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Synthesis and Characterization of Iron(III) Peroxy-Chromate

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Iron(III) chromate, $FeCrO_4(OH){\cdot}H_2O$, has been prepared with modified method and characterized by IR, Mössbauer, magnetic moment and elemental analysis. The prepared bluish-violet iron(III) peroxy-chromate belongs to violet series of peroxy-chromates. The isolated iron(III) peroxy-chromate has been formulated as $Fe(Cr_2O_{10})_3$. The probable mechanism of the formation of $Fe[CrO(O_2)_2OH]_3$ and its transformation into stable $Fe(Cr_2O_{10})_3$ has also been worked out.

Key Words: Iron(III) Chromate, Mössbauer, Iron(III) peroxy-chromate, Decomposition products, Violet series.

INTRODUCTION

Peroxy-chromates associated with iron(III) seem to be unknown in the literature. However, some workers have reported[1-3] the preparation of iron(III) peroxy-chromate and study of its water, alkali, silver(I) oxide and lead dioxide decomposition products. This situation is enticing and demands a thorough characterisation of the aforesaid peroxy-chromate.

EXPERIMENTAL

All chemicals used were of either GR or AR grade. Iron(III) was estimated as Fe_2O_3, chromium(VI) by iodometric method and hydrogen with usual combustion technique. The peroxy oxygen was determined by potassium permanganate and sodium arsenite methods[4]. IR (KBr) were recorded on FTIR 8201. Mössbauer spectra were recorded with a constant velocity spectrometer (BARC) using Co^{57}(Rh) source and SNP as standad. For pH and colorimeteric measurements the Toshniwal's pH-meter CL-49 and colorimeter CL-05 were used. The magnetic susceptibility was measured with Gouy method.

Iron(III) Chromate[5, 6]: It was prepared by slightly modified method. The freshly precipitated ferric hydroxide (7.0 g) was mixed with M-CrO_3 solution, taking care that the ratio of Fe(III) and Cr(VI) is 1 : 1 by weight. The mixture was heated at 65–70°C for about 20 h with occasional shaking. The reddish-brown emulsion so obtained was transferred to a hard glass tube (length = 25 cm, external diameter = 12.5 cm and thickness = 3 mm, closed at one end and open capillary on the other), and concentrated at 90–95°C till it reduced to a reddish-black dry mass. Now the narrow end of the glass tube was sealed and the contents were heated at 120–130°C in an oven for about 25 h. The hot tube was then slowly cooled to room temperature and the sealed end was opened with the help of file mark. The fine amorphous black deposit was taken out, washed with diethyl-ether, dried at 50–60°C and stored in a vacuum desiccator over silica-gel. Yield: 14.32 g.

The presence of Fe(III) and Cr(VI) was tested positive by usual qualitative tests. The compound was found insoluble in common organic solvents but resolved to some extent in water into chromic acid and ferric oxide. For a mixture of iron(III) chromate (0.5 g) and water (50 mL), the pH was noted to be 5.95 at 25°C. FTIR (KBr): 3300 br s, $\nu(H_2O/OH^-)$, 1620 s, $\nu(H_2O)$; 956 s and 800 br s cm^{-1} $\nu(CrO_4^{2-})$. Mössbauer (298 K): $\delta = 0.69$ and ΔE = negligible (mm/sec) (HS, Fe^{3+}). μ_{eff} (25°C) = 5.74 B.M. Analysis: Found: Fe = 26.96, Cr = 25.22 and H = 1.56%; Calcd. for $FeCrO_4(OH){\cdot}H_2O$: Fe = 27.00, Cr = 25.14 and H = 1.45%.

Iron(III) Peroxy-Chromate[1–3, 7, 8]: Ice-cold solutions of 10% ethyl acetate extracted anhydrous hydrogen peroxide (5 mL, minimum possible amount) and ethyl acetate (50 mL) were mixed (pH = 4.50–4.55). To this 1 g ice-cold solid $FeCrO_4(OH){\cdot}H_2O$ was added. The contents were shaken from time to time and kept cold by freezing mixtue for 30 min, (pH = 2.45–3.15, optical density = 0.28–3.00), In the beginning a faint purple colour was observed which gradually darkened to violet colour with bluish tinge. The bluish-violet ethyl acetate layer was then separated and stored at 0°C. Due care was taken to use the stored peroxy compound within 3 h as after that an apparent decomposition (optical density decreases) was noticed. The washing of the prepared compound with ice-cold water should not be done because the entire bluish-violet substance gets washed out with water.

The amount of peroxy oxygen in 50 mL of the blush-violet compound was found to be 0.00362 g. The water decomposition product was prepared by decomposing bluish-violet compound (50 mL) in contact with water (100 mL). The studies were repeated[2] and it was noticed that Fe(III) and $Cr_2O_7^{2-}$ are present in the cationic and anionic portion of the water decomposition product. Further, the concentration of Fe(III) and Cr(VI) was determined and found to be 0.00278 and 0.00784 g respectively. These values are equivalent to $Fe_2(Cr_2O_7)_3$.

