FORMAL REDOX POTENTIAL VALUES OF Co^{3+}/Co^{2+} SYSTEM REGARDING THE USE OF COBALT(III) ACETATE AS VOLUMETRIC OXIDIMETRIC TITRANT

Muhammad Hanif, Naseem Asghar Ginai* and M. Anwar Chaudhry*

PCSIR Laboratories, Lahore 16

The values of formal redox potential of Co^{3+}/Co^{2+} system have been measured in hydrochloric, perchloric, acetic and sulphuric acids. The change in the values with changing concentrations of these acids have also been investigated.

Recently, investigations on the use of cobalt(III) acetate as volumetric titrant have been made for the quantitative oxidation of organic and inorganic systems.[1] Cobalt(III) acetate exhibits very strong oxidising properties and its redox potential, the main cause of its vigor, has been measured to be 1.84 V in $4N$ HNO_3.[2] The titrant has yielded very useful results and a lot still remains to be investigated. Hanif[1] has successfully tried various quantitative determinations of organic and inorganic substances in various acidic media. It was, therefore, advisable to study the value of redox potentials which could positively confirm and give information about the possible utility of the titrant and the medium before actually trying the Co^{3+}/Co^{2+} system. These studies have been conducted in those media which could be safely used for such further important studies and the results of these findings have been reported in this communication.

Experimental

Reagents.—Cobalt(III) acetate solution in glacial acetic acid was electrolytically prepared according to the method of Sharp and White[3] modified by Hanif.[1] The factor of this solution was determined with ferrous sulphate using potentiometric end point method.

Cobalt(III) acetate solutions of other strengths were also prepared in glacial acetic acid by diluting stock solution and checking their strengths as above. All other chemicals used were also of analytical grade.

Apparatus.—Potential measurements were made with an electronic pH meter with platinum indicating and saturated calomel reference electrodes. After each reading both electrodes were washed with distilled water and the platinum electrode was rubbed between the folds of filter paper to remove any possible adherence of the reactants to its surface. All the potential values were converted for standard hydrogen electrode.

Method of Measurement of Formal Redox Potential.— Formal redox potential values were measured either through the courses of potentiometric titration curves of suitable systems, measuring the potential value at double the reagent consumption required for equivalence, or measureing these values of an equimolar mixture of oxidised and reduced forms of the system Co^{3+}/Co^{2+}. These studies were conducted at a temperature of 25°C. All the values of formal redox potential reported in this work are the average of multiple measurements.

Results

Formal Redox Potential of Co^{3+}/Co^{2+} in Hydrochloric Acid Medium.—The first method of potential measurement was used. Advantage was taken of the fact that divalent iron in $2N$ HCl reacts quantitatively with trivalent cobalt. For 1, 3 and $4N$ HCl no suitable system was available, hence the second method of measurement was used. The results of the findings have been reported in Table 1.

Formal Redox Potential of Co^{3+}/Co^{2+} in Perchloric Acid Medium.—According to the previous studies,[1] perchloric acid from 1 to 10% was found to be well suited to redox measurements with cobalt(III) acetate as oxidizing titrant. It was, therefore, rational to measure formal redox potential values of Co^{3+}/Co^{2+} system in perchloric acid medium as this could give very important advance information regarding the suitability of this medium for redox studies of any substance with cobalt(III) acetate. These experiments were conducted only according to the second method of measurement as no suitable system was available regarding the application of the first one. The results of the investigations are given in Table 1.

Formal Redox Potential of Co^{3+}/Co^{2+} in Acetic Acid Medium.—The values of formal redox potential of Co^{3+}/Co^{2+} system were measured in acetic acid ranging from 50 to 99%. Results of these measurements have been exhibited in Table 1.

*Government College Lahore.

Medium	Formal potential (mV vs. S.H.E.)	Normality of the medium	Formal potential (mV vs. S.H.E.)
1n HCl	1273	50% acetic acid	945
2n ,,	1252	70% ,,	930
3n ,,	1243	80% ,,	924
4n ,,	1217	99% ,,	847
2% perchloric acid	1062	1n H_2SO_4	1439
5% ,, ,,	1053	4n ,,	1384
10% ,, ,,	1046	7n ,,	1360
		11n ,,	1349
		15n ,,	1332

Formal Redox Potential of Co^{3+}/Co^{2+} *in Sulphuric Acid Medium.*—Sulphuric acid (1–15n) has been used as a medium in a number of oxidimetric determinations with cobalt(III) acetate as oxidising titrant.[1] It was, therefore, justifiable to find the formal redox potential values of Co^{3+}/Co^{2+} system in all these media. The method of measuring formal redox potential value of an equimolar solutions of trivalent and divalent cobalt in an appropriate strength of acid was employed. The other method of titrating divalent iron in 2n H_2SO_4 was also used for the potential measurements because of the quantitative oxidation of iron(II) by cobalt(III) in this medium. The results of these experiments are reported in Table 1.

