

# Studies in the Oxinate derivatives of Chromium

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With 2 Figures

## Summary

Conditions for preparation of chromium (II) oxinate have been defined. The analysis of the product, as well as the conditions, under which it is precipitated, confirm that the product is initially different from chromium (III) oxinate.

The redissolution of chromium (II) oxinate in hydrochloric acid gives a solution with no reducing properties. It has been shown that oxine itself in acidic solutions is not capable of oxidising chromous ions and hence the conversion of chromous to chromic appears to occur at the dissolution stage.

Conditions of precipitation of chromium (III) oxinate have been studied in detail and it has been shown that complete precipitation occurs in the  $p_H$  range 4–8, on boiling the solution.

A chloroform solution of chromium (III) oxinate obeys BEER's law and can be estimated colorimetrically.

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Chromium in its bi- and tri-valent states shows electropositive character. The oxinate derivatives, corresponding to both the valency states, have already been reported. However, there has been a controversy in the literature about the existence of chromium (II) oxinate. Its preparation was first claimed by HUME and STONE<sup>1</sup>), by adding chromous chloride (0.2 M) to an excess of oxine solution (5% in 2 M acetic acid). Although chromium under these conditions got precipitated quantitatively in the form of a voluminous orange-yellow precipitate, the analysis of the purified product did not correspond with the chromous compound. KING and GARNER<sup>2</sup>), also could not find any evidence for the existence of chromous derivative in the above product by magnetic susceptibility measurements. They further criticised the work of HUME and STONE<sup>1</sup>), on the ground that the reported analysis of the product (10.24% Cr and 7.8% N<sub>2</sub>) also corresponded nearly to the trivalent chromium derivative.

As regards the existing state of our knowledge about chromic oxinate, the quantitative precipitation of chromium as chromium (III) oxinate

<sup>1</sup>) D. N. HUME and H. W. STONE, J. Amer. I. chem. Soc. **63**, 1200 (1941).

<sup>2</sup>) R. W. KING and J. R. and C. S. GARNER, chem. Physics **18**, 689 (1950).

has been studied empirically by a number of workers<sup>3)4)5)6)</sup>. However, no attempts appear to have been made to study the precipitation in different pH ranges, and to work out simple conditions for the complete precipitation of chromium as the oxinate.

Thus it is evident that both chromium (II) and chromium (III) oxinates, need further study. In the present investigations, attempts have been made to isolate the chromium (II) oxinate and to study the quantitative precipitation of chromium as the tri-oxinate, in different ranges of pH.

In a detailed study of the formation and properties of chromium (II) oxinate, it was found that even in acidic solution (about 0.2 N), addition of oxine (2% in acetic acid, neutralized by ammonium hydroxide) to excess of chromous salt or vice – versa gave an immediate yellow – orange precipitate. The work of TAYLOR-AUSTIN<sup>6)</sup>, confirmed under corresponding conditions in these laboratories, clearly indicated that chromium (III) oxinate would not be precipitated so instantaneously in solutions of such high acidity.

The precipitate, thus obtained under slightly varying conditions, was dried at 105–110 °C and analysed (table I) for chromium and oxinate contents and the analyses correspond closely to that of chromium (II) oxinate, although the precipitate appeared to lose the last molecules of water of crystallization rather slowly.

In determining the character of the precipitated product by analysis, the % of chromium and the ratio of chromium: oxine are much more important than the % of oxine or that of nitrogen, carbon or hydrogen. However, the fact that the product does not depict any reducing power on redissolution in hydrochloric acid, and the work of KING and GARNER<sup>2)</sup> regarding the magnetic susceptibility, throw some doubt to the valency state of chromium (II) oxinate formula, found by chemical analysis.

In contrast to the above, the ease of precipitation particularly in acidic solution (about 0.2 N) lends support that the compound is entirely different to the chromium (III) oxinate, which can be precipitated only on boiling the reactants in the pH range of approximately 4–8.

