STUDIES ON METALLIC HALIDE DIOXANATES

II. Dioxanates of Cupric and Ferric Chlorides

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INTRODUCTION

Molecular addition compounds of metallic halides with several ethers have been extensively studied and dioxanates of several metallic halides are reported.\(^1\)\(^-\)\(^8\) Rheindboldt \textit{et al.}\(^7\) in the course of their systematic investigations of the dioxane complexes of the halides of mono-, di- and trivalent metals have reported cupric chloride dioxanate with the formula CuCl\(_2\)·C\(_4\)H\(_8\)O\(_2\) as a relatively unstable compound. Later studies by Virginia \textit{et al.}\(^8\) have shown that cupric chloride forms a di-dioxanate. The method of preparation followed by the earlier workers is the direct mixing of dioxane and the metallic halide and subsequent purification. In view of the reported differences in the composition of cupric chloride dioxanate and in view of the absence of any previous studies on ferric chloride dioxanate, the present investigations have been made by the authors. The new method developed by the present authors\(^9\) for the preparation of mercuric chloride dioxanate is employed for the isolation of the dioxanates described in this paper.

The freshly prepared dry metallic oxide or hydrous oxide is suspended in pure dry dioxane and treated with dry hydrogen chloride gas. The hot solution is filtered under dry conditions to remove unreacted or hydrolysed materials and the filtrate is cooled overnight at 0\(^\circ\) C. when crystals of the dioxanate separate. The crystals are collected in a dry sintered funnel, washed with dry petroleum ether and treated with a current of dry air. The samples if necessary can be recrystallised from dioxane. The pure samples are then analysed for metal and chloride.

DISCUSSION

Cupric chloride dioxanate thus prepared and analysed is found to be the mono-dioxanate, the analytical values agreeing with the formula CuCl\(_2\)·C\(_4\)H\(_8\)O\(_2\). Cupric chloride dioxanate is very sparingly soluble in...
dioxan and this fact makes the method of preparation less convenient and efficient. On treatment with hydrogen chloride gas, a brownish product gets precipitated, covering the unreacted copper oxide and thus preventing completion of the reaction. This difficulty is observed with precipitated copper oxide and to a larger measure with ignited oxide, but when cupric hydroxide dried to constant weight at 160° C. is used, a homogeneous product is obtained. Solubility of the complex in dioxane is considerably low and only a small quantity of the crystals could be obtained on cooling the filtrate. The crystals are brownish in colour, needle-shaped and highly hygroscopic. On exposure to air, the colour changes to bluish green. The complex is very soluble in water, the concentrated solution becoming blue. The dioxanate is very stable and remains unchanged even after heating to 140° C. or after evacuation at 1 mm. pressure for 2 hours. No change in composition occurs when crystallised from alcohol. But when crystallised from water the dioxanate is destroyed and cupric chloride dihydrate is obtained. At no stage in the present investigations, the authors were able to get the didioxanate of cupric chloride as reported by Virginia et al.

Ferric chloride is found to form the tridioxanate with the formula FeCl₃·3 C₄H₈O₂. Trivalent halides of arsenic, antimony and bismuth form molecular addition compounds with dioxane with the general formula 2 MCl₃·3 C₄H₈O₂ (where M = As; Sb or Bi) and aluminium halides form both mono- and didioxanates. Among the transition elements, Cobalt is reported to form CoI₃·3 C₄H₈O₂; CoI₃·2 C₄H₈O₂ and CoI₃·C₄H₈O₂. Ferric chloride shows close resemblance to cobalt iodide in the number and stabilities of their dioxanates. The present method of preparation is highly suitable for isolating ferric chloride dioxanate. Both hydrous and ignited ferric oxides are found to be equally good as starting material. Ferric oxide suspended in dioxane is rapidly and vigorously attacked by hydrogen chloride gas. No unreacted oxide remains and no ferric chloride complex gets precipitated. However, the solubility of the complex in dioxane is so high that the yield on crystallisation is small. The dioxanate is obtained as pale green thin plates. It is extremely hygroscopic and changes to an yellowish brown viscous liquid on exposure to air. The crystals can be best preserved in petroleum ether or in an atmosphere of dioxane vapour. When kept in a desiccator, slow changes in colour and crystalline form set in, with loss of dioxane. A product approximating to the composition 2 FeCl₃·3 C₄H₈O₂ can be obtained by crystallisation of the tridioxanate from alcohol. When kept in a vacuum, the tridioxanate slowly changes to give first 2 FeCl₃·3 C₄H₈O₂ and finally FeCl₃·C₄H₈O₂. The monodioxanate can be obtained within 90 minutes if the evacuation is done at 110° C. The
dioxanate is more highly soluble than ferric chloride itself in alcohol and acetone. However, the acetone solution undergoes colour change and slow decomposition even at 0°C.

