STUDIES ON HEXACHLOROCERIC ACID

VI. Pyridinium Ceric Chloride Complex

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ABSTRACT

Pyridinium ceric chloride has been prepared and analysed. Its structure is elucidated from studies on mode of formation, spectral characteristics and vapour pressure data. Attempts to prepare complexes with sodium and ammonium chlorides are also presented.

ALTHOUGH Koppe failed in his attempt to isolate ceric chloride or hexachloroceric acid, he succeeded in isolating the pyridinium complex of hexachloroceric acid and assigned it the formula $(C_6H_5NH)_2CeCl_4$. Koppe’s work was later extended by Destifano and Caglioti. Bradley and co-workers have used this type of pyridinium salts of quadrivalent metals for the preparation of alkoxides of Th, Zr, Hf and Ce. They have assumed the general formula $(C_6H_5NH)_2 MCl_4$ for the salt. But, in view of the evidence presented by the authors on the structure of hexachloroceric acid in methyl alcohol solution, the presence of cerium in the anion complex of the pyridinium salt is to be doubted. Bradley’s alkoxylation mechanism can as well be explained, if the pyridinium salt is assumed to be $CeCl_4 \cdot 2(C_6H_5NH\cdot Cl)$, a molecular addition compound of ceric chloride with pyridinium hydrochloride, analogous to the structure $CeCl_4 \cdot 2 HCl$ for hexachloroceric acid in methyl alcohol. This formulation of the structure of pyridinium salt is very well supported by the excellent agreement in the absorption maxima of the salt and the acid in methyl alcohol, now reported by the authors with the absorption maxima for ceric salts in aqueous solutions.

The absorption maximum of the ceric pyridinium chloride in methyl alcohol is found to be at $310 \mu$. There is no absorption in this range for a solution of pyridinium hydrochloride in methyl alcohol. The absorption maximum

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† Part V of the Series.
at 310\( \mu \) is reported to be characteristic of only Ce\(^{4+} \) ions and not of [Ce(SO\(_4\)]\(^{2-} \) ion. In the same manner, the absorption at 310\( \mu \) is attributable to the following mode of dissociation in methyl alcohol:

\[
\text{CeCl}_4 \cdot 2 \text{C}_6\text{H}_5\text{NHCl} \rightarrow \text{CeCl}_4 + 2 \text{C}_6\text{H}_5\text{NHCl}
\]

\[
\text{CeCl}_4 \rightarrow \text{Ce}^{4+} + 4 \text{Cl}^-
\]

The ionic dissociation may be stepwise and incomplete. The degree of dissociation and nature of the species present in dilute methyl alcohols are being investigated.

Details of preparation and analysis of the pyridinium salt are presented. Attempts are made to find if an acid salt could be prepared by mixing methanol solutions of hexachloroceric acid and pyridinium hydrochloride in different molar ratios. The products obtained were found to be the same in all cases.

In all the earlier methods of preparation, a methanol solution of the acid, containing large quantity of dissolved hydrogen chloride, had to be used, as the hexachloroceric acid had not been isolated. Hence it was not possible, so far, to study the mode of formation of the salt. It has now been established by the present investigations, at least qualitatively, that hydrogen chloride is displaced when pyridinium hydrochloride is added to hexachloroceric acid solution without any free hydrogen chloride. This observation gives additional support to the proposed structure of the acid and the corresponding preparation can be represented as:

\[
\text{CeCl}_4 \cdot 2 \text{HCl} + 2 \text{C}_6\text{H}_5\text{NHCl} \rightarrow \text{CeCl}_4 \cdot 2 \text{C}_6\text{H}_5\text{NHCl} + 2 \text{HCl}
\]

The fact that the acid crystals and the pyridinium salt contain one equivalent of active chlorine, readily liberating one equivalent of iodine from potassium iodide solution, is also better explained by the above structures, the ceric chloride getting reduced to cerous chloride. The formulation, with the cerium atom and all the six chloride atoms in the anion complex, thus, fails to explain most of the properties shown by the acid and the pyridinium salt.

In view of the remarkably higher values of the vapour pressure of the complex as compared with those of pyridinium hydrochloride (Table II) the composition of the vapour-phase was determined. The vapour pressure of the ceric complex increases from 1.75 mm. at 0°C to 9.00 mm. at 25°C, while the corresponding increase with pyridinium hydrochloride is only from 1.10 mm. to 2.70 mm. The vapour-phase has been shown to contain chlorine besides pyridinium hydrochloride. This is due to the slight
decomposition of the salt under vacuum. Attempts to prepare the sodium or ammonium ceric chloride were unsuccessful. There was immediate reduction, accompanied by decolourisation and precipitation of cerous chloride. This could be attributed to the sodium or ammonium ion combining with the labile chlorine in ceric chloride before salt formation with the hydrogen chloride.

**Experimental**

Materials used.—Hexachloroceric acid was prepared by the method reported by the authors. The acid crystals were preserved in petroleum ether.

