

Oxidation of Some Organic Substances with Cobalt (III) Acetate as Redox Titrant

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Summary: Cobalt (III) acetate solution, prepared in glacial acetic acid by the anodic oxidation and showing as high redox potential as about 1.4 in various acidic media has been successfully utilised as a Volumetric redox titrant for the determination of hydroquinone, p-tetrachlorohydroquinone, ascorbic acid, p-aminophenol and p-phenylenediamine.

Introduction

Salts of trivalent cobalt exhibit high redox potentials¹; hence cobalt (III) acetate prepared in glacial acetic acid by anodic oxidation shows a redox potential of the order of about 1.4V in some acidic media and its solution has a long keeping quality³. It has been successfully used as a redox titrant for the determination of a variety of substances²⁻¹².

The titrant, therefore, has a great future and hence in order to extend its usefulness, studies of the oxidations of a few organic substances were undertaken. Consequently methods of the determination of hydroquinone, p-tetrachlorohydroquinone, ascorbic acid, p-aminophenol and p-phenylenediamine were evolved using this titrant and some of the results of these studies are reported here (see table 1 & figure 1).

Experimental

Reagents:

Cobalt (III) Acetate. A stock solution of the reagent was prepared in glacial acetic acid by anodic oxidation and it was standardised potentiometrically against standard ferrous sulphate² solution.

Hydroquinone. 0.1 N aqueous solution was prepared (p.a. Lachema, Czechoslovakia) and its exact strength was determined with dichromate in 4 N sulphuric acid using diphenylamine as indicator.

Tetrachloro-p-hydroquinone. 0.1 N aqueous solution was prepared (p.a. Lachema, Czechoslovakia) and standardised against dichromate.

Ascorbic acid. Aqueous solution of ascorbic acid (p.a. Lachema, Czechoslovakia) was also standardised before use¹⁻¹².

p-Aminophenol. 0.1 N aqueous solution was prepared (p.a. Lachema, Czechoslovakia) and standardised against dichromate¹³.

p-Phenylenediamine. 0.01 N aqueous solution was prepared (p.a. Lachema, Czechoslovakia) and was also

standardised potentiometrically against dichromate using 0.1N K₂Cr₂O₇ and sulphuric acid. The strength was always checked before use.

Apparatus:

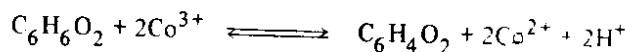
All potential measurements were made with a potentiometer Multoscop V (Metra Co., Czechoslovakia) using platinum and saturated calomel electrodes.

All "A" grade calibrated volumetric glass-ware was used during the investigations.

Results and Discussion

Oxidation of Hydroquinone:

In hydrochloric acid medium the oxidation of hydroquinone was not accurate and its reaction with cobalt (III) acetate was so slow that one titration could not be completed in about 75 minutes. At equivalence point the reaction was too sluggish. In glacial acetic acid although the system worked stoichiometrically, yet the rate of reaction was even slower than in HCl and one titration was accomplished in 2-hours. In 5N H₂SO₄ the reaction was faster than in both media mentioned earlier and results of determination were much more accurate. One titration could be completed in about 40-45 minutes. There was a two-electron change from one molecule of hydroquinone. The reaction proceeded according to the following equation:



Oxidation of p-Tetrachlorohydroquinone:

p-Tetrachlorohydroquinone on oxidation gave a quinonoid structure and its reaction with cobalt (III) proceeded according to the following equation:

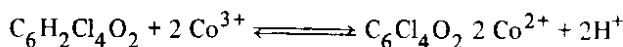


Table:- Showing the results of Oxidation of Hydroquinone, *p*-Tetrachlorohydroquinone, Ascorbic acid, *p*-Aminophenol and *p*-Phenylenediamine.

