

A Comparative Study of the Decomposition Products of Iron(III) Peroxy-chromate

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Iron(III) peroxy-chromate has been prepared by the interaction of iron(III) chromate with anhydrous hydrogen peroxide. The ratio of Fe(III) : Cr(IV) : peroxy-oxygen has been found to be 1 : 2.79 : 1.30, which supports the formulation of studied peroxy-chromate as $\text{Fe}_2(\text{Cr}_2\text{O}_{10})_3$. For this, the water, silver(I) oxide and lead dioxide, decomposition products of the prepared iron(III) peroxy-chromate, have been investigated with the help of ion-exchange resins, electronic absorption, IR, pH-metric and colorimetric techniques.

Key Words: Iron(III) peroxy-chromate, Water, Silver(I) oxide, Lead dioxide, Decomposition products.

INTRODUCTION

The peroxy iron compounds are usually formed in the catalytic decomposition of hydrogen peroxide by ferrous or ferric salts¹⁻⁸. The peroxide-iron(III) complexes are of major importance in respect of mechanism of catalysis or operation of iron(III) containing enzymes, such as peroxidase and catalase, and also as oxygen carriers. The preparation of iron(III) peroxy-chromate [$\text{Fe}_2(\text{Cr}_2\text{O}_{10})_2$] and studies on its water alkali decomposition products have been reported^{9, 10}. In the present study an attempt has been made to confirm the earlier findings with reference to composition of the prepared iron(III) peroxy-chromate.

EXPERIMENTAL

All chemicals used were of AR grade. The UV-Vis (aqu.) and IR (KBr) spectra were recorded on Shimadzu-UV-Vis-160 PC controlled and Perkin-Elmer 1800 FTIR spectrophotometers respectively. For pH and colorimetric studies Toshinwal's pH-meter CL-49 and colorimeter CL-05 were employed. Peroxy oxygen was estimated by sodium arsenite and potassium permanganate methods^{11, 12}.

Iron(III) peroxy-chromate being an oxidizing agent was prepared by known methods^{9, 10, 13} by dissolving 0.00774 g of peroxy oxygen per 100 mL.

Water Decomposition Product: Ten sets of this product were prepared by decomposing the iron(III) peroxy-chromate (30 mL) in contact with water (60

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mL). After decomposition (*ca.* 65 min, 25°C) the colourless organic layer was removed and the yellow aqueous layer was exchanged^{9, 10, 14} with Dowex-50 (Na) and Amberlite-120 (Na) ion-exchange resins. The presence of iron(III) in the elutriant and of dichromate ions in the effluent was confirmed with the help of known qualitative tests. R_f values [elutriant: 0.718, effluent: 0.316; FeCl_3 : 0.725, $\text{Na}_2\text{Cr}_2\text{O}_7$: 0.312], absorption and IR data [effluent vs. $\text{Na}_2\text{Cr}_2\text{O}_7$: λ_{max} at 233 and 350 nm; sharp absorptions at 950, 890 and 770 cm^{-1}]. The changes in pH on dilution of effluent with water were noted in the range of 4.76 to 4.85, which is in agreement with usual dichromate solutions^{9, 10, 14}.

The colorimetric determination of the concentration of iron(III) and chromium(VI), in a set of water decomposition products, gave the ratio (0.00168: 0.00472) equal to 1 : 2.81.

