Studies on Basic Chromic Compounds

A Contribution to the Theory of Hydrolysis

NIELS BJERRUM

Studier over basiske Kromiforbindelser. Bidrag til Hydrolysens Teori. Dissertation. Copenhagen (1908). Only the author's summary has been translated for the present volume.

SUMMARY

1. There are two distinct classes of *basic chromic compounds* which, owing to their different reactivities toward acids, may be called *manifestly basic* and *latently basic*, respectively.

2. *Manifestly basic compounds* are formed in lesser quantities when chromic salts are dissolved in water, in greater quantities when a base is added to the solution. Typical of these compounds is their *instantaneous* formation even at room temperature.

3. From the bluish-violet hexaquochromic chloride two soluble, green, manifestly basic chromic chlorides, $Cr(OH)Cl_2$ and $Cr(OH)_2Cl$, and the insoluble, grayish-green, manifestly basic chromic hydroxide, $Cr(OH)_3$, are formed. $Cr(OH)_2Cl$, however, never is present in great amounts, and a precipitate of chromic hydroxide is obtained only on addition of base. These compounds are hydroxo compounds, i.e., they contain hydroxyl attached directly to the chromium atom. Their content of constitutional water presumably is that given in the following formulae:

$$[Craq_5(OH)]Cl_2,\ [Craq_4(OH)_2]Cl,\ Craq_3(OH)_3$$

4. The quantities formed of these three compounds may be calculated from the following three equations (ξ is the concentration of free acid):

$$\frac{Cr(OH)Cl_2}{CrCl_3} \cdot \xi = K_h, \qquad \frac{Cr(OH)_2Cl}{Cr(OH)Cl_2} \cdot \xi = K'_h, \qquad (1)\ (2)$$

$$Cr(OH)_3 = 0 \qquad (3)$$

as long as $Cr(OH)Cl_2/\xi^2$ is less than or equal to K_b. But if these equations give a $Cr(OH)Cl_2/\xi^2$ greater than K_b (indicating supersaturation with chromic hydrox-

ide), the state of equilibrium (with a precipitate of chromic hydroxide) is found by replacing equation 3 with

$$\frac{Cr(OH)Cl_2}{\xi^2} = K_b \tag{3a}$$

The constants in these equations have the following values (in decimillimolar units of concentration):

	0° C.	17° C.	25° C.
K_h:	0.22	0.62	0.98
K_h':	$\leq$0.0025*	0.0059	—
K_b:	36000*	10200*	—

From the changes of these values with temperature are calculated:

1) The evolution of heat in the reaction $Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3\,H_2O$: 21200 cals.; Recoura found 20700 cals.

2) The evolution of heat in the reaction $Cr(OH)_2Cl + HCl \rightarrow Cr(OH)Cl_2 + H_2O$: at least 8060 cals.

3) The evolution of heat in the reaction $Cr(OH)\,Cl_2 + HCl \rightarrow CrCl_3 + H_2O$: 9600 cals.; Recoura found 8200 cals.

The constants vary somewhat with the nature and the concentration of electrolytes in the solution. Thus *the presence of potassium chloride and of chromic chloride lowers the value of the hydrolysis constant* K_h.

5. The validity of these formulae shows that *even in rather involved cases the law of mass action in combination with the theory of electrolytic dissociation gives a correct evaluation of the factors governing hydrolysis* when one confines oneself to the investigation of dilute solutions. Furthermore, it should be emphasized that this investigation has shown that freshly precipitated chromic hydroxide is a definite chemical compound of well-defined solubility.

6. *Solutions of nitrates* are hydrolyzed to manifestly basic products to the same extent as dilute solutions of chlorides, but *solutions of sulphates* behave differently. Thus the hydrolysis constant K_h in chrome alum solutions is smaller than in chromic chloride solutions. This may be explained by assuming that sulphates have a stronger decreasing influence on the hydrolysis constant than chlorides. And the precipitate obtained on addition of base to dilute solutions of chrome alum is neither chromic hydroxide nor dihydroxochromic sulphate nor a mechanical mixture of the two, but probably a single phase of varying composition.