Pyridinium hydrochloride was prepared by passing dry hydrogen chloride gas into a solution of 50 c.c. pyridine (A.R.) and 150 c.c. of dry ether. The white precipitate of pyridinium hydrochloride was collected in a dry sintered funnel, washed with ether, dried in a current of dry nitrogen and stored in sealed bottles.

Other materials used were of A.R. or C.P. grade.

1. Preparation and analysis

Methyl alcohol solution (100 c.c.) containing 4 g. of hexachloroceric acid crystals was taken in each of the four flasks. Pyridinium hydrochloride solution in methyl alcohol was then added to each flask in such amounts that molar ratios of the acid to pyridinium hydrochloride were respectively

<table>
<thead>
<tr>
<th>Molar ratio of acid to py. hydrochloride</th>
<th>Cerium %</th>
<th>Active chlorine %</th>
<th>Total chloride %</th>
<th>Nitrogen %</th>
</tr>
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<tbody>
<tr>
<td>2:1</td>
<td>26.80</td>
<td>6.68</td>
<td>40.05</td>
<td>5.02</td>
</tr>
<tr>
<td>1:1</td>
<td>27.00</td>
<td>6.82</td>
<td>40.94</td>
<td>5.18</td>
</tr>
<tr>
<td>1:2</td>
<td>26.75</td>
<td>6.70</td>
<td>40.85</td>
<td>5.00</td>
</tr>
<tr>
<td>1:4</td>
<td>26.92</td>
<td>6.66</td>
<td>40.48</td>
<td>5.12</td>
</tr>
<tr>
<td>Calculated values for CeCl₄.2 C₅H₅N.HCl</td>
<td>27.30</td>
<td>6.91</td>
<td>41.46</td>
<td>5.46</td>
</tr>
</tbody>
</table>
as 2:1, 1:1, 1:2, and 1:4. The pyridinium complex that separated was filtered off and washed with methyl alcohol and ether. The four samples of the pyridinium complex thus obtained were then analysed for cerium, active chlorine, total chloride and nitrogen.

2. To find if hydrogen chloride is displaced during the addition of pyridinium hydrochloride

50 c.c. of 0·05 M hexachloroceric acid solution in methanol and 50 c.c. of 0·1 M pyridinium hydrochloride solution in methanol were mixed. When the pyridinium complex got precipitated, dry ether was added to diminish the solubility of the complex and the mixture was filtered. The filtrate was still slightly yellowish in colour. A vigorous current of dry nitrogen was passed through the solution, the gas carrying the hydrogen chloride was passed through a standard solution of silver nitrate when silver chloride was produced. Quantitative estimation of the silver chloride did not give concordant values although the presence of hydrogen chloride was definitely confirmed.

**Table II**

*Vapour pressure of ceric pyridinium chloride and of pyridinium hydrochloride*

<table>
<thead>
<tr>
<th>Temperature ° C.</th>
<th>V.P. in mm. of mercury</th>
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<tbody>
<tr>
<td></td>
<td>Complex</td>
</tr>
<tr>
<td>± 0·1</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1·75</td>
</tr>
<tr>
<td>5</td>
<td>2·50</td>
</tr>
<tr>
<td>10</td>
<td>3·60</td>
</tr>
<tr>
<td>15</td>
<td>5·20</td>
</tr>
<tr>
<td>20</td>
<td>6·90</td>
</tr>
<tr>
<td>25</td>
<td>9·00</td>
</tr>
<tr>
<td>30</td>
<td>14·65</td>
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<tr>
<td>40</td>
<td>..</td>
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<tr>
<td>50</td>
<td>..</td>
</tr>
<tr>
<td>60</td>
<td>..</td>
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</table>
3. Vapour pressure measurements

The vapour pressure of the pyridinium ceric chloride and pyridinium hydrochloride was determined by the static method for the temperature range 0° to 60° C. A liquid air-bath was used to evacuate the system. The tube containing the substance was maintained at known temperatures for 2 hours before the pressure readings were taken. The pressure could not be measured beyond 30° C, since the complex decomposed giving chlorine which attacked the mercury in the manometer.

4. Spectral characteristics

The absorption spectrum of ceric pyridinium chloride in methyl alcohol was studied with a Beckmann Du quartz spectrophotometer. Very dilute solutions had to be used to avoid complete absorption. The absorption maximum was found to be at 310 μ. A solution of pyridinium hydrochloride in methyl alcohol showed no absorption in this range. For comparison, the absorption curve for a solution of the acid crystals in methyl alcohol is also given (Fig. 1).

![Absorption spectra of solution of the pyridinium complex in methyl alcohol.](image)

5. Attempts to prepare the sodium and ammonium salts

Solutions of the acid crystals in methyl alcohol were added to equivalent quantities of sodium hydroxide, sodium methoxide and ammonia in methyl alcohol in separate vessels. There was sudden decolourisation of the acid solution followed by precipitation of cerous chloride. Pure, dry, solid sodium chloride was added in another vessel to a methanol solution of the acid crystals. The decolourisation was not very rapid, but on standing, a
white precipitate appeared, thus indicating that the corresponding sodium or ammonium complexes could not be prepared. This is in conformity with the observations of Koppel.\textsuperscript{3}

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\textbf{REFERENCES}