

## Some Investigations on Basic Chromic Compounds

NIELS BJERRUM and CARL FAURHOLT

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1. If chromic salt solutions are heated with or without addition of bases, part of the chromium is transferred to “*latently basic*” compounds. In these compounds the chromic hydroxide will bind less than three equivalents of acid, even in the presence of an excess of acid. Consequently part of the hydroxyl of the chromic hydroxide is masked. These latently basic compounds may be sharply discerned from the “*true basic*” compounds, which immediately combine with acids even at low temperatures<sup>1a,2</sup>.

Formerly<sup>1a,2</sup> the quantity of masked hydroxyl was determined by means of hydrogen-ion concentration measurements in the cooled solutions. But in the present investigations on the formation of latently basic chromic compounds we have used another method, viz. determination of the quantity of chromium which still after heating existed in the original form of the hexaquo chromic cation,  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ , or which could quickly be converted into this form at normal temperature by means of an acid (true basic compounds). As nitrate solutions were used, and the nitrate ion forms no complexes with chromium under the experimental conditions employed, we may assume that the remaining part of chromium existed as latently basic compounds.

2. In the present investigations, the hexaquo chromic ion had to be determined in rather dilute solutions (down to 0.01 molar). Consequently precipitation of the chloride<sup>1b,3</sup> by hydrogen chloride or the sulphate<sup>1c,4</sup> by sulphuric acid and alcohol could not be used. And precipitation of the potassium alum<sup>4</sup> required such large quantities of alcohol that new difficulties arose. We found, however, that it is possible to precipitate hexaquo chromic salt quantitatively as caesium alum in the following manner:

3. *Determination of the Hexaquo chromic Ion by Precipitation as Caesium Alum.* 20 cc. about 0.01 molar chromium solution is mixed with 0.2 to 0.3 cc. about 2 normal sulphuric acid and 1 g. caesium sulphate. After 25 minutes 10 cc. 96 per cent alcohol is added, and after standing another 5 minutes the precipitate

of caesium alum is filtered off on a small filter and washed four times, each time with 8 cc. dilute alcohol (2 volumes of water + 5 volumes of 96 per cent alcohol). The amount of chromium left on the filter was then determined according to R. Weinland<sup>5</sup> by oxidation in alkaline solution by hydrogen peroxide, addition of hydrochloric acid and potassium iodide, and finally titration with thiosulphate.

Control experiments showed that by this procedure the amount of hexaquo-chromic salt remaining in the mother-liquor and in the washings only corresponded to some 0.0002 molar chromium in the original solution. A corresponding small correction is consequently introduced for this amount. To obtain as complete a precipitation in the form of potassium alum, 8 volumes of alcohol instead of  $\frac{1}{2}$  volume would have been necessary.

In a number of cases we encountered the particular difficulty at the alum precipitation that a green basic compound was precipitated besides the alum. This green precipitate may best be described as colloidal chromic hydroxide. It occurred already on addition of sulphuric acid and was somewhat increased by addition of caesium sulphate and alcohol. Some analyses of precipitates obtained by sulphuric acid and sulphuric acid + alcohol, respectively, showed that they were basic chromic sulphates with only from 0.28 to 0.47 equivalents  $\text{SO}_4^{--}$  per Cr.

To overcome this difficulty the alum precipitate was treated with 50 cc. of water, and the alum precipitation was repeated in 20 cc. of the latter solution. The precipitate from the second alum precipitation was dissolved in 50 cc. of water, and the electrical *conductivity* of this solution was determined. From the result obtained the hexaquo-chromic ion content was calculated. For now we could assume that the conductivity was exclusively due to alum. Beforehand, freshly prepared chromic nitrate solutions (which contained chromium exclusively as hexaquo-chromic salt) had been subjected to the same treatment so as to determine the relation between the conductivity of the solution of the second alum precipitate and the hexaquo-chromic salt content of the original solution. All hexaquo-chromic ion contents of table 1 are obtained conductometrically in this way.