Discussion

The formal redox potential of Co^{3+}/Co^{+2} system, as evident from Table 1, decreases with increasing concentrations of hydrochloric acid. These values when compared with those in other media, are next to those in sulphuric acid. This fact has clearly supported the idea that because of these higher values many of the substances have been oxidized in HCl.[1]

In order to verify whether this dependence is only due to the acidity or the character of the acid also, experiments were carried out for the measurement of formal redox potential values in 2–10% perchloric acid. It can be seen from Table 1 that the values of formal redox potential in perchloric acid are less by about 200 mV besides their being next to those in hydrochloric acid. These values like those in hydrochloric acid decrease with increasing concentration of the acid. It is also exhibited by the results in Table 1 that with changing concentrations of acid the formal redox potential values change a little less in perchloric acid than in hydrochloric acid. In view of the facts, it can be concluded that substances which cannot be oxidised in perchloric acid have better chances of oxidation in hydrochloric acid, a fact

experienced in our previous studies.[1]

The increase in redox potential values of the system, with the increase in the amount of water in hydrochloric acid and perchloric acid media could be attributed to the increasing amount of water providing greater chances of complex formation with Co^{2+} and Co^{3+} species which results in lesser electronic movements.

The studies for redox potential measurements in acetic acid were restricted from 99% to 50% because of the quick reduction of trivalent cobalt below 50% acetic acid. Potential stabilisation was quite slow due to the complex-forming nature of acetic acid with cobalt. The change in redox potential values, as shown in Table 1, was about 100 mV from glacial to 50% acetic acid. This change can be attributed to higher chances of complex formation at higher concentrations of acetic acid with cobalt. Such low values of redox potential of Co^{3+}/Co^{2+} system in acetic acid medium, have proved the limited application of cobalt(III) acetate as an oxidising agent in this acid. This fact has also been proved previously.[1] Although, the redox potential values of the system in acetic acid are lower than those exhibited in other media, yet the medium has its unique importance especially where the oxidation of most of the organic substances, by many reasons, is the most suited.

Both the methods of formal redox potential measurements were applied in suitable concentrations of sulphuric acid and results were the same (Table 1). Formal redox potential values of Co^{3+}/Co^{2+} system also decrease with increasing concentration of sulphuric acid. This phenomenon, as observed in hydrochloric acid could also be attributed to the complex formation of Co^{2+} and Co^{3+} with water. A decrease of about 100 mV in formal redox potential values, when going from 1 to 2 n sulphuric acid is obviously a proof of the above speculation. According to the results it has been proved that because of the higher formal redox potential values of the system in sulphuric acid medium many of the substances could be studied in this medium. These values in sulphuric acid are higher than those in other media so far studied. This fact has clarified the maximum possible oxidations of many substances studied earlier.[1]

Hydrochloric acid stands second to sulphuric acid and hence will also lend many possibilities for such studies with cobalt(III) acetate. Perchloric acid is too close to the properties of those exhibited by hydrochloric acid. It has also lent chances to many substances for their redox studies. Acetic acid has proved to show the minimum redox potential values of the Co^{3+}/Co^{+2} system whereas this value in about 50% acetic acid is a little close to those in perchloric acid. These lower values have given a clue that they were the main cause of

restricted application of acetic acid as a medium for such experiments. Also the quick reduction of trivalent cobalt by water in lower than 50% acetic acid restricted the use of acetic acid below 50% concentrations. Inspite of this, acetic acid as a medium, especially glacial acetic acid, has its importance in the oxidation of organic substances, where the reaction proceeds at a much lower rate and in the absence of this acid other acids (aqueous solutions) will be reducing the titrant to add much error to the results. This utility of glacial acetic acid medium has also been supported by recent studies on the oxidation of organic substances with cobalt(III) acetate.[4] According to this communication glacial acetic acid has been employed as medium for the oxidation of substances like hydroquinone, monochlorohydroquinone, 1,4-dihydroxynaphthalene p-aminophenol, p-phenylenediamine, metol, α-tocopheroel. Summing up the above, formal redox potential values of Co^{3+}/Co^{2+} system are in the following decreasing order: $H_2SO_4 > HCl > HClO_4 > HOAc$.

These studies have given a ready information for the selection of proper media for the oxidation of various substances with cobalt(III) acetate and thus avoiding much of hit and trial methods. At the same time these studies,[4] combined with the previous,[1] conclude that it is always not so simple though the present investigations have given very valuable conclusions and guidance, to explain the peculiarity of the oxidation behaviour of this salt in many cases, which is another separate problem requiring a different approach.

References

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