STUDIES ON HEXACHLOROCERIC ACID

I. Isolation of Hexachloroceric Acid

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The reason for the marked instability of ceric halides have not been fully understood. Only the fluorides are known as normal salts of both cerous and ceric cerium.[1-3] Ceric chloride has not been isolated in the free state. When ceric hydroxide is dissolved in concentrated hydrochloric acid, a dark-red solution containing ceric chloride or the acid H_2CeCl_6 is obtained which rapidly decomposes with evolution of chlorine. The possibility of obtaining ceric chloride or hexachloroceric acid in absence of water was first reported by Koppel[4] and following his method, several double salts of the acid with organic bases have been prepared.[5-7] It is of interest to note that while the sulphato- and nitrato-ceric acids are stable in aqueous solutions, the chlorato-ceric acid is quite unstable. Although Koppel, for the first time, tried to isolate ceric chloride by carrying out the reaction between ceric oxide and hydrogen chloride in methyl alcohol, he only succeeded in preparing the pyridinium double salt of hexachloroceric acid. This paper deals with a systematic study for the isolation of hexachloroceric acid by using methyl alcohol and dioxane as reaction media to increase the stability of the products.

The reaction of hydrated ceric oxide and hydrogen chloride in methyl alcohol did not yield useful results in the isolation of hexachloroceric acid. The failure to isolate the reaction product from methyl alcohol solution could be either due to the high solubility of the product in methyl alcohol or due to the incapacity of the solvent to co-ordinate with the product as a solvate to yield a stable complex or due to both. Dioxane was next employed as the solvent. Dioxane was expected to be a good solvent to prepare ceric chloride since the solvent might increase the stability of the compound by forming a type of oxonium compound. Several inorganic halide dioxinates have been reported.[8-12]

It has been found in the present investigation that hexachloroceric acid crystallises out, under suitable conditions from a dioxane solution with four molecules of dioxane for every mole of the acid. The exact nature of the mechanism of reaction of hydrated ceric oxide and hydrogen chloride in dioxane and the formation of the crystalline product is not understood with certainty. Although the formation of hexachloroceric acid is noticed when various other organic solvents are used as reaction media, *viz.*, methyl alcohol, ether, ethylene glycol mono methyl ether, etc., the crystalline product is obtained only in presence of dioxane. Evidence has been adduced to suggest that an anion complex of the type $CeCl_6$ is absent but that the product is a molecular compound of ceric chloride and hydrogen chloride of the formula $CeCl_4 . 2\,HCl$, co-ordinated with four molecules of dioxane. If the hexachloroceric acid and its pyridinium salt were complexes with cerium attached to the six chlorine atoms in a stable anion, silver nitrate solution (in non-aqueous medium) should give no precipitate. Again, if it is assumed that the anion consists of all the chlorine atoms combined with the cerium atom, there is no reason why one chlorine atom should behave differently in liberating iodine from potassium iodide. Studies on the physico-chemical properties like conductivity, molecular weight, vapour pressure and spectral characteristics—details of which are to be published in another part of the series—strongly support the view that the compound does not contain an anion complex of the type $CeCl_6^{--}$.

EXPERIMENTAL

Materials used

(1) *Hydrated ceric oxide.*—Pure ceria was prepared from ceric ammonium nitrate by the iodate method. The ceric oxide thus obtained was converted into nitrate, dissolved in water and made alkaline with dilute ammonia. The precipitated hydroxide was oxidised with hydrogen peroxide and let stand for 12 hours. The yellow product was filtered, washed thoroughly with water, dioxane and petroleum ether when a free flowing yellow powder ($CeO_2 \cdot 2\,H_2O$) was obtained.

(2) *Hydrogen chloride.*—Hydrogen chloride gas was prepared by the method of Harwood Tucker.[13]

(3) Methyl alcohol, dioxane and petroleum ether (30–75° C.) were purified and dried by standard methods.[14]

Analytical

(1) *Cerium.*—Cerium was precipitated as the oxalate, ignited and weighed as ceria.

(2) *Active chlorine.*—A known quantity of the material was put into acidified potassium iodide solution and the iodine liberated was estimated by standard sodium thiosulphate.

(3) *Total chlorine.*—A known weight of the substance was dissolved in 1 N sodium hydroxide solution and the contents acidified with chloride-free

nitric acid until the precipitated cerous hydroxide redissolved. The decomposition of the hypochlorite was effected by warming the solution with a little urea. The chloride content of the solution was estimated volumetrically by the silver nitrate method.

