STUDIES ON HEXACHLOROCERIC ACID

V.* Stability, Spectral Characteristics and Electrical Conductance

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Received September 17, 1958

Suitable conditions for preserving hexachloroceric acid crystals without decomposition have been found out from stability studies under various conditions. From studies on spectral characteristics and electrical conductivity in dioxan and methyl alcohol solutions, a mode of dissociation has been postulated.

It has been shown by the authors¹, ² that hexachloroceric acid could be prepared when dry hydrogen chloride diluted with nitrogen is allowed to react with hydrated cerioxide (CeO₂₄H₂O) at −20 °C. to −15 °C. It was not possible to isolate the free acid in a pure state, but the acid was crystallised out in dioxan solution and these acid crystals had the composition (H₂CeCl₆₄C₄H₈O₂) with 4 molecules of dioxan of crystallisation. Several difficulties were encountered in handling the acid crystals during the course of isolation, purification and analysis. Results of investigations of some of the salient properties of these acid crystals are presented in this paper.

Results obtained from the decomposition studies clearly explain the difficulties in handling and keeping the crystals. About 40% decomposition takes place in 9 hours when the crystals are exposed under dry conditions and when the volatile products of decomposition are swept off. The rate of decomposition is quite high in the beginning, but falls off with the progress of time, the rate being only 3.4% per hour at the end of 9 hours. Temperature is found to have a marked effect on the stability of the substance, 30% decomposition taking place at 40 °C. in one hour. At about 70 °C., the entire crystals appeared to melt accompanied by sudden decomposition, leaving a white residue of cerous chloride. Similarly, exposure to direct sunlight was found to decompose the crystals completely within one hour. The corresponding decomposition in diffused light was only 32%.

(Table III).

* Part IV, This Journal, 1956, 43, 272.

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Preliminary experiments indicated that the crystals are best preserved under dry petroleum ether, free from reducing substances at 0°C. in the dark. In this way the pure hexachloroceric acid crystals can be kept for weeks without undergoing any change.

The vapour pressure of the acid crystals has been measured from 0°C. to 30°C. Measurements beyond 30°C. could not be recorded as decomposition occurred. The straight line obtained by plotting $1/T$ against $-\log p$ can be represented by the equation, $-\log p = (2200/T) - 8.81$ and the heat of dissociation was found to be 10.96 k.cal./mol. The heat of vaporisation of dioxan is 8.96 k.cal./mol.

The dioxan solution of the crystals showed (Fig. 2) two absorption maxima at 255μ and 370μ. The hydrogen chloride solution in dioxan of nearly corresponding strength was found to have the absorption maximum at 260μ. Hence it was clear that the absorption maximum at 370μ was due to the hexachloroceric acid. The methyl alcohol solution of the acid crystals, however, showed only one absorption maximum at 310μ. This value was in agreement with the reported absorption maximum for aqueous ceric salt solutions. The shift to 310μ in methyl alcohol solutions could therefore be attributed to ionisation of CeCl₄ to Ce²⁺ which might be absent in dioxan solution. This assumption is supported by the result obtained by the conductivity measurements. Dioxan solutions of the acid showed very poor conductivity, indicating the absence of dissociation of the compound. While the values for molecular weight of the acid crystals in dioxan definitely indicated dissociation, the electrical behaviour of the solution made it necessary to exclude the presence of any ionic species in the solution. It may, therefore, be assumed that in dioxan, the compound undergoes dissociation according to the equation $\text{CeCl}_4·2\text{HCl} \rightarrow \text{CeCl}_4 + 2\text{HCl}$.

In methyl alcohol, it appears that ionic dissociation of CeCl₄ takes place probably in successive steps as $\text{CeCl}_3^{+1}$, $\text{CeCl}_2^{+2}$ and $\text{CeCl}^{+3}$ and finally $\text{Ce}^{+4}$. The excellent agreement in absorption maximum at 310μ of the crystals in methyl alcohol with that of dilute ceric sulphate solution of low acidity where the presence of $\text{Ce}^{+4}$ or $\text{CeSO}_4^{+2}$ has been established, lend support to the above assumptions. It can also be seen that the higher values of specific conductivity of dilute solutions (0.025 to 0.0125 M) of ceric acid crystals as compared with the specific conductivity of hydrogen chloride of corresponding strength (Table V) suggest that the conductivity of the solution of the crystals in methyl alcohol is not due to the ionised HCl alone.