STUDIES ON HEXACHLOROCERIC ACID

II. Reaction of Hydrated Ceric Oxide with Hydrogen Chloride Gas in Non-Aqueous Solvents

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RESULTS of the reaction of hydrated ceric oxide and hydrogen chloride in methyl alcohol and dioxane have been detailed in Part I of the series. The reaction was studied in various liquids—both polar and non-polar—which are usually good solvents. Reaction was found to take place in some of the solvents, although in the absence of dioxane, no crystalline product could be isolated. The reaction is found to take place in such solvents which can form oxonium type of compounds with hydrogen chloride. The failure to isolate hexachloroceric acid from solutions in methyl alcohol, ether and ethylene glycol mono-methyl ether, in the absence of dioxane clearly shows that a suitable solvate is necessary for the complex formation in a crystalline form. Addition of dioxane to concentrated solutions in various solvents results in the formation of crystals having the composition \( \text{H}_2\text{CeCl}_6, 4 \text{C}_4\text{H}_8\text{O}_2 \). It appears that the solubility of the product is very much enhanced by the presence of OH group in the solvent as evident from the high solubility in methyl alcohol. The extremely rapid reaction in ethylene glycol mono-methyl ether and the non-separation of a second layer or crystals, support the view that the presence of tetravalent oxygen favours the reaction and that the presence of OH group in the solvent increases the solubility of the product formed. The separation of a second layer in ether shows the relatively low solubility of the product in ether which does not have the hydroxyl group. The exact nature of the mechanism of reaction in these solvents is not understood with certainty.

EXPERIMENTAL

Material used.—Hydrated ceric oxide and hydrogen chloride were prepared by the method detailed in Part I of the series. Dioxane, petroleum ether, benzene, chloroform, acetone, ether, ethylene glycol mono-methyl ether, formamide, and cyclohexanol were purified and dried by the standard methods.\(^1\),\(^2\)

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Studies on Hexachloroceric Acid—II

Reactions in acetone, cyclohexanol, formamide, anisole, benzene, and carbon tetrachloride:

(a) Acetone.—A mixture of hydrated ceric oxide (5 g.) and acetone (100 c.c.) was subjected to the action of hydrogen chloride for three hours. The acetone turned only light yellow in colour. When the flask was left at 2–3°C for a day, the liquid became dark brown in colour with the formation of mesitylene oxide due to the polymerisation of acetone in presence of hydrogen chloride. Acetone was therefore considered unsuitable for the preparation of hexachloroceric acid.

(b) Cyclohexanol.—The previous experiment was repeated with cyclohexanol as the reaction medium. The ceric oxide remained unreacted. The solvent became slightly brownish in colour but no crystals separated on cooling the solution.

(c) Formamide.—When this solvent was used as the reaction medium, there was no change in the ceric oxide. The formamide became slightly brownish in colour but very little of the hydrochloroceric acid was produced.

(d) Anisole.—In this case also, the ceric oxide remained practically unreacted. But on keeping, the liquid became dark brown but no hydrochloroceric acid was produced.

(e) Reaction in benzene and carbon tetrachloride.—These solvents were tried as reaction media. As before, hydrated ceric oxide was suspended in these solvents and hydrogen chloride was passed. In both cases, there was no reaction and the ceric oxide remained unchanged.

1. Reaction in ether.—Hydrated ceric oxide (5 g.) and ether (150 c.c.) were taken in a flask and hydrogen chloride was passed at 10°C for three hours, with stirring. The reaction was very slow, most of the gas being unabsorbed. Finally, the colour of the solution became orange. The flask was cooled at 2–3°C. The colour of the solution slowly became deeper and at the end of a week, about 5 c.c. of an oily red liquid got collected at the bottom. The ether layer had become red in colour. After another week, more of the red liquid had formed and then the contents of the flask were filtered. The residue on the filter was found to be mostly unreacted ceric oxide. The clear filtrate consisting of about 10 c.c. of the red oily lower layer and about 120 c.c. of the upper layer, was kept at 0°C for several days. Crystallisation did not take place. All attempts to crystallise the substance were unsuccessful.

The two layers were separated and portions of each analysed for cerium and active chlorine. Both layers gave the atomic ratio of cerium to active
chlorine as $1:1$. It was clear that small amounts of the hexachloroceric acid were formed in this solvent.

A portion of the lower layer was added to some dioxane. The two liquids mixed well on shaking. The solution was then kept at $2-3^\circ$C., when orange red, needle-shaped crystals separated out. The crystals were removed, washed with petroleum ether, dried and analysed. The composition of the crystals was found to agree with the formula $\text{H}_4\text{CeCl}_8 \cdot 4 \text{C}_4\text{H}_8\text{O}_2$. Hence it can be assumed that the red liquid that separated contained hexachloroceric acid, probably with ether of solvation.

2. Reaction in ethylene glycol mono-methyl ether.—When this solvent was used as the reaction medium in the above reaction, more vigorous reaction and quicker changes were noticed. Within about half an hour, nearly the whole of the ceric oxide dissolved and the solution became red and viscous. The temperature of the flask rose to about $60^\circ$C. The flask was disconnected from the hydrogen chloride system and the contents filtered. There was very little residue left on the filter and a clear, red viscous solution was obtained as the filtrate. Analysis showed that the gram atom ratio of cerium to active chlorine was $1:1$.

Attempts were made to isolate a pure compound from this solution. Keeping the solution at $0^\circ$C. for several days did not effect crystallisation. Cooling to $-15^\circ$C. also did not make any change. Further cooling in solid carbon dioxide bath caused solidification of the entire solution without any separation of the acid. The solution was washed with petroleum ether. A larger number of washings with petroleum ether gave a pasty product. A pure product with a constant composition could not be obtained. Removal of solvent by evacuation was also not successful in getting the pure acid.

A portion of the solution was mixed with an equal volume of dioxane and kept at $2-3^\circ$C. Within a few hours needle-shaped orange coloured crystals appeared, which were removed, washed with petroleum ether, dried and analysed. The results indicated that the compound had the formula $\text{H}_4\text{CeCl}_8 \cdot 4 \text{C}_4\text{H}_8\text{O}_2$. These facts clearly show that hexachloroceric acid is formed during the above reaction in presence of ethylene glycol mono-methyl ether but the solid acid could not be crystallised.

**Summary**

(1) Benzene, carbon tetrachloride, formamide, cyclohexanol, anisole and acetone are not suitable media for the reaction of hydrated ceric oxide and hydrogen chloride.
(2) The reaction is found to take place to a limited extent in ether and nearly to completion in ethylene glycol mono-methyl ether forming hexachloroceric acid.

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REFERENCES

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(2) A. I. Vogel