

## SOME FUNDAMENTAL STUDIES WITH COBLAT(III) ACETATE FOR ITS USE IN REDOX REACTIONS WITH ORGANIC SUBSTANCES IN NONAQUEOUS MEDIA

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**Abstract.** Result of fundamental studies regarding the use of Cobalt (III) acetate for the study of oxidation of organic substances in nonaqueous media have been reported.

The high redox potential of cobalt(III) acetate has been utilized for the determination of variety of compounds in aqueous media.<sup>1-14</sup> Due to their high solubility in nonaqueous solvents and interesting oxidation behaviour, organic substances form an important field for study with cobalt(III) acetate as volumetric oxidimetric titrant. However, these are less investigated. It is important to have a practical knowledge of the stability of the reagent in the media to be used, since it was planned to add an excess of the reagent and then to back titrate the excess. Such methods have been developed. It was also considered necessary to look for the decomposition of various concentrations of Co(III) acetate in glacial acetic acid medium.

### Experimental

**Reagents.** Cobalt(III) acetate solution was prepared by the anodic oxidation of cobalt(II) acetate in glacial acetic acid to which sodium acetate was added to increase conductivity after the method of Sharp and White<sup>2</sup> as modified by Hanif.<sup>15</sup> Solution of other strengths were prepared of cobalt(III) acetate by its exact dilution with glacial acetic acid. A solution of cobalt(III) acetate free of sodium acetate was also prepared according to the above method.

All other chemicals were of analytical grade or of equivalent purity.

**Apparatus.** Potential measurements were made with a potentiometer Multoscope V (Metra, Czechoslovakia) using a platinum foil indicating electrode and saturated calomel reference electrode.

**Procedure.** Stability studies were carried out by measuring the redox potential of the reagent in glacial acetic acid medium at regular intervals. A 0.1-ml of 0.0922N Co(III) acetate solution free of sodium acetate, was mixed with 55 ml of glacial acetic acid, potential values were noted after every 10 min. Similarly study was made with cobalt(III) acetate containing sodium acetate in glacial acetic acid medium. The concentrations of the reagent in both cases were the same.

The above procedure was followed for various further low concentrations of the reagent.

Back titrations were carried out by adding an excess of cobalt(III) acetate in a definite volume of the test nonaqueous media to which a known amount of the organic substance under investigation had been added. After a predetermined interval the

excess cobalt(III) was back titrated with the titrant to be examined.

### Result and Discussion

Although the present investigations were to determine the suitability of the media for nonaqueous studies of the reagent with organic substances the reagent itself contained about 1% of water from the glacial acetic acid used in its preparation. This amount of water was tolerable as it did not affect the decomposition of the reagent or the oxidizing behaviour of cobalt(III), whose complexing nature remains unaltered and it reacts normally.

Apart from initial studies sodium acetate was added to Co(II) acetate solution in glacial acetic acid to increase the conductivity of the solution during its electrolysis, without this addition the time of electrolysis was almost double.

It was also designed to treat organic substance with an excess of cobalt(III) acetate in glacial acetic acid medium and then to determine the actual amount of reagent used up during a certain reaction time. It was also deemed necessary to examine the rate of extent of decomposition of different concentrations of Co(III) acetate in the medium employed, under the influence of time. Table 1 reveals that glacial acetic acid medium does not appreciably decompose cobalt(III) even if it is in low or higher concentrations. Hence this could be used safely in further studies.<sup>1-2</sup> Iron(II) sulphate, the usual reagent used for Co(III) acetate standardization, was tried in back titrations and worked well. The reaction is quite fast with reasonable potential break at equivalence point. The reaction is sluggish only near and after equivalence point after which precipitation also takes place due to the fairly low solubility of iron(III) in glacial acetic acid and an unusually long time of about 1½-2 hr is required to complete one titration. The approach of end point can be noted visually by a sharp change in solution colour from reddish yellow to blackish red. In order to increase the rate of reaction, effect of various catalysts, influence of mineral acids, rapid addition method and temperature were examined. To the reagent solution prepared in glacial acetic acid, containing 1% sodium acetate further additions of sodium acetate were of no effect in increasing the rate of reaction between Co(III) and Fe(II). The time of one titration was cut short from 2 to 1 hr with 1% sodium acetate addition (Table 2). Other possible catalysts such as potassium acetate, silver nitrate, Ce(IV) sulphate, potassium iodide and

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TABLE 1. PER CENT DECREASE IN THE CONCENTRATION OF Co(III) ACETATE (0.1386N), IN THE MEDIUM OF GLACIAL ACETIC ACID UNDER THE INFLUENCE OF TIME.