In order to establish the identity of chromium (II) oxinate, obtained above, the conditions of precipitation of chromium (III) oxinate, were investigated in detail. It was found that chromium is quantitatively

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<sup>3)</sup> A. ABLOV, Bull. Soc. chim. France (4) **53**, 234 (1933).

<sup>4)</sup> O. HACKL, Z. analyt. Ch. **109**, 91 (1937).

<sup>5)</sup> T. DUPUISAND u. C. DUVAL, C. R. Acad. Sci. Paris **227**, 772 (1948).

<sup>6)</sup> E. TAYLOR-AUSTIN, Analyst. **63**, 710 (1938).

precipitated as trioxinate in the pH range 4–8 (table III), but over the whole pH range, the reaction mixture requires boiling before precipitation starts. The chromium (III) oxinate precipitate was found to be

soluble in chloroform and the solution found to have a maximum absorption at 425 m $\mu$ . Further, the absorption of light appears to obey BEER'S law in low concentrations of chromium (III) oxinate.

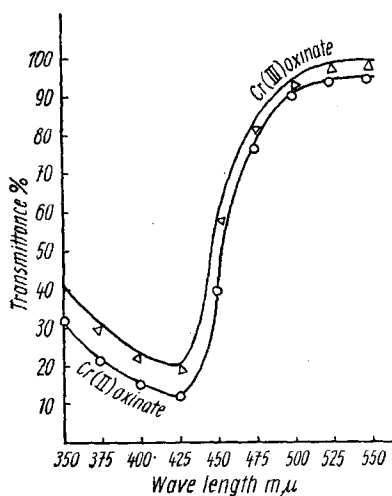


Fig. 1

A colorimetric estimation of chromium (III) oxinate is therefore possible. Attempts were made to study the absorption curve of chromium (II) oxinate also with a view to develop a colorimetric method of analysis for a mixture of the two. However, this could not be possible as the absorption curves of the two are quite similar. [Figure 1].

It was also shown volumetrically, that the chromous ions are not oxidised in solution by the oxine molecule in the acidic medium (table II) but during precipitation or may be during dissolution, the two are brought together to such close proximity that the oxidation does occur. This is not very surprising in view of the very low redox potential of Cr<sup>++</sup>/Cr<sup>+++</sup> system itself, and this is further reduced considerably by such ligands as salicylic acid<sup>7)</sup> or acetyl acetone<sup>8)</sup>.

## Experimental

### Materials

8-Hydroxyquinoline, acetic acid, ammonium hydroxide, granulated zinc, mercuric chloride, potassium bromate, potassium bromide (B. D. H., A. R.). Chromium chloride (T. T., A. R.), hydrochloric acid (Merck, G. R.), sodium acetate, chrome alum violet, sodium thiosulphate and redistilled chloroform of C. P. quality, were used.

### Solutions used

(i) Chromous solution: About 10–20% solution of chrome alum violet in about 0.5 N sulphuric acid was reduced, as described in the earlier communication<sup>9)</sup>.

<sup>7)</sup> R. L. PECOK and J. J. LINGANE, *J. Amer. chem. Soc.* **72**, 189–93 (1950).

<sup>8)</sup> G. COSTA and A. PUXEDDUE, *I. Inorg. Nuclear, Chem.* **8**, 104 (1958).

<sup>9)</sup> J. P. TANDON and R. C. MEHROTRA, *Z. analyst. Chem.* **158**, 20 (1957).

(ii) Oxine solution: 2 gms. of oxine was dissolved in 100 ml of 2 N acetic acid and ammonia added dropwise, till a slight precipitate was produced. It was dissolved out by warming, cooled and saturated with carbon-dioxide.

(iii) Chromic chloride solution: About 2 gms. of green salt was dissolved per litre of water, and its exact strength found out.

