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A Direct Titrimetric Determination of Malic, Tartaric and Thioglycollic Acids with Ammonium Hexanitratocerate(IV)

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The use of ammonium hexanitratocerate (IV) in oxidimetry has not been studied in considerable detail, although the salt can be obtained in a high degree of purity. Conditions have now been established for the direct and also reverse titration of malic, tartaric and thioglycollic acids with this reagent at room temperature and also slightly elevated temperatures in nitric acid medium using ferroin as indicator. The procedures developed give reasonably precise results and they constitute a definite improvement over those involving cerium(IV) sulphate.

INTRODUCTION

Smith, Sullivan and Frank[1] described the preparation of ammonium hexanitratocerate(IV) in a high degree of purity and later on Smith and Fly[2] advocated its use as a primary standard. Several advantages are associated with the use of this salt as an oxidant: (1) high equivalent weight, (2) high degree of stability in the crystalline condition, (3) the attainment of a high oxidation potential in perchloric acid (1.70–1.87 V from 1–8 N) or in nitric acid (1.61–1.56 V from 1–8 N) media. The use of ammonium hexanitratocerate (IV) in nitric acid medium does not appear to have been studied in a considerable detail although Smith, Sullivan and Frank[1] have established that **the nitrate had no influence upon the oxidimetric titrations.** A survey of literature has shown that so far no one has extensively studied this reagent in nitric acid medium, using ferroin as indicator for the quantitative estimation of these commercially important organic acids.

EXPERIMENTAL

A known weight of the crystalline ammonium hexanitratocerate (IV) is dissolved in nitric acid and the solution made up to 1 litre with the requisite amount of dilute nitric acid so that the overall concentration of nitric acid is 1.0 N. The solution is stored in an amber coloured Jena glass bottle. The solution is standardised against a solution of Mohr's salt in sulphuric acid medium, using ferroin as indicator, the Mohr's salt solution having been previously standardised against a standard potassium dichromate solution employing diphenyl amine sulphonate as an internal indicator. All other reagents, *viz.*, nitric, malic, tartaric and thioglycollic acids were of analytical reagent grade. The solutions of these organic acids were previously standardised through different oxidimetric procedures[3,4].

Recommended Procedure

Take an aliquot of 0.01 M organic acid in a 100 ml Erlenmeyer flask and add 10 ml of 1 N nitric acid, 0.5 ml of 0.001 M ferroin and 1 ml of a mixture of potassium iodide and potassium iodate (equivalent to 10^{-3} N iodine). Titrate with a solution of ammonium hexanitratocerate(IV) till the ferroin red colour just changes to very pale blue. The titration should be performed as slowly as possible i.e., waiting for 30 sec. after each addition.

The above titration can be performed in a better way by heating the reaction mixture to 40°C excluding the intial addition of the catalyst, potassium iodide-potassium iodate mixture. However, near the equivalence point when the ferroin red colour has faded very much, add 0.5 ml of potassium iodide-iodate mixture (equivalent to 10^{-3} N iodine) and continue the titration, waiting for 10 sec. after each addition. If the blue colour reverts to a pale red tinge in 10 to 15 sec., a fraction of a drop of the cerate solution may be added to obtain a permanent pale blue colour.

The reverse titration of ammonium hexanitratocerate (IV) in 0.5 N nitric acid with 0.01 M organic acid solution can be carried out without any difficulty. This titration is smooth and rapid and further does not warrant the addition of the above said catalyst using ferroin as indicator. Evidently, ferroin is quite stable in contact with an excess of ammonium hexanitratocerate(IV) solution in 0.5 N nitric acid without losing its intensity during its reversibility as an indicator. Slightly higher temperatures i.e. 40–50°C further facilitate the rapidity of the reaction.

A large number of titrations are made according to the above procedures. Some typical results are given in Tables 1 and 2.