(1) *Reaction of hydrated ceric oxide and hydrogen chloride in methyl alcohol*

Hydrated ceric oxide (5 g.) and methyl alcohol (100 c.c.) were taken in a flask at 20° C. and hydrogen chloride was passed for nearly three hours with constant stirring, at the rate of about 6 litres per hour. The methyl alcohol solution turned orange-red in colour. The flask was kept at 2–3° C. for two days when the solution became more intensely coloured. The solution was filtered, out of contact with moisture and the residue on analysis was found to consist of 97·1% $CeO_2 \cdot 2\ H_2O$ and 3% $CeCl_3$. The filtrate was analysed for active chlorine and cerium contents. The estimation of total chloride was not attempted as it was not possible to free the solution completely of dissolved hydrogen chloride. It was noticed that for every gram atom of active chlorine, a corresponding quantity of cerium was present in the methyl alcohol solution. These results in general indicated that about 3% of ceric oxide was converted into ceric chloride or hexachloroceric acid which dissolved in alcohol producing the orange-red colour.

The above experiment was repeated at 0° C., − 15° C. and − 75° C. In the first two cases, there was not much difference in the rate of reaction and development of colour from the previous experiment. There was practically no reaction at − 75° C. The reaction could not be carried out for a long time as the methyl alcohol solution became very viscous, preventing the free passage of hydrogen chloride.

The product obtained by the reaction of 7·5 g. of ceric oxide and hydrogen chloride in 150 c.c. of methyl alcohol for three hours, was kept at 0° C. The progress of reaction was followed by estimating the active chlorine in aliquots of the solution every twelve hours. From these values, the amount of cerium (IV) in the solution was calculated. The results are presented in Table I.

These results show that in thirty-six hours, the ceruim (IV) content has increased nearly seven-fold, after which the rate of reaction is very slow.

Attempts at the isolation of hexachloroceric acid from methyl alcohol solution

About 100 c.c. of the ceric chloride in methyl alcohol, was subjected to vacuum desiccation when the intensity of colour and viscosity of the alcohol solution were found to increase. During the final stages an yellowish-red solid separated which on further desiccation yielded only cerous chloride. Presence of free chlorine in the exit vapour was detected towards the final stages of evaporation. Concentration by cooling at 0° C. and at − 20° C. gave no better results.

TABLE I

Progress of reaction between ceric oxide and hydrogen chloride in methyl alcohol with time

Time (in hours)	% Ce (IV) in soln.
3	0·33
12	1·25
24	1·89
36	2·22
48	2·36
60	2·58
72	2·68

Removal of methyl alcohol from the solution was also attempted by passing a current of hydrogen chloride to maintain the acidity at a high value. The solid that separated was found to be merely cerous chloride. Separation of the ceric chloride by fractional freezing of the alcohol did not result in higher concentration of the ceric chloride. Fractional precipitation of the chloride by the addition of benzene, carbon tetrachloride, chloroform, ether, dioxane and petroleum ether did not yield any fruitful results. It can therefore be concluded that methyl alcohol is not a suitable medium for the preparation of hexachloroceric acid.

(2) *Reaction in presence of dioxane*

Hydrated ceric oxide (5 g.) suspended in dioxane (100 c.c.) was next treated with hydrogen chloride for nearly three hours. As there was considerable rise in temperature, the flask was cooled in water at 25° C. The development of the orange colour in the solution was much quicker than with methyl alcohol and left only a small quantity of residual solid. The flask was stoppered and left overnight at 2–3° C. when some orange-red, needle-shaped crystals were formed. At the same time the colour of the solution had become paler. The solution was filtered through a sintered glass funnel, out of contact with moisture. The filtrate on analysis was found to contain cerium and active chlorine in the gram atom ratio of 1 : 1.

The residue in the funnel consisting of the crystalline mass and unreacted ceric oxide was dried in a current of dry air after washing with a small quantity of dioxane to remove the adsorbed solution and hydrogen chloride. The solid was then extracted with 50 c.c. of dioxane and filtered when a deep red filtrate was obtained, leaving a white residue on the filter. The white residue thus obtained was found on analysis to be a mixture of 87% ceric oxide and 13% $CeCl_3$. The deep red filtrate was then analysed for cerium, active chlorine and total chlorine and the ratio was found to be 1 : 0·994 : 6·10. From this, it was concluded that the crystals had the empirical formula H_2CeCl_6 with or without dioxane of crystallisation.