4. Besides determining hexaquo-chromic salt by alum precipitation we determined the amount of "colloidal chromic hydroxide" which was precipitated in 20 cc. of chromium solution by 0.2 cc. 2 normal sulphuric acid and 10 cc. 96 per cent alcohol. In that way it became possible to differentiate between two kinds of latently basic chromium: the typically colloidal form which is precipitated by sulphuric acid and alcohol, and the slightly colloidal or non-colloidal form which is not precipitated by sulphuric acid and alcohol.

5. In table 1 we have collected the results obtained from the investigation of chromic nitrate solutions heated to 75°C, with or without addition of sodium

hydroxide. The chromic nitrate used was prepared from chromium trioxide, which was reduced by means of 3 per cent hydrogen peroxide in the presence of a small excess of nitric acid, evaporated until crystallization and twice re-crystallized from water.

The percentage distribution of chromium on 1) hexaquochromic salt, 2) latently basic chromium not precipitable by sulphuric acid and alcohol, 3) latently basic chromium precipitable by sulphuric acid and alcohol, is shown in the table. But no greater accuracy than a few per cent can be reckoned with in these figures.

It can be seen from the figures that in a short time, one day or a few days, at 75° C an equilibrium seems to be established between the hexaquochromic ion and the latently basic chromium which is not precipitable by sulphuric acid and alcohol. On the other hand the formation of the latently basic chromium which is precipitable by sulphuric acid and alcohol sets in very slowly; it cannot be seen from the data of the table whether equilibrium has been attained with regard to this formation in the experimental period of three or four months.

It is interesting to observe how the equilibrium between the hexaquochromic ion and chromium not precipitable by sulphuric acid is shifting towards an increase of the hexaquochromic ion content when there is an increasing formation of chromium precipitable by sulphuric acid. No doubt there is a relation between this fact and the increasing acidity of the solution.

6. The following two experiments are instructive with regard to the behaviour of chromic salt solutions at heating over a long period. In these experiments the solutions were refluxed for a long time, the small quantity of evaporated water being replaced.

A 0.1 molar chromic nitrate solution was still clear after 74 days' boiling; but after another 30 days' boiling the solution was quite turbid, and after standing deposited a greyish white precipitate which was easily filtered off. An analysis of the filtrate showed that 91 per cent of the chromium had deposited. Out of the remaining 9 per cent, 8 per cent was hexaquochromic salt and 1 per cent latently basic chromium which was not precipitable by sulphuric acid. A titration with sodium hydroxide and phenolphthalein showed that the solution was still 0.3 normal with regard to nitric acid, free or bound to chromium. This fact can be taken as a proof that during the long period of boiling the solution has not to any perceptible degree absorbed any bases from the Jena glass flask used.

After desiccation over sulphuric acid the greyish white precipitate was to a rather close approximation of the composition  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (determined by ignition loss).

After eight days' boiling a 0.1 molar solution of  $\text{Cr}(\text{NO}_3)_3 + 2\text{NaOH}$  contained 83 per cent basic chromium which could be precipitated by sulphuric acid. After 38 days the solution was still clear. After a total boiling time of 68 days an

Table 1. Chromic Nitrate Solutions Heated to 75° C without or with Addition of Sodium Hydroxide