Like water decomposition product the studies in respect of alkali, silver(I) oxide and lead di-oxide decomposition products of the bluish-violet compound were repeated[1, 3]. It was observed that the cationic and anionic parts of the bluish-violet compound contain Fe(III) and Cr(VI) respectively and the ratio between these ions is 1 : 2.8–2.9.

RESULTS AND DISCUSSION

Iron(III) chromate, $FeCrO_4(OH){\cdot}H_2O$, has successfully been prepared by the modified method and characterised with the help of IR (H_2O/OH^-, CrO_4^{2-}), Mössbauer (HS, Fe^{3+}), μ_{eff} (5.74 B.M.) and elemental analysis. It is insoluble in ethyl acetate and such other organic solvents, but slightly resolves in water (pH 5.95, 25°C) into soluble chromic acid and insoluble ferric oxide.

In the preparation of iron(III) peroxy-chromate the initial pH of the ethyl acetate and anhydrous peroxide mixture is 4.50–4.55, which is favourable for the formation of violet species of the peroxy-chromate[9]. On adding solid iron(III) chromate, to above ethyl acetate-hydrogen peroxide mixture, the pH first decreases to 2.45 and then gradually (30 min) rises to 3.15. This change in pH may be attributed to generation of some H^+ ions through the following reactions[10]:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$2Fe^{3+} + H_2O_2 \longrightarrow 2Fe^{2+} + O_2 + 2H^+$$

$$2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O_2$$

On the other hand Fe^{3+} has a tendency to hydrolyse (even at pH = 2–3) in aqueous solution and then dissociation of aquo ion may provide H^+ as:

$$[Fe(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_5OH]^{2+} + H^+$$

and

$$[Fe(H_2O)_5OH]^{2+} \longrightarrow [Fe(H_2O)_4(OH)_2]^+ + H^+$$

After the lapse of 30 min the pH (3.15) becomes constant and may suggest that the catalytic decomposition of hydrogen peroxide, in presence of Fe^{3+} and CrO_4^{2-} is complete. Secondly the maximum optical density (3.0) value is attained within the aforesaid time and then it remains constant for about 3 h. Hence a time of 30 min seems to be rational to cover up all changes pertaining to the formation of the iron(III) peroxy-chromate.

The changes in pH (4.55–3.15) may also indicate that limited number of H^+ ions are produced in the course of reaction between Fe^{3+}, CrO_4^{2-} and H_2O_2. This condition is therefore responsible to form the bluish-violet product, iron(III) peroxychromate, in place of pure blue peroxy compound (CrO_5). The washing of the prepared iron(III) peroxy chromate with ice-cold water was found not possible because the entire bluish-violet compound got washed out with water. This situation therefore indicates that the studied peroxy-chromate is more soluble in water than in ethyl acetate and belongs to violet class[11] of the peroxy-chromates.

The studies on water[2], alkali[1], silver(I) oxide and lead dioxide[3] decomposition products have revealed that the cationic and anionic portions of the prepared bluish-violet compound contain Fe(III) and Cr(VI) respectively and the ratio between these ions is approximately 1 : 3. Further, the water decomposition product has been formulated as $Fe_2(Cr_2O_7)_3$. Also the amounts of Fe(III), Cr(VI) and peroxy oxygen in 50 mL of bluish-violet compound have been found to be 0.00278, 0.00784 and 0.00362 g respectively, which show that the ratio between Fe(III) : Cr(VI) : Peroxy oxygen is 1 : 2.82 : 1.302. The peroxy oxygen : chromium(VI) ratio is 0.4617.

It is an established fact[12] that like blue pentoxide (CrO_5) the violet salts contain two peroxy groups per chromium atom. On this basis the peroxy oxygen/chromium(VI) ratio would have been equal to 0.6152, which is greater than the observed ratio of 0.4617 for the bluish-violet compound. This difference may be due to the fact that the violet peroxy-chromates are less stable than CrO_5.

The formulations[7, 8, 11–14] of other peroxy chromates and their water decomposition products have earlier been done as below:

$M_2^+Cr_2O_8$, $M_2^+Cr_2O_{11}$, $ZnCr_2O_{10}$, $CuCr_2O_{10}$, $Sn(Cr_2O_{10})_2$, $Cr_2(Cr_2O_{10})_3$, $ZnCr_2O_7$, $CuCr_2O_7$, $Sn(Cr_2O_7)_2$ and $Cr_2(Cr_2O_7)_3$ [$M^+ = NH_4^+, Li^+, Na^+, K^+, Tl^+$, etc.].

In the light of the above formulations and observed results, the bluish-violet compound may be formulated as $Fe_2^{3+}\ (Cr_2^{4+}O_{10})_3$.

