by a stream of dry nitrogen through a. When the salt had dissolved, dry N_2 was led through b and the stopcocks c and d opened. With c closed, some solution was transferred through d to C (filtration at f), after which c was opened again and d closed. The vessel D was cooled with a freezing mixture, and AsCl_3 was evaporated from C by evacuation at v (9 mm Hg). Crystals of $(\text{CH}_3)_4\text{NAsCl}_4 \cdot 2\text{AsCl}_3$ were formed in C.

Analyses. The crystals were dissolved in 1 M NaOH. The solution was slightly acidified with conc. HNO_3 , and Cl determined by a potentiometric titration with 0.1 M AgNO_3 (silver electrode). As was determined by a potentiometric titration with 1/60 M KBrO_3 (platinum electrode). A silver/silver-chloride electrode was used as reference electrode. *Results:* Found, Cl 54.5, As 34.5; calc. Cl 54.3, As 34.4.

Desolvatisation. It was proved that two of the three AsCl_3 molecules are loosely bound in $(\text{CH}_3)_4\text{NAsCl}_4 \cdot 2\text{AsCl}_3$ by deter-

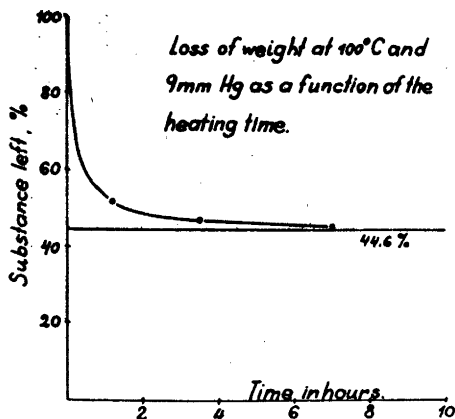


Fig. 2.

mining the loss of weight of the salt after heating at a pressure of 9 mm Hg to 100°C (Fig. 2). The calculated loss of weight is 55.5 %, that found 54.6 %.

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On the Synthesis of Methoxinine

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Methoxinine, the oxygen analog of methionine, has been prepared by Roblin¹ by alkylating ethyl phthalimidomalonate with β -methoxyethyl bromide, followed by

hydrolysis and decarboxylation of the resultant ethyl (β -methoxyethyl)phthalimidomalonate.

In an attempt to repeat this synthesis, using ethyl acetamidomalonate and either β -methoxyethyl chloride or β -methoxyethyl *p*-toluenesulfonate it was found difficult to obtain the intermediate ethyl β -methoxyethyl acetamidomalonate in a pure state. The substance was therefore prepared by the method of Barry and Hartung² using γ -methoxy- α -oximino butyric acid as an intermediate. Hydrogenation of this oximino acid in aqueous ammonia gave methoxinine in a pure state.

Experimental. (Micro analyses are made by Mr. P. Hansen. All melting and boiling points are uncorrected.)

Ethyl- β -methoxyethylmalonate was prepared in conventional manner³ from ethyl malonate, sodium ethoxide and β -methoxyethyl chloride in 69 % yield. B.p. 124—5°/10 mm; n_D^{25} 1.4228; $C_{10}H_{16}O_5$ (218.2): Calc. C 55.0; H 8.3. Found C 54.9; H 8.0.

γ -Methoxy- α -oximinobutyric acid was prepared according to the directions of Barry and Hartung² in 80 % yield. M.p. 112—3° (from ethyl acetate). $C_5H_9NO_4$ (147.1): Calc. C 40.8; H 6.2; N 9.5. Found C 41.0; H 6.1; N 9.2; Acid eqv. 147.

Methoxinine: A solution of 36 g of γ -methoxy- α -oximino butyric acid in 360 ml of 10% aqueous ammonia was treated with hydrogen at 50° and 100 atm for 6 hours using 10 g of Raney-nickel as a catalyst. The catalyst was filtered off and the solution concentrated to 100 ml in vacuum, treated with hydrogen sulfide to remove some dissolved nickel salts, filtered, and the solution concentrated to approx. 50 g, 150 ml of 99 % ethanol added, and the solution left in the ice box for 15 hours. Filtration gave 18 g (55 %) of colorless leaves, decomposing at 220—250° without melting (Roblin² gives m.p. 253° (dec. with effervescence)). $C_5H_{11}NO_3$ (133.1). Calc. C 45.1; H 8.3; N 10.5. Found C 44.9; H 8.0; N 10.5; Formol titr. 134.

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