**EXPERIMENTAL**

**Materials Used**

(1) *Cupric oxide.*—(a) A.R. grade copper sulphate (50 g.) was dissolved in water and a dilute solution of sodium hydroxide added till precipitation was complete. The precipitate was allowed to stand at 80°C for one hour, filtered and washed free of soluble impurities. It was then dried at 160°C to constant weight, powdered and stored. Analysis of the sample showed it to be pure cupric oxide.

(b) A.R. grade copper carbonate (25 g.) was ignited in a platinum dish at 800°C. The copper oxide thus obtained was cooled and stored.

(c) A.R. grade copper sulphate (50 g.) was dissolved in water and 1 N ammonium hydroxide was added in drops till precipitation was complete. The precipitated cupric hydroxide was filtered off, washed free of sulphate and dried at 160°C to constant weight.

*Ferric oxide.*—(a) A.R. grade ferric ammonium sulphate (100 g.) was dissolved in water and 1 N ammonium hydroxide added to precipitate the ferric hydroxide. The precipitate was filtered off, washed free of sulphate and dried at 160°C to constant weight.

(b) The hydrated ferric oxide (10 g.) prepared as in (a) was ignited at 900°C, cooled and stored.

*Dioxane.*—C.P. grade B.D.H. make dioxan was refluxed with sodium, distilled and stored over sodium wire.

*Dry hydrogen chloride* gas was prepared as and when required.

**Analytical.**—Pure samples of the dioxanates were analysed for metal and chloride by standard methods.

**Preparation of Cupric Chloride Dioxanate**

Cupric oxide (5 g.) sample (a) was suspended in dioxan (200 ml.) and treated with dry hydrogen chloride gas. The contents of the vessel were cooled in cold water. A brown product was formed which got mixed up with the unreacted cupric oxide. As the reaction proceeded, the amount of the brown product increased, but even after one hour some cupric oxide was found to remain. The contents of the vessel were filtered under dry
conditions and the filtrate let stand overnight at 0°C. Light brown needle-shaped crystals of the dioxanate separated at the bottom of the vessel. The crystals were collected on a dry sintered funnel, washed with petroleum ether, dried in a current of dry air and analysed for copper and chloride. Found: per cent., Cu: 28·34; Cl: 31·98. Calculated per cent. values for the formula CuCl₂·C₄H₇O₂: Cu: 28·56; Cl: 31·86. Most of the dioxanate formed by the reaction was admixed with unreacted copper oxide. When the ignited copper oxide, sample (b) was used in the above reaction, the behaviour was nearly identical, except that the reaction was slower and the amount of unreacted oxide was larger. But when cupric hydroxide sample (c) was made to react, the entire copper reacted rapidly and a brownish homogeneous product was obtained. This product after washing with petroleum ether was analysed. Found: per cent., Cu: 28·85; Cl: 31·21. Because of the very low solubility in dioxane, it could not be recrystallised successfully. The filtrate after removal of the brownish product gave, on cooling, needle-shaped crystals of the dioxanate CuCl₂·C₄H₇O₂.