Time (hr)	Vol. of Co(III) acetate taken (ml)	Vol. of the reagent un-decomposed	Difference	Inflection potential (mV)
1	2.00	2.00	+0.00	370
	3.00	3.01	+0.33	370
	5.00	5.02	+0.40	370
	7.00	7.04	+0.57	390
	10.00	10.06	+0.60	390
2	-do-	1.99	-0.50	370
		2.99	-0.33	370
		4.98	-0.40	370
		6.98	-0.28	390
		9.98	-0.20	390
3	-do-	1.99	-0.50	370
		2.98	-0.66	370
		4.98	-0.44	370
		6.98	-0.28	380
		9.98	-0.20	390
4	-do-	1.98	-1.00	360
		2.98	-0.66	370
		4.98	-0.44	370
		6.97	-0.42	380
		9.97	-0.30	380
6	-do-	1.98	-1.00	360
		1.97	-1.00	360
		1.97	-0.60	360
		1.96	-0.57	380
		1.95	-0.50	390
8	-do-	1.97	-1.50	360
		1.97	-1.00	360
		1.96	-0.80	360
		1.96	-0.57	360
		1.95	-0.50	390

TABLE 2. THE INFLUENCE OF SODIUM ACETATE ON THE RATE OF TITRATION AND ON THE PER CENT ERROR, IN THE DETERMINATION OF Co(III) ACETATE (0.0942N) WITH Fe(II) SULPHATE (0.0875N) IN GLACIAL ACETIC ACID AT LABORATORY TEMPERATURE.

Co(III) acetate taken (ml)	Co(III) determined (ml)	Difference (%)	Infl. in pot (mV)	Time for one titration (min)
In the presence of 1% sodium acetate in Co(III) acetate				
2.00	2.01	+0.50	370	60-80
3.00	3.02	+0.66	370	80-90
5.00	5.04	+0.80	370	80-90
7.00	7.05	+0.71	390	80-160
In the absence of sodium acetate				
2.00	2.02	+1.00	360	80-100
3.00	3.04	+1.33	360	80-110
5.00	5.06	+1.20	360	90-110
7.00	7.13	+1.86	360	90-110

TABLE 3. INFLUENCE OF TEMPERATURE ON THE RATE OF TITRATION AND ON THE RESULTS OF THE DETERMINATION OF Co(III) ACETATE (0.1279N) WITH Fe(II) SULPHATE (0.098N) IN THE MEDIUM OF GLACIAL ACETIC ACID.

Temp (°C)	Co(III) taken (ml)	Co(III) determined (ml)	Difference (%)	Inflection potential (mV)	Time for one titration (min)
Temperature maintained throughout titration					
20	5.00	5.04	+0.80	370	90-100
30	5.00	5.03	+0.60	370	60-70
40	5.00	4.96	-0.80	370	40-50
50	5.00	4.95	-1.00	350	30-35
60	5.00	4.93	-1.40	350	25-30
Temperature maintained only near the equivalence point					
20	5.00	5.04	+0.80	370	80-100
30	5.00	5.05	+1.00	370	70-80
40	5.00	5.04	+0.80	370	45-50
50	5.00	5.02	+0.40	370	40-50
55	5.00	4.98	-0.40	365	30-45
60	5.00	4.96	-0.80	350	30-40

TABLE 4. DETERMINATION OF Co(III) ACETATE (0.1204N) WITH 0.99N HYDROQUINONE SOLUTION PREPARED IN GLACIAL ACETIC ACID IN THE MEDIUM OF GLACIAL ACETIC ACID AT LABORATORY TEMPERATURE.

Vol. of Co(III) acetate taken (ml)	Vol. of Co(III) back titrated (ml)	Difference (%)	Inflection potential (mV)
1.00	0.99	-1.00	460
2.00	2.00	—	460
3.00	3.01	+0.33	460
4.00	4.03	+0.50	460
5.00	4.97	-0.60	480
7.00	7.03	+0.43	480
10.00	9.95	-0.50	480

osmium tetroxide gave no positive effect.

Addition of mineral acids  $H_2SO_4$ , HCl and  $HClO_4$  had marked influence on the rate of titration, especially 2N HCl but unfortunately they proved to have adverse effect on the decomposition of the reagent.

The method of rapid addition as in case of Fe(II) salts with  $K_2Cr_2O_7$  titration did not work for the present purpose.<sup>16</sup>

The influence of temperature to increase the rate of reaction between Fe(II) sulphate and Fe(III) acetate was investigated and a temperature of 40-50° was the optimum. This temperature was maintained

only near equivalence point. The time of titration was 45–50 min (Table 3).

Hydroquinone in nonaqueous media was tried in place of Fe(II) sulphate for the determination of the excess of Co(III) acetate via back titration. The results (Table 4) are satisfactory but the titration time was unacceptably long. Similarly thallium(I) acetate and ascorbic acid could not be used.

Hence Fe(II) sulphate was the best titrant available.

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