STUDIES ON THE FORMAL REDOX POTENTIAL VALUES OF Co^{3+}/Co^{2+} REGARDING THE VOLUMETRIC USE OF HEXAMMINECOBALT(III) TRICARBONATOCOBALTATE(III)

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Abstract. The values of the measured formal redox potential of Co^{3+}/Co^{2+} system in sulphuric, hydrochloric, perchloric and acetic acids, with regard to the possible use of $Co(NH_6)_3Co(CO_3)_3$ as a volumetric oxidimetric titrant, have been reported.

Hexamminecobalt(III) tricarbonatocobaltate(III) $Co(NH_6)_3.Co(CO_3)_3$, prepared according to the method of Bricker et al.,[1] has been successfully used by us for the estimation of a number of organic and inorganic substances.[2-5] Since we have found the titrant very useful for volumetric estimations based on redox measurements, it seemed quite desirable to study its formal redox potentials in the acid media. The values of the measured formal redox potentials of the system in acid media like hydrochloric, sulphuric, acetic and perchloric acids, have been reported here.

Experimental

Reagents. A stuitable solution of $Co(NH_6)_3-Co(CO_3)_3$ was prepared and its factor checked after the method described earlier.[1]

The solution of Co(II) which was equimolar with respect to $Co(CO_3)_3$ as given in the above formula, was prepared from analytical grade substance by Merck and its factor was checked according to conventional method.

All other reagents used were either of A.R. grade or equivalent purity.

Apparatus. A pH meter (model 290, Pye, Cambridge) with saturated calomel as reference and platinum foil as indicator electrodes was used for potential measurements.

All officially calibrated glassware (A grade) was used during these investigations.

Procedure. To a 250-ml beaker, exactly equal volumes of Co(III) and Co(II) equimolar solutions were added. To the same beaker water and a particular acid were added so as to give a definite total volume which was of the required exact strength with reference to the particular acid. The contents were mixed with magnetic stirrer and the potential reading was noted on its stabilisation. The procedure was repeated with various acids and their various strengths, previously [1-4] found most suited to be used as media for oxidations of many organic and inorganic substances.

Results and Discussions

Formal Redox Potential of Co^{3+}/Co^{2+} System in Sulphuric Acid. The values of the formal redox

potential of Co^{3+}/Co^{2+} system were measured in a total volume of 50 ml which was from 0.03 to 14.83N with regard to sulphuric acid. The values of the formal redox potential increase with increasing concentrations of sulphuric acid but after a certain increase in the concentration of the acid, further increase results in decrease of formal redox potential. The possible explanation could be the complex formation of the Co^{3+} and Co^{2+} with the medium due to higher concentration of acid and low concentration of water. The rise in the measured value shows that from 0.03 to 9.93N acid the increase is about 300 mV, while from 4.96 to 9.93N acid the increase is not so appreciable. This shows that it would not be so advisable to use higher concentrations of sulphuric acid in many of the cases for redox studies with the titrant. Anyhow there is no bar, wherever these higher concentrations are necessarily needed for their use as medium. Sulphuric acid stands second to hydrochloric acid in using it as a medium. On the whole sulphuric acid is a good medium for the study of the oxidizing behaviour of $Co(NH_6)_3Co(CO_3)_3$ (Table 1), and the fact is supported by our previous studies.[2-5]

Formal Redox Potential of Co^{3+}/Co^{2+} System in Hydrochloric Acid. The value of formal redox potential of Co^{3+}/Co^{2+} couple in various strengths of hydrochloric acid measured in a total volume of 50 ml shows a more rapid increase (with increase in acid concentration) than those in sulphuric acid. The rise in the value, with the rise of hydrochloric acid concentration from 0.03 to 0.15N is about 532 mV and with further increase in the acid concentration, although the value of formal redox potential decreases yet up to 4.58N hydrochloric acid the decrease is not more than about 103 mV. This means that this value is fairly constant over a fair range of the acid concentration (0.03–4.58N). Further increase in the acid concentration (5.53N) lowers the value of the formal redox potential comparatively at a higher rate than the increasing rate of the acid. The decrease in the measured values with the increase in the acid concentration could be attributed to the liberation of chlorine, at very high rate, from hydrochloric acid at higher concentration and thereby affecting the potential of the indicating electrode.