### Preparation of Chromium (II) oxinate

The following two alternative procedures were used:

(i) About 100 ml of chromous sulphate solution was taken out in an atmosphere of carbon-dioxide, acidified with conc. hydrochloric acid (about 2 ml) and treated with deficient amount of oxine solution (about 80 ml.). A greenish yellow precipitate was obtained immediately and some yellowish-orange precipitate appeared towards the end. It was quickly filtered in an atmosphere of carbon di-oxide, and washed twice with water, saturated with carbon-dioxide. A little of it was tested for reducing power. It was then washed repeatedly with water and dried at 105–110 °C.

(ii) About 150 ml. of chromous solution was run in a saturated solution of sodium acetate. The precipitated chromous acetate was filtered and washed in an atmosphere of carbon dioxide. It was then dissolved in hydrochloric acid and treated with deficient amount of oxine as described above, or alternatively the chromous solution was added to the oxine solution.

### Determination of the ratio of Cr: Oxine

About 0.15 gm. of the oxine compound was dissolved in 150 ml. of glacial acetic acid and made upto 250 ml. In 25 ml. of this solution chromium was estimated volumetrically, by the method of KOLTHOFF and SANDELL<sup>10</sup>) after oxidation with potassium bromate. In the same solution the oxine content was also determined by the well-known bromate method. The ratio of Cr:Oxine, found out in a few samples, has been recorded below (table I).

Table I

	% of Cr	% of Oxine	Molar ratio of Oxine:Cr
1.	13.82	73.04	1.909:1
2.	14.13	80.05	2.046:1
3.	14.90	82.80	2.007:1
4.	15.60	84.71	1.961:1

The last two samples were also analysed for carbon, hydrogen and nitrogen and following are the results:

	% C	% H	% N
Found (i)	63.1	4.0	8.37
(ii)	63.53	3.55	8.12
Calculated	63.50	3.52	8.23

<sup>10</sup>) I. M. KOLTHOFF and E. B. SANDELL, *Ind. Eng. Chem. Analyt.* **2**, 140 (1930).

### To study reduction of oxine by chromous sulphate

5 ml. of chromous solution was taken in an atmosphere of carbon-dioxide in a wide mouthed 100 ml. bottle, fitted with a three-bored cork, one for the delivery tube, another for the separating funnel and the third for introducing the tip of the burette. It was then titrated with methylene blue solution and later on in presence of hydrochloric acid also. Different volumes of oxine solution were then added and the titrations carried out in the same manner. The following are the observations (table II).

Table II

	Volume (ml) oxine sol. added to 5 ml of chromous sulphate sol.	Vol. (ml) of HCl (conc) added before or after addition of oxine sol.	Vol.(ml) of methylene blue required to oxidise the chromous solution.
1. (a)	0.0	— (No HCl)	33.6
2. (a)	0.0	20.0	33.6
(b)	1.0	20.0 (before)	33.6
(c)	1.0	— (No HCl)	31.8
(d)	1.0	20.0 (after)	31.8
3. (a)	0.0	20.0	33.6
(b)	2.0	20.0 (before)	33.6
(c)	2.0	— (No HCl)	31.7
(d)	2.0	20.0 (after)	31.5
4. (a)	0.0	20.0	33.6
(b)	5.0	20.0 (before)	33.6
(c)	5.0	— (No HCl)	28.2
(d)	5.0	20.0 (after)	28.1

(N. B. (i) No precipitation of oxinate occurred in observations 2(b), 3(b) and 4(b).

(ii) Precipitation of oxinate occurred in 2(c), 3(c), 4(c) and 2(d), 3(d) and 4(d).

The precipitate was dissolved in hydrochloric acid before titration in the last three).

The data in the table (II) indicated that the presence of oxine itself in strongly acidic solutions of chromous salts does not reduce its titre value. However, if oxinate is allowed to be precipitated, the titre value is reduced. Further even if the precipitated oxinate is redissolved in acid under most inert conditions, the titre value is not increased, indicating that the redissolved chromium oxinate has no reducing capacity.

