

Studies on Chromic Chloride. III.

Hydroxoquo chromic Chlorides

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THE HYDROLYSIS OF HEXAQUOCHROMIC CHLORIDE

During the work it proved necessary to undertake some electrometric determinations of the degree of hydrolysis of chromic chloride in potassium chloride solutions. The results, recorded in table 1, show that the hydrolysis constant in this case is considerably smaller than in pure water. μ is the decimillimolar concentration of chromic chloride, i.e. the number of moles in 10000 litres. The constant of hydrolysis in these units, $k_h = [\text{CrOH}^{++}][\text{H}^+]/[\text{Cr}^{+++}]$, is 10^4 times as great as when molar concentrations are used.

Table 1. The hydrolysis constant of hexaquo chromic chloride

μ	t	without KCl	0.1 N KCl	0.2 N KCl
100	18°C	0.65	0.48	
33.33	18	0.88	0.51	0.32
6.25	18	1.05	0.44	
33.33	0	0.27	0.156	

Of course, the great influence of potassium chloride on the hydrolysis constant makes it necessary in calculations of hydrolysis to employ a value corresponding to the actual quantity of potassium chloride present.

Without entering upon a discussion of the theory of this effect of potassium chloride, I wish to make the following remark. One might conceive that the decrease of the hydrolysis constant with increasing concentrations of chromic chloride is an effect similar to the decrease of the hydrolysis constant with increasing concentrations of potassium chloride, and that it is an Arrhenius neutral salt effect. In 0.1 N potassium chloride the neutral salt effect of chromic chloride

is negligible compared with that of potassium chloride and consequently the hydrolysis constant is only slightly dependent on the concentration of chromic chloride.

THE CONSTITUTION OF MANIFESTLY BASIC CHROMIC CHLORIDES

Hitherto we have not been quite justified in calling the manifestly basic hydrolysis products of chromic chloride hydroxo compounds, for we have estimated only the numbers of acid equivalents and of chromium atoms per molecule of each compound.

In order to form a well-founded opinion regarding the constitution of these unstable basic aquochromic compounds we must go a circuitous way (compare^{1a,2,3}). Among the more stable basic chromammines we seek out analogous compounds of established constitution; and from the constitution of these amines we draw inferences regarding the constitution of the corresponding aquo compounds. The *basic* chromammines may be classified into three groups. The first group comprises the latently basic compounds. To this group belong the rhodo-, erythro-, and rhodoso-compounds found by Jørgensen, and two series of basic ethylenediamine-containing compounds prepared by Pfeiffer. In a second group we may collect the numerous manifestly basic salts of a weakly basic nature similar to that of ammonia. Such compounds have been prepared by Jørgensen, by Pfeiffer, and by Werner. Finally, to the last group belong some strongly alkaline compounds known only in solution. Jørgensen has prepared such strongly alkaline solutions from purpureo chloride and from rhodo and erythro chlorides with silver oxide, and Christensen from nitropentaminechromic chloride with silver oxide.

There can hardly be any doubt that the constitution of the manifestly basic aquo compounds mentioned in the present paper is analogous to that of the likewise manifestly basic compounds belonging to the second group of amines. This view is supported not only by their analogous behaviour towards acids but even more by the fact that both these groups contain only one chromium atom in their nucleus while the latently basic chromammines and, as I shall show later on, also the latently basic aquochromic salts are polynuclear, "condensed" compounds.

With respect to the constitution of the manifestly basic chromammines resembling ammonia, the present state of knowledge is as follows: In 1902 Pfeiffer⁴ advanced the opinion that in certain dipyridinechromic compounds the basic hydroxyl must be attached directly to the chromium atom and must occupy the same place as the complexly bound anions in chloro, bromo, and nitro compounds. Consequently, these basic compounds were hydroxylo salts or, using an abbreviated term introduced by Werner, *hydroxo salts*. Pfeiffer supported his view by the observation that the basic dipyridinechromic compounds contained

one molecule of water less than the corresponding normal salts. In 1906 Pfeiffer⁵ defined these concepts more precisely and after that he wrote: "If one accepts the opinion of Werner that aqueous solutions of salts of heavy metals contain no metal ions but exclusively hydrated metal ions and that, consequently, constitutional formulae of the salt hydrates should be written $[\text{Me}(\text{OH}_2)_n] \text{X}_n$, then I consider it justified to infer that, generally speaking, in the case of heavy metal hydroxides having hydroxyl groups attached directly to the heavy metal atom, salt formation is primarily an addition reaction. However, in most cases it will be difficult to furnish experimental proof of this assumption".

Even before Pfeiffer had written this, I^{1b} had arrived at the conclusion that all bases and basic salts of chromium and of chrom- and cobaltammines hitherto prepared, apart from basic salts of a complexly basic nature, were to be regarded as hydroxo compounds. This opinion I supported not merely on the water content of these compounds but also on their colours which are different from those of the normal salts and on their slight electrolytic dissociation. I made it probable that direct addition compounds of ions — and only such — always possess the colour of their ions and show a normal degree of dissociation just as common strong electrolytes. "On dissolution in water they (the basic chromic salts) to a slight extent are converted into *real bases* containing hydroxyl ions and the unchanged cation of the series of salts in question combined to each other. The fraction of the basic salt transformed in this manner, by its normal electrolytic dissociation, proceeding in accordance with Ostwald-Walden's law, controls the hydroxyl-ion concentration of the solution, i.e. the strength of the base".

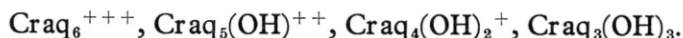
Werner in 1907 accepted this notion of many basic compounds being hydroxo compounds. He has furnished a copious experimental material demonstrating that basic salts, apart from polynuclear compounds, always contain one molecule of water less than the corresponding normal salts. And he claims to have found further evidence in support of this view in the fact that the basic salts regarded as hydroxo salts yield carbonato salts with carbon dioxide and acetato salts with acetic anhydride⁶.

This new proof, however, does not seem very convincing to me; for we have no reason to believe that hydroxo compounds should form acido compounds with acid anhydrides with special ease. —

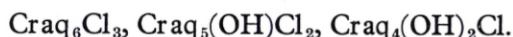
Immediately it may seem strange that just the manifestly basic salts are regarded as hydroxo compounds. We know that other radicals attached directly to the chromium atom are bound so firmly or rather so inertly that they cannot be exchanged instantaneously. It must be borne in mind, however, that when a hydroxo ion is transformed by acid into an aquo ion this process need not consist in an exchange of hydroxyl against water; we must imagine that a hydrogen ion combines with the hydroxyl group. So if we assume that hydroxo groups

capable of adding a hydrogen ion do this almost instantaneously we have an explanation of the manifestly basic nature of the hydroxo compounds. —

These considerations lead us to the conclusion that our manifestly basic aquochromic compounds are to be regarded as hydroxo compounds. Their ions are derived from the hexaquo chromic ion by exchange of water for hydroxyl and must be constituted in the following way:



And the corresponding chlorides are:



Even if the compounds probably do contain the quantities of water indicated in these formulae I generally prefer to omit the water both in the formulae and in the names. For the direct experimental determination of the quantities of water has not yet been accomplished*. And that this determination is not superfluous may be inferred e.g. from the existence of compounds (bisaquo compounds⁷) in which for no obvious reason two molecules of water appear in a place where in analogous compounds only one is present.

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* In the hydroxide three molecules of water have been found (Fremy and Prudhomme); but it is beyond doubt that the hydroxide is changed on drying.