Comparing with the values of the measured formal redox potential of Co^{3+}/Co^{2+} system in sulphuric acid, these values in hydrochloric acid media are relatively on higher side. Hence it could be safely concluded, and as observed earlier,[2-4] that hydro-

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Table 1. Formal Redox Potential of the System Co^{3+} / Co^{2+}.

Acid concn (N)	Formal potential vs. S. H. E. (mV*)
H_2SO_4	
0.03	887.00
0.17	1022.00
0.88	1128.50
2.90	1129.50
4.96	1148.50
9.93	1184.75
14.83	930.00
HCl	
0.03	696.00
0.15	1228.50
0.42	1221.00
0.92	1189.50
4.58	1123.50
5.53	998.25
$HClO_4$	
0.04	648.25
0.22	862.00
0.42	915.75
0.88	940.75
1.87	945.75
CH_3COOH	
0.38	458.25
0.97	495.74
2.83	542.00
4.96	578.28
7.63	634.50
11.47	643.25
H_3PO_4	
0.05	400.75
0.43	899.50
0.93	1105.75
4.36	633.66
9.43	568.25
14.00	557.00

*Average of multiple readings.

chloric acid is of more use to the studies of $Co(NH_6)_3$-$Co(CO_3)_3$ for various redox estimations. This acid is suitable for use as medium for showing high formal redox potential values of Co^{3+}/Co^{2+} system when compared with other acids.

Formal Redox Potential of Co^{3+}/Co^{2+} System in Perchloric Acid. The values of the formal redox potential of Co^{3+}–Co^{+2} system in perchloric acid-have an increasing trend with the increase in concentration of the acid (Table 1). After 0.88N acid, further increase does not give appreciable increase in the formal redox potential values. Even then the values exhibited in the media show that this acid stands almost after sulphuric acid. The studies were made in 50 ml as total value of the reactants whereas in case of 0.04N it was 100 ml.

Formal Redox Potential of Co^{3+} / Co^{2+} System in Acetic Acid. The values (Table 1) of the system Co^{3+} / Co^{2+} in various concentrations of acetic acid observe (total volume 50 ml) almost a uniform increase with the increase in the concentration of the acid. The values of the measured formal redox potential show that the acid has limited applications for the studies, whereas it too could be quite important in the estimation of organic compounds which could only be dissolved in it (Table 1.)

Formal Redox Potential of Co^{3+} / Co^{2+} System in Phosphoric Acid. The formal redox potential values in phosphoric acid increase with increasing acid concentrations. The total volume of the reactants was 50 ml with the exception of 0.05N medium where it was 100 ml. The increase in the formal redox potential is about 705 mV with an increase from 0.05 to 0.93N of the acid (Table 1). With further increase in the acid concentration the value falls suddenly and remains almost constant with further higher acid concentrations. This acid like other acids could also be quite safely used for the oxidation studies of $Co(NH_3)_6Co(CO_3)_3$.

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Short Communication

DETERMINATION OF PEROXYDISUL-PHATE BY EDTA

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(Received May 28, 1975)

The standard procedures for the determination of alkali peroxydisulphates, based on redox reactions, are (a) iodometric method[1]. (b) reduction of acidified peroxydisulphate with an excess of ferrous salt,[2,3] followed by the determination of unreacted Fe^{++} by $KMnO_4$ or ceric sulphate,[2] (c) reduction of peroxydisulphate as in (b) followed by the determination of Fe^{+++} by mercurous nitrate,[2] and (d) reduction of peroxydisulphate with excess of oxalic acid[2] followed by the determination of unreacted oxalic acid by $KMnO_4$. Besides these redox reactions, peroxydisulphates dissolve many metals,[4] e.g. zinc (redox potential –0. 7628 V [5,6] disolves in $K_2S_2O_8$ (redox potential 2.01 V [5,7,8] according to the following reaction.[4]

$$Zn + K_2S_2O_8 \longrightarrow ZnSO_4 + K_2SO_4$$
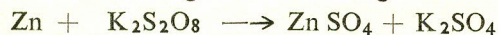
The reaction between zinc metal dust and $K_2S_2O_8$ is exothermic and does not appear to be accompanied by the evolution of any gas. The solution, obtained after shaking aqueous $K_2S_2O_8$ with zinc metal dust for 5 min, did not liberate iodine from KI and gave positive test for Zn^+. According to these observations the reaction between zinc metal dust and $K_2S_2O_8$ appeared to be quantitative and reasonably fast. In the present communication, a method is described for the determination of potassium peroxydisulphate by reacting it with an excess of zinc metal dust followed by the determination of Zn^{++} by EDTA.[2]