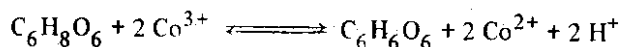
Substance	Medium	Substance			Inflection Potential mV	$\Delta mV/\Delta ml$ for 0.02 ml of 0.1N Co(III) Ac.
		taken (mg)	found (mg)	error %		
Hydroquinone	5N H ₂ SO ₄	60.29	61.66	+ 2.28	645	10.8
		52.77	52.82	+ 0.09	650	10.5
		41.04	41.06	+ 0.04	650	10.5
		29.32	29.68	+ 1.22	645	10.5
		23.45	23.86	+ 1.74	645	10.5
<i>p</i> -tetrachlorohydroquinone	5N H ₂ SO ₄	18.59	18.59	+ 0.00	710	170.0
		24.79	24.79	+ 0.04	715	170.0
		30.98	30.99	+ 0.03	710	170.0
Ascorbic acid	10N H ₂ SO ₄	39.76	39.76	+ 0.00	675	16.0
		62.49	62.49	+ 0.00	655	16.0
		78.11	78.15	+ 0.05	630	16.0
		116.90	116.90	+ 0.00	580	11.0
		140.29	140.29	+ 0.00	545	7.0
	2N HCl	39.36	39.39	+ 0.07	600	35.0
		51.29	51.29	+ 0.00	600	30.0
		78.73	79.44	+ 0.91	660	46.0
		87.94	88.03	+ 0.12	650	16.0
		109.90	109.90	+ 0.00	650	13.0
<i>p</i> -aminophenol	65% HOAc	23.16	23.52	+ 1.56	540	14.0
		32.62	32.73	+ 0.34	545	14.0
		37.28	37.76	+ 1.29	545	14.0
		41.94	42.77	+ 1.97	535	14.0
		46.60	47.03	+ 0.92	530	14.0
<i>p</i> -phenylenediamine	50% HOAc	30.18	31.48	+ 4.31	450	11.0
		20.12	20.76	+ 3.18	450	11.0
		15.09	15.74	+ 4.31	450	11.0
		10.00	10.50	+ 5.00	450	10.0

There was a fairly high potential jump at the equivalence point and one titration took 45-60 minutes. As in the case of hydroquinone, it was also quantitatively oxidised by Co(III) in 5N H₂SO₄, there being a 2-electron transfer. There appeared a light yellow precipitate after the substance was completely oxidised. The reaction proceeded quantitatively in glacial acetic acid but the rate of reaction was too slow.

Oxidation of Ascorbic acid:

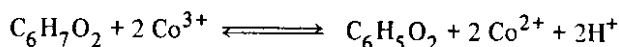
Although ascorbic acid in 1-2 N HCl was quantitatively oxidised by Co(III) yet the rate of reaction was too slow and the titration was completed in about 3 hours. In the case of acetic acid, (60% to glacial) one titration took about 4 hours and the error was too high. In 10N sulphuric acid however the rate of reaction was

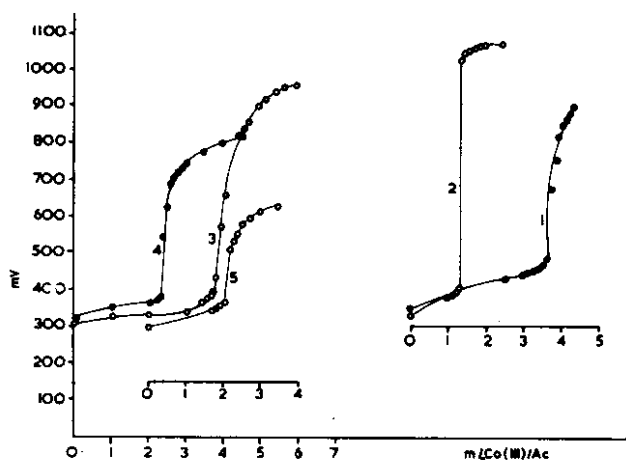
faster and the titration took 2 hours. All the titrations were carried out in an inert atmosphere to avoid possible interference from atmospheric oxygen. The reaction proceeded as follows:



Oxidation of *p*-Aminophenol

In hydrochloric acid media *p*-aminophenol could not be quantitatively oxidised with Co(III). In H₂SO₄ and HClO₄ (1 to 20%) the errors were high. In all the cases the reaction was too slow. More accurate results were obtained by using CH₃COOH (60% to glacial) particularly so in 65% CH₃COOH as under:





Representative Potentiometric Titration curves.

Curve No: 1. 29.30 mgs of hydroquinone against 0.147N Co (III)/AcOH.

Curve No: 2. 12.39 mgs of p-tetrachlorohydroquinone against 0.073N Co (III)/AcOH.

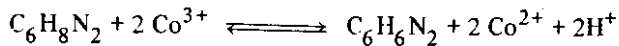
Curve No: 3. 62.49 mgs of ascorbic acid against 0.1795N Co (III) AcOH.

Curve No: 4. 23.16 mgs of p-aminophenol against 0.1823N Co (III)/AcOH.

Curve No: 5. 20.12 mgs of p-phenylenediamine against 0.1869N Co (III)/AcOH.

Oxidation of p-phenylenediamine.

The oxidation was tried in HCl, H₂SO₄, HClO₄, and CH₃COOH but better results were obtained with 50% CH₃COOH.



On the basis of the above findings it is quite obvious that Co(III) Ac can be used for the determination of a variety of compounds.

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