### Precipitation of chromium (III) oxinate

The quantitative precipitation of chromium as the oxinate has been studied by HACKL<sup>4</sup>) and TAYLOR AUSTIN<sup>6</sup>). The later worker, however describes that only in sodium hydroxide and ammonium acetate solution, does the precipitation approach completion. In these investigations, its precipitation was studied in different ranges of  $p_H$ . To the chromic chloride solution, reagent was added and the  $p_H$  adjusted with the help of 4 N ammonium hydroxide, using PHILIPS  $p_H$  meter (P R 9400).

Method. 25.0 ml. of chromic solution was taken and about 17.0 ml. of oxine solution was added. Now different volumes of dilute ammonia solution were added and the  $p_H$

of the resulting solution was read by the  $p_H$  meter. It was then heated on a low flame for about  $1\frac{1}{2}$  hour, with constant stirring, till the excess of oxine got dissolved and the brownish precipitate of chromium (III) oxinate settled down completely. After the supernatant liquid had become clear, it was then filtered in the hot state and washed with hot water. It was dried at  $110^\circ\text{C}$ . The results of these determinations are given in the following table (III).

Table III

	$p_H$ of the resulting solution	Weight of the precipitate obtained (mg)	Theoretical weight (mg)
1.	1.05	No ppt.	87.10
2.	1.70	No ppt.	87.10
3.	3.01	83.00	87.10
4.	4.01	87.00	87.10
5.	4.97	82.60	82.10
6.	4.98	82.10	82.10
7.	6.00	84.10	84.10
8.	6.02	81.80	82.10
9.	7.00	84.20	84.10
10.	7.14	84.40	84.10
11.	8.00	80.50	80.70
12.	8.11	84.10	84.00
13.	8.92	79.70	82.10
14.	8.95	78.40	82.10
15.	8.97	80.70	82.10
16.	9.97	80.60	82.10

It is clear from the above table (III) that above  $p_H$  8.11, inconsistent and low results were obtained.

#### Testing of BEER'S law

The chromium (III) oxinate was found to be readily soluble in chloroform, giving yellowish red solution and showed a maximum absorption at  $425\text{ m}\mu$ . Attempts were made to measure the absorption curve of chromium (II) oxinate also. For this purpose, freshly precipitated sample was extracted directly with chloroform and the percentage transmission was measured at various wave-lengths keeping the system out of contact from atmospheric oxygen. A chloroform solution of Chromium (II) Oxinate has also been found to show absorption in the region of  $425\text{ m}\mu$  (Figure I).

In the subsequent determinations it was also found that dilute chloroform solution of Chromium (III) Oxinate obeys BEER'S law (table IV, Figure II) BAUSCH and LOMB spectronic 20 model was used.

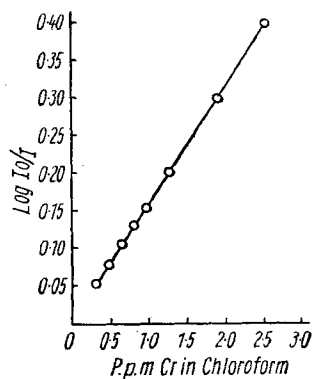


Fig. 2

With Spekker absorptiometer also, using filter No. 1 (which covers nearly from 400–460  $m\mu$ ), satisfactory results were obtained.

Table IV

	Parts per million of Cr in Chloroform (g)	% Transmittance	$\frac{\text{Log } I_0}{I}$
1.	0.3124	89.00	0.0506
2.	0.4686	84.10	0.0752
3.	0.6250	79.30	0.1007
4.	0.7810	74.90	0.1255
5.	0.9372	70.70	0.1506
6.	1.2500	62.70	0.2027
7.	1.8750	50.10	0.3002
8.	2.5000	39.50	0.4034

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