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Oxidizing power determination of mercury peroxychromate and its water decomposition product

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Abstract
To arrive at the correct idea of constitution of mercury peroxychromate, the oxidizing power of mercury peroxychromate and its water decomposition product have been determined. Present investigation suggested that mercury peroxychromate and its water decomposition products contain $Cr_2O_{10}^{-2}$ and $Cr_2O_8^{-2}$ ions respectively.

Keywords: Mercury peroxychromate, oxdising power, water decomposition product

1. Introduction
Nowadays correlation between one-electron reduction and oxygen- oxygen bond strength in transition metal peroxo complexes of Cr (VI) and V (V) is done. The correlation holds for complexes of the same metal containing different ligands as well as for complexes of the various metals containing the same ligand. The nature of the ligands in affecting the one-electron -oxidizing ability of the peroxo complexes appears to play a more important role than the nature of the metal[1]. The coordination of dioxygen to transition metals is a subject of extreme interest due to its utilization by biological systems [2]. In biological processes, activation of molecular oxygen occurs by coordination in metalloproteins which catalyse oxygen insertion reactions and oxidation. Various formulas are given by several workers to peroxy compounds i.e., $Cr_2O_7.H_2O$, $H_2Cr_2O_8$, $CrO_3.H_2O_2$, Cr_2 $(Cr_2O_{10})_3$ etc. In aqueous systems the peroxychromate anions decomposes readily to release several species capable of causing lipid peroxidation. These species are singlet oxygen, hydrogen peroxide, hydroxyl ion etc. During the decomposition of peroxychromate, produced singlet oxygen has been suggested as one of the primary lipid oxidant.
CrO_5 formula was also given to peroxychromate compounds. Peroxy complexes of various metals are prepared and investigated by many workers [3-10]. In the present investigation, the oxidizing power of mercury peroxychromate and its water decomposition product have been determined.

2. Experimental
All the reagents used were of AR [Analytical Reagent] and GR [Guaranteed Reagent] grade. Mercury peroxychromate was prepared by adding ethyl acetate extracted hydrogen peroxide (anhydrous) to solid dry mercury chromate at 0ºC. The solution of blue or violet color thus obtained. The oxidizing power of mercury peroxychromate was determined by titrating it iodometrically using sodium thiosulphate solution as intermediate and starch as indicator. The end point was marked when the color of the solution changed from blue to light yellow. In second stage, the above reaction mixture was acidified with 2N sulphuric acid and the iodine thus liberated was titrated against the same standard sodium thiosulphate solution to the characteristic green end point.
To prepare water decomposition product, 5 ml. of mercury peroxychromate were taken into four erlenmayer flask. To each flask add 100 ml. of distilled water. After one hour mercury peroxychromate decomposed and colorless aqueous solution is obtained. Oxidizing power of water decomposition product is determined in two different ways:-
(i) Without oxidizing the water decomposing product
(ii) After oxidizing the water decomposition product.

In without oxidizing the water decomposition product, the oxidizing power is determined in two stages. In first stage, the contents of two flasks were titrated iodometrically using sodium thiosulphate as intermediate and starch as indicator. When color changes from blue to yellow, end point was marked. In second stage, the above reaction mixture was acidified with 2N sulphuric acid and the iodine liberated was titrated against the same standard $Na_2S_2O_3$ solution to the characteristic green end point.

The oxidizing power of water decomposition product, after its oxidation is one-step process. To the contents of remaining two flasks of water decomposition product of blue compound add 10 ml. of N-NaOH followed by 5ml. of 30% hydrogen peroxide solution. The reaction mixture was thoroughly agitated and boiled slowly and then gently. Small quantity of distilled water is also added time to time to make loss of water. After cooling the contents, add $2N.H_2SO_4$ and titrated iodometrically. The experimental results have been recorded in table –1.