In subsequent experiments, 10 g. of ceric oxide were treated with hydrogen chloride, using the dioxane solution left as the filtrate, and the unreacted ceric oxide was removed by filtration. The filtrate separated into two layers, the heavier one being deep red and the lighter one orange-red in colour. On cooling the heavier layer to 2–3° C. for about 6 hours, a large crop of needle-shaped, bright, orange-coloured crystals separated, leaving behind pale orange coloured mother liquor. It was also noticed that the presence of hydrogen chloride was necessary for efficient crystallisation.

Analysis of the crystals

The crystals prepared as above were washed several times with petroleum ether and dried in a current of dry air, and analysed for cerium, active chlorine and total chlorine. The mean values of six different crops of crystals were: Ce = 19·48%; active chlorine = 4·94%; and total chlorine = 29 69%. Calculated percentage composition of $H_2CeCl_6 \cdot 4\,C_4H_8O_2$ is: Ce = 19·80%; active chlorine = 5·02% and total chlorine = 30·13%. The cerous chloride obtained by thermal decomposition of the crystals was also analysed. A known weight of the crystals was heated to 150° C., out of contact with moisture and cooled in a current of nitrogen and weighed. It was then analysed for cerium and chloride. The average value was 33·62% residue analysing to 56·18% Ce and 42·85% Cl. Calculated value of $CeCl_3$ from H_2CeCl_6, $4\,C_4H_8O_2$ is 34·87 % with 56·79% Ce and 43·21% Cl. These results conclusively show that the residue on decomposition of the acid crystals is cerous chloride, and the per cent. weight of $CeCl_3$ obtained agrees with the calculated value when the acid has the formula $H_2CeCl_6 \cdot 4\,C_4H_8O_2$. Because of the high reactivity of the crystals towards light and moisture, experiments to estimate carbon and hydrogen did not give consistent results.

Preparation of salts

Koppel prepared the organic derivatives of hexachloroceric acid by treating the methyl alcohol solution with organic bases. The hexachloroceric acid crystals as prepared above, were also employed to prepare these compounds as follows. To a solution of the crystals in dioxane was added a solution of pyridinium chloride in methyl alcohol. Yellow shining crystals were thrown out, the amount of which increased by the addition of ether. The crystals were filtered off, washed with ether and analysed. The percentage composition was Ce = 26·80, active chlorine = 6·72, total chlorine = 39·26 and nitrogen = 5·12 agreeing well with the formula $(C_5H_5NH)_2 CeCl_6$, for the complex.

With a view to prepare the sodium salt, the following methods were tried. Samples of methyl alcohol solution of the acid crystals were added to a methyl alcohol solution of sodium hydroxide, a solution of sodium methoxide in methyl alcohol and dry solid sodium chloride respectively. In the first two cases, there was immediate decolourisation with precipitation of cerous chloride. In the experiment where sodium chloride was added there was no immediate change, but on standing the solution got slowly decolourised, with deposition of white residue. Further studies on the preparation of salts of the acid are in progress.

Attempts to prepare the acid without dioxane of solvation

A portion of the heavy layer of liquid that is formed during the reaction of ceric oxide and hydrogen chloride in dioxane at 50° C. was subjected to evacuation at 25° C. and 0·1 mm. pressure. As the solid dried up, a pale yellow powder was left which was identified as cerous chloride. Repeated washing of the liquid with petroleum ether also resulted in getting cerous chloride as the residue. When the acid crystals were subjected to evacuation, decomposition took place leaving behind cerous chloride. Gentle heating of the crystals also resulted in decomposition. It was thus concluded that the acid got easily decomposed when the dioxane of solvation was removed.

SUMMARY

(1) The reaction of hydrated ceric oxide with hydrogen chloride in methyl alcohol under controlled conditions did not result in the isolation of hexachloroceric acid.

(2) Hexachloroceric acid has been obtained as a crystalline product from the reaction of hydrated ceric oxide and hydrogen chloride in dioxane.

(3) Conditions have been worked out for obtaining the crystals in a pure form. Analytical results agree with the formula H_2CeCl_6, $4\,C_4H_8O_2$. It has not been possible to obtain the acid without the dioxane of solvation.

(4) The pyridinium salt of the acid has been prepared, the analytical values agree with the formula $(C_5H_5NH)_2CeCl_6$ for the complex.

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