Silver(I) oxide decomposition product: Many sets of this product were prepared by decomposing the iron(III) peroxy-chromate (10 mL) in contact with water (20 mL) and silver(I) oxide (0.3 g). After 10 min (25°C) the bluish-violet organic layer changed to colourless and the aqueous layer became brownish-red. These decomposition products were filtered and the residue was washed over filter paper (No. 42) thoroughly with water. The washings with filtrate were concentrated to 100 mL by heating, treated first with ammonia (to faint smell) and then with SO_2 at 100°C for 0.5 h. The iron(II) solution so obtained was cooled in an atmosphere of CO_2 , acidified with dil. H_2SO_4 (1 : 6) and titrated with standard KMnO_4 solution. The presence of iron(III) and acetate ions was tested positive in aqueous layer of these decomposition products. The IR spectra of the same product showed absorptions at the following frequencies (cm^{-1}): 3600–3000 (br max with hump), 1690–1510 (s-br), 1435 (s), 1375 (s), 1190–1000 (s-br), 670–550 (s-br) and 425 (m). These absorptions indicate the association of water/ OH^- and acetate ions with iron(III). The iron(III) has a tendency to hydrolyse in aqueous solution and liberate H^+ ions. By this the ethyl acetate may hydrolyze^{15–17} to generate acetate ions in presence of silver(I) and iron(III) species.

The silver chromate residue was mixed with water (150 ml), warmed and treated with 1 N HCl. The precipitated AgCl was filtered out and washed thoroughly with water containing few mL of dil. HNO_3 . The filtrate and washings were boiled together to decompose excess of acid and then chromium(VI) was estimated iodometrically.

In 100 mL of iron(III) peroxy-chromate, silver(I) oxide decomposition product, the amount of iron(III) and chromium(VI) were found to be (0.00536 : 0.1498) in the ratio of 1 : 2.79.

Lead dioxide decomposition product: Several sets of this product were prepared by decomposing the iron(III) peroxy-chromate (10 mL) in contact with 0.3 g of dried lead dioxide, (12 h, 25°C). The decomposition product of each set was then treated with hot water and filtered (No. 42). The residue was washed well with hot water.

The washings and brownish-red filtrate were acidified with 2 N H_2SO_4 ; precipitated PbSO_4 was filtered out; filtrate was made distinctly acidic with 2 N H_2SO_4 and iron(III) was reduced to iron(II) by H_2S . This iron(II) was estimated

by KMnO_4 method. The presence of iron(III) and acetate ions was tested positive in these products, as in case of silver(I) oxide decomposition products. The IR spectra of the aforesaid product exhibited absorptions at the following frequencies (cm^{-1}): 3680–3000 (br max with hump), 1695–1510 (s-br), 1460–1360 (s-br), 11900–1000 (s-br), 660–580 (s-br) and 435 (m). These absorptions are almost similar to those of silver(I) oxide decomposition products and indicate the association of water/ OH^- and acetate ions with iron(III)¹⁵⁻¹⁷.

The lead chromate residue was mixed with water (150 mL), treated with 2 N H_2SO_4 and the precipitated PbSO_4 was filtered out. The chromium(VI) was then estimated iodometrically in the collected washings and filtrate.

In 100 mL of iron(III) peroxy-chromate, lead dioxide decomposition product, the amount of iron(III) and chromium(VI) were observed to be (0.00494 : 0.001372) in the ratio of 1 : 2.78.

RESULTS AND DISCUSSION

The ion-exchange, electronic absorption, IR, colorimetric and pH-metric studies confirmed the presence of iron(III) in the cationic while of dichromate ions in the anionic part of the water decomposition product of ions in the anionic part of the water decomposition product of iron(III) peroxy-chromate. The ratio between Fe(III) and Cr(VI) was found to be 1 : 2.81, which is equivalent to $\text{Fe}_2(\text{Cr}_2\text{O}_7)_3$.

Similarly the study of silver(I) oxide and lead dioxide decomposition products of iron(III) peroxy-chromate, have revealed that the ratio between Fe(III) and Cr(VI) is 1 : 2.78–2.79 in the studied peroxy-chromate.

On the basis of observed data the ratio of Fe(III) : Cr(VI) : peroxy oxygen, in the studied iron(III) peroxy-chromate, comes to 1 : 2.79 : 1.30. This relationship is in good agreement with the formulation of investigated iron(III) peroxy-chromate as $\text{Fe}_2(\text{Cr}_2\text{O}_{10})_3$.

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