Stability studies.—(1) The crystals on heating in a melting point tube underwent slight colour change to greyish brown at 140°C. There was no noticeable change till 300°C and on further heating the substance charred leaving a black residue. The dioxanate was found to remain unchanged for several weeks when kept in a dry atmosphere. Evacuation at room temperature at 1 mm. pressure for two hours did not bring about any change in composition.

(2) Effect of crystallising from water.—A saturated solution of the dioxanate in water was prepared at 60°C and the clear solution kept overnight at 0°C. Bluish green crystals that separated were removed, dried between folds of filter-paper and analysed. Found: per cent., Cu: 37·03; Cl: 41·14. Calculated per cent. values for the formula CuCl₂·2H₂O: Cu: 37·26; Cl: 41·58.

From alcohol.—The dioxanate is fairly soluble in alcohol, the solution acquiring an olive green colour which becomes deeper with concentration. A saturated solution of the dioxanate crystals in about 50 ml. absolute alcohol was prepared at 40°C and the clear solution cooled to 0°C. A solid phase got separated after two days, as hard plates with brick-red colour. However, the solid on analysis gave the same values as the original dioxanate. The crystallised product was heated under vacuum for two hours and there was no loss in weight showing that it was a very stable compound.

From acetone.—Cupric chloride dioxanate is only very sparingly soluble in acetone, the solution acquiring a pale brownish colour. A product with definite crystalline shape or composition could not be isolated.
Preparation of Ferric Chloride Dioxanate

The procedure adopted was the same as described earlier. Ferric oxide (5 g.), sample (a) suspended in 100 ml. dioxane was treated with hydrogen chloride gas. The reaction was very fast and a dull green clear solution was obtained within fifteen minutes. All the ferric oxide had gone into solution and the complex had not precipitated during the reaction. The solution was kept overnight at 0°C. when the dioxanate separated. The crystals were transferred to a sintered funnel, washed several times with petroleum ether and kept in a current of dry air for 30 minutes. The sample was then analysed for iron and chloride. Found: per cent., Fe: 13.22; Cl: 25.15. Calculated per cent. values for the formula FeCl₃·3C₄H₈O₂: Fe: 13.10; Cl: 24.97.

The experiment was then repeated with ignited ferric oxide (sample b). Reaction proceeded in almost identical manner except for the slower rate and the same product was obtained.

Stability studies.—Ferric chloride tridioxanate even on keeping under dry conditions is found to be unstable. In about 10-12 days it becomes black and sticky. However, it can be preserved indefinitely under petroleum ether. When exposed to air, it rapidly absorbs moisture and behaves like ferric chloride. It is readily soluble in water, at first giving an yellowish green solution which on keeping becomes more yellow and finally yellowish-brown, possibly due to hydrolysis and formation of colloidal ferric hydroxide.

The dioxanate dissolves readily in alcohol imparting a pale yellow colour to the solution. Even after cooling a saturated solution to —20°C., only a small amount of the crystals could be obtained. Analysis of this product does not give any concordant results, but the values approximate for the formula 2FeCl₃·3C₄H₈O₂.

The dioxanate crystals are equally highly soluble in acetone, the solution becoming pale brown in colour. But within 30 minutes, even at 0°C the colour was found to deepen and in two hours, the solution became dark brown in colour. On cooling to —20°C., a dark brown solid got deposited, together with a tarry oily matter on the top of the solution. Attempts to identify the products were unsuccessful.

The dioxanate crystals, on slowly heating with a naked flame, melt and then burn with a smoky flame. On stronger heating ferric oxide is obtained. When kept in a vacuum there was progressive loss in dioxane and two lower dioxanates 2FeCl₃·3C₄H₈O₂ and FeCl₄·C₄H₈O₂ could be isolated. These lower dioxanates are more stable than the tridioxanate, the monodioxanate being most stable.
Studies on Metallic Halide Dioxanates—II

SUMMARY

Cupric chloride dioxanate has been prepared by the new method developed by the authors and shown to be the monodioxanate. Stability studies and effects of crystallisation from different solvents are reported.

The tridioxanate of ferric chloride is prepared and studied. Existence of two lower dioxanates of ferric chloride has been indicated.

REFERENCES

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