Table 1: Oxidizing Power of Mercury Peroxychromate & Its Water Decomposition Products

Volume (ml.) of Mercury Peroxychromate	Volume (ml.) of Sodium Thiosulphate Solution used in titrating				Oxidised water decomposition product	Ratios		
	MercuryPeroxychromate		Unoxidised water decomposition product					
	Ist Stage	IInd Stage	Ist Stage	IInd Stage		$\frac{a}{b}$	$\frac{a+b}{c+d}$	$\frac{c+d}{e}$
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
5 ml.	7.3	9.6	7.6	5.0	16.2	0.76	1.42	0.77
5 ml.	7.3	9.7	7.5	4.8	16.8	0.75	1.40	0.73
5 ml.	9.2	12.1	4.5	11.6	22.2	0.76	1.32	0.72
3 ml.	10.6	13.6	8.2	8.7	22.4	0.77	1.43	0.75
2 ml.	3.8	5.0	4.3	3.1	9.9	0.76	1.38	0.74
2 ml.	5.3	7.2	5.1	4.0	12.8	0.73	1.38	0.71

3. Result and Discussion

If it is assumed that both mercury peroxychromate and its water decomposition product contain $Cr_2O_7^{-2}$ ion then it must have only one step of titration while in the present study, there are two stages of titration for mercury peroxychromate and its water decomposition product. This clearly indicate that mercury peroxychromate and its water decomposition products do not have $Cr_2O_7^{-2}$ ion but some other ion, which after the first stage of titration gives $Cr_2O_7^{-2}$ ion liberating oxygen in the first stage. The second stage is due to the liberation of $Cr_2O_7^{-2}$ ion in acidic medium represented by the equation (i):–

$$(Cr_2O_7^{-2}) \longrightarrow 2Cr_2O_3 + 8\,(O) \text{ ---------- (i)}$$

If we assume that mercury peroxychromate has $Cr_2O_{10}^{-2}$ ion, then this idea of two stages of titration, can therefore be formulated.

The formation of $Cr_2O_7^{-2}$ ion and $Cr_2O_{10}^{-2}$ ion in the first stage may be explained as:-

$$(Cr_2O_{10}^{-2})_2 \xrightarrow{\text{Ist Stage}} (Cr_2O_7^{-2})_2 + 6(O) \text{ ----------(a)}$$

$$(Cr_2O_7^{-2})_2 \xrightarrow{\text{IInd Stage}} 2\,Cr_2O_3 + 8(O) \text{ ----------(b)}$$

In this, we see that 6 and 8 oxygen atoms are evolved respectively in two stages i.e. first stage and second stage. The ratio a/b in the above reactions is 6 : 8 or 0.75 : 1.

In the table 1 the values of the ratio a/b ranges between 0.73 to 0.77. This experimental values concide with the theoretical values.

The ratio (a+b)/ (c+d) = 1.4: 1 shows that water decomposition product of mercury peroxychromate contain $Cr_2O_8^{-2}$ ion in the solution.

$$Cr_2O_{10}^{-2} \longrightarrow Cr_2O_8^{-2} + 2\,(O) \text{ ---------- (ii)}$$

The resulting $Cr_2O_8^{-2}$ ion in water decomposition product is titrated in two stages, given by equation (c) and (d).

$$(Cr_2O_8^{-2})_2 \xrightarrow{\text{Ist Stage}} (Cr_2O_7^{-2})_2 + 2(O) \text{ ---------- (c)}$$

$$(Cr_2O_7^{-2})_2 \xrightarrow{\text{IInd Stage}} 2\,Cr_2O_3 + 8\,(O) \text{ ---------- (d)}$$

Further, the water decomposition product which contain $Cr_2O_8^{-2}$ ion is oxidized by H_2O_2 in presence of N-NaOH. The oxidized product is then treated with dil. H_2SO_4. The reaction can be represented by the following equation –

$$Cr_2O_8^{-2} + 4\,NaOH + H_2O_2 \longrightarrow 2Na_2CrO_4 + 3\,H_2O + 3(O)$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

This oxidized product on titration evolve 12 atoms of oxygen, as follows–

$$4Na_2Cr_2O_7 \xrightarrow{\text{aq. KI}} 4Na_2O + 4\,Cr_2O_3 + 12\,(O) \text{ --------(e)}$$

The ratio c+d/e=10:12 or 0.83:1 obtained from above equation on calculation comes to nearly 0.80:1, which is in close agreement with the experimental values in table 1 column (h). These facts lead to the conclusion that mercury peroxychromate and its water decomposition product contains $Cr_2O_{10}^{-2}$ and $Cr_2O_8^{-2}$ ions respectively.

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