From the above conclusions the bluish-violet compound has been regarded as a violet peroxy-chromate. Hence, it should have the formula $Fe[CrO(O_2)_2OH]_3$. Its formation may be explained through the following mechanism:

In presence of Fe^{3+} and CrO_4^{2-} the ethyl acetate extracted anhydrous hydrogen peroxide decomposes as:

$$3H_2O_2 \longrightarrow 3H_2O + 3O$$

Now in presence of water the solid iron(III) chromate gives[5, 10]:

$$3FeCrO_4(OH)\cdot H_2O + 3H_2O \longrightarrow 3Fe(OH)_3 + 3CrO_4^{2-} + 6H^+$$

After this the CrO_4^{2-} ions react with hydrogen peroxide, in presence of H^+ ions, to form CrO_5 as:

$$3CrO_4^{2-} + 6H_2O_2 + 6H^+ \longrightarrow 3CrO_5 + 9H_2O$$

Further the CrO_5 hydrolyses to produce hydrated pentoxide, *i.e.*, the parent acid[12] of the violet salts, as:

$$3CrO_5 + 3H_2O \longrightarrow 3CrO(O_2)_2\cdot OH_2 \xrightarrow{-H^+} 3CrO(O_2)_2\cdot OH^- + 3H^+$$

In turn the parent acid anions of the violet salt react with ferric hydroxide to form the bluish-violet compound as:

$$Fe(OH)_3 + 3CrO(O_2)_2\cdot OH^- + 3H^+ \longrightarrow Fe[CrO(O_2)OH]_3 + 3H_2O.$$

Hence

$$3FeCrO_4(OH)\cdot H_2O + 9H_2O_2 \longrightarrow Fe[CrO(O_2)_2OH]_3 + 2Fe(OH)_3 + 9H_2O + 3O$$

and

$$2Fe[CrO(O_2)_2OH]_3 \xrightarrow{+H_2O} \underset{\text{Water decomposition product}}{Fe_2(Cr_2O_7)_3} + 3H_2O + 12O$$

During pH-metric and colorimeteric studies of the reaction between ethyl-acetate extracted anhydrous hydrogen peroxide and solid iron(III) chromate at 0°C, it has been observed that in the beginning a faint purple colour is generated and that gradually darkens to a stable violet colour with bluish tinge. On this we can assume that $Fe[CrO(O_2)_2OH]_3$ is first formed and then it changes to a stable bluish-violet compound, $Fe_2(Cr_2O_{10})_3$, as:

$$2Fe[CrO(O_2)_2OH]_3 \longrightarrow Fe_2(Cr_2O_{10})_3 + 3H_2O + 3O$$

This type of change may explain that the observed ratio between peroxy oxygen and chromium(VI), for the studied bluish-violet compound, is less than the theoretical value.

Now with $Fe_2(Cr_2O_{10})_3$ the formation of $Fe_2(Cr_2O_7)_3$, water decomposition product, can be shown as:

$$Fe_2(Cr_2O_{10})_3 \xrightarrow{+H_2O} Fe_2(Cr_2O_7)_3 + 9O$$

From this the ratio between Fe(I), Cr(VI) and peroxy oxygen will be:

$$2\,Fe : 6\,Cr : 9\,O \quad \text{and} \quad 6\,Cr : 9O$$

$$1 : 2.79 : 1.28 \qquad\qquad 1 : 0.4614$$

These ratios are well in agreement with the observed ratio and therefore facilitate the formulation of prepared iron(III) peroxy-chromate as $Fe_2(Cr_2O_{10})_3$.

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REFERENCES

1. N. Mishra and B.M.L. Tiwari, *Acta Ciencia Indica*, **11C**, 211 (1985).
2. ———, *J. Indian Chem. Soc.*, **63**, 245 (1986).
3. N. Richharia, R. Bajpai, S. Tiwari and B.M.L. Tiwari, *Asian J. Chem.*, **16**, 995, 1001 (2004).
4. I.M. Kolthoff and E.B. Sandell, Text Book of Quantitative Inorganic Analysis, McMillan, N.Y., Vol. 3, pp. 575, 600–601 (1955).
5. A. Bonnin and A. Lecerf, *Compt. Rend. Acad. Sci.*, **262**, 1782 (1966); **267**, 1137 (1968).
6. K. Yabuta, K. Kinomura, K. Shimada, F. Kanamaru and M. Koijumi, *J. Solid State Chemistry*, **33**, 253 (1980).
7. S.P.S. Jadon and D.S. Rathore, *J. Indian Chem. Soc.*, **53**, 527 (1976); *J. Res. Sci.*, **27**, 7 (1978).
8. S.P.S. Jadon, *Rev. Roum. Chem.*, **26**, 1107 (1981).
9. M. Bobtelsky, A. Glasner and L. Bobtelsky-Chaikin, *J. Am. Chem. Soc.*, **67**, 966 (1945).
10. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry—A Comprehensive Text, Wiley Eastern, New Delhi, pp. 372–74, 852, 858 (1972).
11. R.C. Rai and S. Prakash, in H.J. Emeleus and A.G. Sharpe (Ed.), Advances in Inorganic Chemistry and Radio-Chemistry, Academic Press, NY, pp. 306–307 (1964).
12. W.P. Griffith, *J. Chem. Soc.*, 3948 (1962).
13. K.A. Hofmann and H. Heiendlmaier, *Ber. Deut. Chem. Ges.*, **38**, 3039 (1905); 32, 3181 (1906).
14. E.H. Reisenfield, H.E. Wohlers and W.A. Kutsch, *Ber Deut. Chem. Ges.*, **38**, 1885 (1905); **41**, 3941 (1908).

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