

Studies on Chromic Chloride

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SUMMARY

1. It is shown that if blue chromic chloride is dissolved in water, it instantaneously undergoes, to a greater or lesser extent, hydrolysis according to the equation $\text{CrCl}_3 + \text{H}_2\text{O} = \text{CrCl}_2\text{OH} + \text{HCl}$. This hydrolysis takes place according to the law of mass action, and changes with temperature, as it is to be expected from the heat evolved in the process.

2. The product of hydrolysis, CrCl_2OH , is also formed, when one equivalent of sodium hydroxide is added to a solution of chromic chloride, $\text{CrCl}_3 + \text{NaOH} = \text{CrCl}_2\text{OH} + \text{NaCl}$. It is soluble in water, green, and is slowly transformed on standing. When more sodium hydroxide is added a corresponding amount of the "normal" chromic hydroxide is precipitated, $\text{CrCl}_2\text{OH} + 2 \text{NaOH} = \text{Cr}(\text{OH})_3 + 2 \text{NaCl}$.

3. Dilute chromic chloride solutions become green immediately on warming or on addition of sodium acetate. This is due to the formation of the same product of hydrolysis, CrCl_2OH . The blue chromic chloride is re-formed by rapid cooling or addition of hydrochloric acid, provided that this is done immediately, before the unstable CrCl_2OH has been transformed.

4. The constant of hydrolysis of the green dichlorochromic chloride is about $4 \cdot 10^{-6}$ at 25°C .

5. In dilute solution, the rate of the green dichlorochromic chloride's conversion to the blue chromic chloride (estimated by conductivity measurements) can only be explained theoretically, when it is assumed that monochlorochromic chloride is first formed, and then converted into blue chromic chloride, and that acids retard the process.

On the basis of measurements of the rate of transformation in hydrochloric acids of different strengths, expressions have been obtained for the influence of acids on the two velocity constants of the process. The transformation of chromic chloride in aqueous solution is in agreement with these expressions, if the amount of acid, which is present in the solution owing to the hydrolysis of the chlorides, is inserted in the expressions.

6. The experimentally found expressions for the negative catalysis by acids

$$(k_1 = a + \frac{b}{s} \text{ and } k_2 = \frac{c}{s} + \frac{d}{s^2}, \text{ where } s \text{ denotes the amount of free acid and } a,$$

b , c , and d are constants) can be theoretically deduced, when it is assumed that the products of hydrolysis are transformed much more quickly than the chromic chlorides themselves. This assumption also explains the large temperature coefficient which is characteristic for the rate of transformation (10°C giving a fourfold increase); not only the rate of transformation of the products of hydrolysis increases at higher temperature, but also their amount.

7. In explaining the analytical findings in concentrated chromic chloride solutions, which have been standing until equilibrium has been reached, it is necessary to assume that the solution contains, besides green and blue chromic chlorides, a third substance. This substance I have prepared. It has the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, is green, crystalline and extremely hygroscopic. It contains only one chlorine atom with a complex bond, and hence is a monochlorochromic chloride. On standing, it is transformed into dichlorochromic chloride. It can be separated from the other two chromic chlorides by its solubility in a mixture of equal volumes of ether and fuming hydrochloric acid. It is the same substance, the formation of which as an intermediate product was necessary for the explanation of the transformation of the green chromic chloride in dilute solution.

8. Some estimations have been carried out of the amounts of the three chromic chlorides present in the solutions which had been allowed to stand until equilibrium between the chromic chlorides was reached. It has been shown that the equilibrium is altered, as the theory requires, by changes in either the concentration or the temperature.

The displacement of the equilibrium by the addition of various salts and hydrochloric acid, is also in qualitative agreement with the law of mass action.

9. A chloro-sulphate, which turns out to be identical with the chlorochromic sulphate prepared by Recoura, can be prepared from the monochlorochromic chloride with sulphuric acid. Since, conversely, monochlorochromic chloride can be prepared from Recoura's sulphate in good yield, Recoura's salt must be the sulphate which corresponds to the monochlorochromic chloride.

10. From a solution of equal parts of green chromic chloride and blue chromic

chloride, sulphuric acid precipitates a compound which is isomeric with Recoura's chloro-sulphate. In agreement with Werner, who has recently prepared the same substance, I find that this compound is dichlorochromic-chromic sulphate, $\text{CrCl}_2 - \text{SO}_4 - \text{Cr} = \text{SO}_4$.

11. By dehydration of the green $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$ over phosphoric anhydride in a vacuum of less than 1 mm mercury, I have prepared a red chromic chloride, the composition of which corresponds most nearly to the formula $\text{CrCl}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, but which could not be prepared with a completely constant composition. It is extremely hygroscopic; its aqueous solution is green.