Composition of the solution	Time of heating in days	Distribution of chromium on		
		Hexaquo-chromic ion %	Latently basic chromium	
			Not precipitable by H <sub>2</sub> SO <sub>4</sub> + alcohol %	Precipitable by H <sub>2</sub> SO <sub>4</sub> + alcohol %
0.1 molar Cr(NO <sub>3</sub> ) <sub>3</sub>	1.5	81.8	18.2	0
	4.4	82.4	17.6	0
	72	83.3	16.7	0
	98	80.0	20.0	0
0.05 molar Cr(NO <sub>3</sub> ) <sub>3</sub>	4.4	78.4	21.6	0
	6.4	79.9	20.1	0
	81	77.7	22.3	0
0.01 molar Cr(NO <sub>3</sub> ) <sub>3</sub>	1.5	70.0	30.0	0
	4.4	68.6	31.4	0
	28	69.1	30.9	0
0.1 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 0.5NaOH]	1.6	54.0	46.0	0
	4.6	54.5	45.5	0
	97	51.8	48.2	0
0.05 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 0.5NaOH]	4.7	52.7	47.3	0
	9.5	50.4	49.6	0
	107	51.7	48.3	0
0.01 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 0.5NaOH]	1.7	49.7	50.3	0
	4.7	50.0	50.0	0
	9.5	47.0	53.0	0
	107	48.3	30.4	20.7
0.1 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 1NaOH]	2.8	30.5	69.5	0
	105	37.0	47.7	15.3
0.05 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 1NaOH]	9.5	33.0	59.9	7.1
	114	41.4	34.0	24.6
0.01 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 1NaOH]	3	35.9	55.9	8.2
	7.5	32.1	53.4	14.5
	21	36.8	33	30
	42	38.4	28.5	33.1
	92	39.2	18.6	42.2
	133	41.5	10.5	48
0.05 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 2NaOH]	2.8	10.9	30	59
	105	18.9	4.8	76.3
0.01 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 2NaOH]	2.9	10.7	25.0	64.3
	11	13.4	15.3	71.3
	31	14.9	7.1	78.0
	82	13.3	3.8	82.9
	133	9.1	3	88

ample amount of green precipitate had appeared. After filtration the filtrate only contained 10 per cent of the chromium, and out of this 8.5 per cent was hexaquo-chromic salt and 1.5 per cent latently basic chromium which could be precipitated by sulphuric acid and alcohol. Titration of the solution and the precipitate deposited in it with sodium hydroxide and phenolphthalein showed that the system was always 0.1 normal with regard to nitric acid, free or bound to chromium, and consequently that no perceptible error due to corrosion of the glass flask was introduced. On the other hand the solution by itself contained only 0.091 normal nitric acid, consequently the precipitate has bound 9 per cent of the nitric acid.

On dialysis in a collodion bag against pure water an opalescent greenish colloidal solution was obtained from the precipitate. But the solution was so unstable that flocculation of a sample was brought about by shaking. When dried up and desiccated over calcium chloride to a constant weight, the colloidal solution gave a chromium hydroxide which according to its ignition loss was of the approximate composition  $\text{Cr}_2\text{O}_3, 2\text{H}_2\text{O}$ .

These experiments show that the latently basic chromium which is precipitable by sulphuric acid is formed very slowly even at  $100^\circ\text{C}$ . Everything indicates that the formation observed at  $75^\circ\text{C}$  of basic chromium which is precipitable by sulphuric acid has not reached its maximum in the experimental period of three or four months.

7. To determine the total amount of chromium in the solutions, we used in most cases oxydation by hydrogen peroxide in alkaline solution and titration of the chromic acid formed with thiosulphate after addition of hydrochloric acid and potassium iodide. However, this method proved impracticable in the presence of colloidal basic chromium precipitable by sulphuric acid, because hydrogen peroxide in alkaline solution was not able to oxidize this chromium completely. In these cases the chromium was precipitated by ammonia and filtered off, the filter was burnt in a platinum crucible, and the remainder melted with a mixture of sodium and potassium carbonate over an intense blow-pipe flame until dissolved, and then another 10 minutes, after which the chromate formed was titrated as usual.

In table 2 the behaviour of various chromic solutions towards alkaline hydrogen peroxide is set out.