---

* In 0.1 normal potassium chloride solution.

7. In dilute hexaquochromic chloride solutions — with or without added base — basic compounds that cannot instantaneously combine with acids are formed *slowly*.

8. These *latently basic chromic chlorides* are easily soluble in water and are green; their inclination to form complex chloro compounds is as slight as that of normal chromic chloride; and they contain *more than one chromium atom per molecule*. If one assumes that two compounds are formed containing one and two latent hydroxyl groups per chromium atom, respectively, the first compound can be proved to contain two chromium atoms per molecule and the second about six. However, it is not improbable that more compounds are formed besides these two.

The latently basic compounds in analogy to the latently basic ammines presumably are either *oxy compounds* the chromium atoms of which are linked through oxygen, e.g.:

$$Cl_2[aq_5Cr.O.Craq_5]Cl_2,$$

or *ol compounds*, i.e. aquo-chromic chloride whose water molecules to a greater or lesser extent have been replaced by hydroxochromic chlorides, e.g.:

$$[aq_4Cr:\begin{matrix}HO\\HO\end{matrix}:Craq_4]Cl_4$$

9. From the temperature change (from 75 to 100° C) in the equilibrium resulting from formation of latently basic compounds, is calculated that the transformation of monohydroxochromic chloride to a latently basic salt evolves 1890 cals. From two different calorimetric determinations by Recoura the values 1000 and 2900 cals., respectively, are calculated.

10. The latently basic chromic chlorides are hydrolyzed to soluble, manifestly basic products to approximately the same extent as is the normal, bluish-violet chromic chloride.

11. *The velocity of formation of latently basic* compounds at 100° C is so great that the process goes to completion during a couple of hours. At 75° C this requires a couple of days and at room temperature equilibrium is not attained even during several years.

From the decreasing *(negatively catalytic)* influence exerted by free acid on the initial velocity of formation of latently basic chromic chloride it can be inferred that the reaction proceeds via manifestly basic chromic chlorides. The lower the temperature, the more basic the chlorides constituting the main proportion of the intermediate products.

At room temperature the latently basic chromic chlorides are not changed measurably during one day by dilute (0.01 — 0.1 normal) hydrochloric acid. And even in fuming hydrochloric acid only 1.5 to 10 per cent is transformed during fifteen minutes at room temperature.

12. The velocity of transformation of normal, freshly precipitated chromic hydroxide into latently basic compounds has been measured under varying conditions at room temperature. In a distinctly alkaline medium the velocity of transformation increases with the alkalinity of the supernatant and a *hydroxide* is formed *in which one hydroxyl group per chromium atom is latent.* This hydroxide is — at least comparatively — stable. The presence of baryum chloride or of sulphates catalyzes the transformation of the hydroxide to a hydroxide that is insoluble in acid (in which all hydroxyl is latently basic).

13. *Dilute solutions of chromic nitrate* are on boiling transformed into latently basic compounds to the same extent as the chloride solutions; the compounds formed possess a stability resembling that of the latently basic chromic chlorides.

On the other hand, *in chromic sulphate solutions* boiling leads to liberation of more free acid than in chromic chloride solutions (in solutions containing 0.1 — 0.05 g. atoms of chromium per litre, nearly twice as much). The difference between sulphate and chloride solutions decreases when the concentration is lowered.

14. There is reason to believe that all the chromic salts of strong acids that do not form complexes in dilute solution and corresponding to which no sparingly soluble basic salts exist, will behave like chromic chloride with respect to hydrolysis. And with modifications of a quantitative kind the scheme of hydrolysis of chromic chloride will also apply to the hydrolysis of salts of other trivalent metals.

15. *Werner's general theory of hydrolysis and of bases* — for the time being, at least — rests on an insufficient foundation; and, anyway, the current hydrolysis theory of physical chemistry remains unaffected by its correctness or incorrectness.