Experimental

Reagents. (1) Ethylenediaminetetraacetic acid disodium salt (EDTA) AR. (2) Erio-chrome Black T indicator[2] (0.2 g of the dyestuff dissolved in 15 ml of triethanol amine and 5 ml of absolute alcohol). (3) Zinc metal dust AR. (4) Potassium peroxydisulphate AR. (5) Buffer solution (142 ml of conc NH_4OH and 17.5 g of NH_4Cl AR).

Method. A standard $K_2S_2O_8$ solution in a dry conical flask, was shaken with zinc metal dust, about 1 g more than the required quantity, for 5–10 min. The solution was filtered through a dry filter paper (Whatman No. 42) into a dry flask. A 25 ml aliquot of the filtrate was diluted to 100 ml, followed by the addition of 2 ml of the buffer solution and a few drops of the indicator. The solution was titrated with standard EDTA solution until the colour changed from wine red to blue. Potassium peroxydisulphate is calculated as given below.

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1.0 ml 0.1M EDTA $\equiv$ 6.538 mg Zn $\equiv$ 27.04 mg $K_2S_2O_8$

This procedure was checked against ferrous ammonium sulphate–permanganante method.[3] The result of these analyses are given in Table 1. The time dependence of the reaction between zinc metal dust and $K_2S_2O_8$ is shown in Table 2.

Results and Discussions

The accuracy of the Zn–EDTA method, for the determination of $K_2S_2O_8$, is comparable with the ferrous ammonium sulphate method[2] (Table 1). In both the procedures the error in the assayed values of $K_2S_2O_8$ is not more than $\pm$ 0.5%. Determination of peroxydisulphates by the methods (a–d) is cumbersome because freshly prepared reagents are required and they need standardization against primary standards. However, in the Zn–EDTA method, no such difficulty is encountered; standard solution of EDTA can be stored for long periods without any appreciable deterioration. Moreover, complete reduction of potassium peroxydisulphate. by Fe^{++} takes 10–15 min[3,2] while the reaction between zinc metal dust and $K_2S_2O_8$ is completed in about 5 min. In place of zinc, magnesium metal powder also be used, perhaps more effectively for dilute and weakly alkaline solutions' of peroxydisulphates because the redox potential of zinc is–0.7628 [5,6] while that of magnesium is–2.37 V,[5] the reaction between magnesium metal powder and $K_2S_2O_8$ is likely to be very fast.

TABLE 1. DETERMINATION OF $K_2S_2O_8$ BY Zn–EDTA METHOD.

Wt of $D_2S_2O_8$ (g/25ml)	Wt. of $K_2S_2O_8$ found (g/25 ml)	
	Zn–EDTA method	Fe++ method[2]
0·5069	0·5082	0·5082
0·5089	0·5055	0·5062
0·5069	0·5062	0·5062
0·5069	0·5082	0·5055
0·5089	0·5062	0·5082
0·6764	0·6758	0·6782
0·6764	0·6744	0·6772
0·6764	0·6772	0·5658
0·6764	0·6758	0·6782
0·6764	0·6758	0·6772

TABLE 2. TIME DEPENDENCE (IN MIN) OF THE REACTION BETWEEN ZINC METAL DUST AND $K_2S_2O_8$.

Wt. of $K_2S_2O_8$ (g/25 ml)	Wt. of $K_2S_2O_8$ found (g/25 ml)			
	2 min	3 min	5 min	10 min
0·3380	0·2677	0·2123	0·3375	0·3380
0·3380	0·2681	0·3232	0·3380	0·3387
0·3380	0·2704	0·3232	0·3366	0·3387
0·5063	0·4056	0·4780	0·5080	0·5073
0·5063	0·4022	0·4860	0·5068	0·5058
0·5063	0·4070	0·4860	0·5068	0·5073

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