Solutions 1 and 2, which only contained hexaquo-chromic salt or basic chromium not precipitable by sulphuric acid, were oxidized even at ordinary temperature. If hydrogen peroxide is added to the solutions which have been made alkaline, they turn yellow at once. This is not the case with the four other solutions. In solution 3 oxidation may, however, still be accomplished satisfactorily by boiling. If the solution contains larger quantities of non-oxidizable chromium,

Table 2. Behaviour of Some Chromic Solutions towards Alkaline Peroxide

No	Composition	Heated	Hex-aquo-chromic ion %	Latently basic chromium		Oxidizable by KOH + H <sub>2</sub> O <sub>2</sub> %
				not pre-cip-itable by H <sub>2</sub> SO <sub>4</sub> %	pre-cip-itable by H <sub>2</sub> SO <sub>4</sub> %	
1	0.01 molar Cr(NO <sub>3</sub> ) <sub>3</sub>	0 days (fresh)	100	0	0	100
2	0.1 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + NaOH]	2.8 days at 75°	30	70	0	100
3	0.05 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 2NaOH]	2.8 days at 75°	11	30	59	99—100
4	0.01 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 0.5NaOH]	107 days at 75°	48	30	21	96
5	0.01 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 1.5NaOH]	160 days at 75°	20	10	70	95
6	0.1 molar [Cr(NO <sub>3</sub> ) <sub>3</sub> + 2NaOH]	38 days at 100°	—	—	80	85

it becomes quite turbid when boiled with alkaline hydrogen peroxide. In solutions 4 and 5, where some 95 per cent of the chromium was oxidized, it was contrived to carry out the oxidation quantitatively after a preceding evaporation with strong hydrochloric acid. This procedure was, however, useless in the case of the most resistant solution: no. 6, in which only 85 per cent of the chromium was oxidized. Here the chromium seemed to be even less oxidizable after the treatment with hydrochloric acid.

8. By means of electrometric hydrogen-ion determinations the quantity of masked hydroxyl in heated chromic salt solutions has previously<sup>1a</sup> been determined. Those investigations were made on the system of chromic chloride + barium hydroxide. We consider it, however, permissible to apply the results obtained to the system of chromic nitrate + sodium hydroxide investigated in this paper.

In table 3 the results are collected for the cases where the same concentrations have been investigated according to both methods. In all cases the solutions have only been heated to 75° C for a few days.

In column 4 the total quantity of latently basic chromium is stated as a percentage of the total quantity of chromium. In column 5 the number of masked hydroxyl groups per 100 chromium atoms is calculated. Finally the number of masked hydroxyl groups occurring in the latently basic compounds per chromium atom is presented in column 6. With a decreasing content of latently basic chromium this figure is approaching 1. The primarily formed latently basic compound thus seems to contain *one* masked hydroxyl group per chromium atom.

Table 3

Molarity of the chromic salt	Equivalents of base added per Cr-atom	Heated to 75° in days	Latently basic chromium in per cent	Number of masked OH per 100 Cr	Number of masked OH per Cr-atom in latently basic chromium
0.1	—	3 resp. 4	17.6	20	1.14
0.05	—	7	20.1	25	1.24
0.01	—	5	31.4	40	1.27
0.05	0.5	1 resp. 5	47.3	57	1.21
0.05	1	2 resp. 9	67.0	103	1.54
0.05	2	2 resp. 3	89	179	2.01

But in the solutions with much latently basic chromium, large quantities of latently basic compounds with more than one masked hydroxyl group per chromium atom are present.

## SUMMARY

1. A method for the determination of the hexaquo-chromic ion:  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$  by precipitation as caesium alum is described.

2. This method is used to determine the quantity of latently basic compounds in chromic nitrate solutions which are heated to 75° C, with or without addition of base.

3. Further, the quantity of colloidal latently basic chromium precipitable by sulphuric acid (and alcohol) in these chromic nitrate solutions is determined.

4. Equilibrium with regard to slightly colloidal or non-colloidal latently basic compounds appears to be attained at 75° C in a few days. On the other hand, the formation of colloidal latently basic compounds at this temperature is not yet complete after three or four months.

5. By application of previous determinations of the quantity of masked hydroxyl in heated chromic salt solutions, the ratio between chromium and masked hydroxyl in the latently basic compounds is calculated.

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