TABLE 1
DETERMINATION OF MALIC, TARTARIC AND THIOGLYCOLLIC ACIDS BY AMMONIUM HEXANITRATOCERATE(IV) IN NITRIC ACID MEDIUM (*ca.* 0.5 N)

Malic Acid			Tartaric Acid			Thioglycollic Acid		
Taken m moles	Found m moles	Error (%)	Taken m moles	Found m moles	Error (%)	Taken m moles	Found m moles	Error (%)
0.0330	0.0326	–1.21	0.0382	0.0384	+0.52	0.0328	0.0326	–0.61
0.0770	0.0768	–0.26	0.0574	0.0569	–0.87	0.0547	0.0549	+0.37
0.0990	0.0985	–0.51	0.0860	0.0855	–0.58	0.0765	0.0760	–0.65
0.1100	0.1111	+1.00	0.0956	0.0962	+0.63	0.0984	0.0980	–0.41
0.1540	0.1540	0.00	0.1147	0.1157	+0.87	0.1093	0.1098	+0.46
0.1650	0.1664	+0.85	0.1434	0.1445	+0.77	0.1202	0.1202	0.00
			0.1721	0.1716	–0.29	0.1421	0.1426	+0.35
						0.1639	0.1635	–0.24
						0.2186	0.2199	+0.59
						0.2405	0.2431	+1.08

TABLE 2

DETERMINATION OF MALIC, TARTARIC AND THIOGLYCOLLIC ACIDS: REVERSE TITRATION OF AMMONIUM HEXANITRATOCERATE(IV) IN 0.5 N NITRIC ACID MEDIUM WITH THE ORGANIC ACID

Malic Acid			Tartaric Acid			Thioglycollic Acid		
Taken m moles	Found m moles	Eror (%)	Taken m moles	Found m moles	Error (%)	Taken m moles	Found m moles	Error (%)
0.0220	0.0222	+0.91	0.0287	0.0289	+0.70	0.0328	0.0330	+0.61
0.0440	0.04367	–0.75	0.0669	0.0667	–0.30	0.0765	0.0770	+0.65
0.0880	0.08778	–0.25	0.0861	0.0861	0.00	0.0984	0.0980	–0.41
0.0990	0.09954	+0.55	0.0956	0.0966	+1.04	0.1093	0.1093	0.00
0.1100	0.1111	+1.00	0.1147	0.1142	–0.41	0.13116	0.1312	+0.03
0.1430	0.1430	0.00	0.1338	0.1350	+0.90	0.1529	0.1543	+0.92
0.1540	0.1536	–0.26	0.1434	0.1424	–0.70	0.1639	0.1633	–0.37
0.1760	0.1767	+0.40				0.1749	0.1770	+1.20

RESULTS AND DISCUSSION

Kirk and Tompkins[5] attempted the microtitration of oxalate with ammonium hexanitratocerate(IV) both in nitric and perchloric acid media. However, they have found that the results are somewhat misleading in that the reaction is too slow for convenience and the end-point was difficult to read with *ortho*-phenanthroline ferrous sulphate (ferroin), particularly in presence of asbestos.

Significant observations made during attempted macrotitrations of malic, tartaric and thioglycollic acids with ammonium hexanitratocerate(IV) in nitric acid medium are summarized as follows:

1. In the initial stages of the titration, the addition of small amounts of cerate solution changes the ferroin red colour to the yellow colour of the cerium(IV) which gradually reverts back to red colour through orange in about 6-8 sec. Further, the intensity of the restored red colour is somewhat less than that at the start of the titration.
2. The intensity of the restored red colour, as stated above, becomes less and less as the equivalence point is approached. Further the loss in intensity of the ferroin red colour increases as the nitric acid concentration (*ca.* 0.5 N) of the titration mixture is increased.

We have made the interesting observation that the addition of a little potassium iodide-iodate mixture (1 ml of 10^{-3} M solution per 50 ml of titration mixture) eliminates the above said difficulties. Probably, the action of the catalyst is more concerned with the functioning of the indicator rather than with the reaction of cerate with the above mentioned organic acids.

From our previous studies[3,6] and also the present study, it was found that eight and six equivalents of Ce^{4+} are consumed per mole of malic acid and tartaric acid respectively. The products of oxidation in both the cases are formic acid and carbon dioxide. However, the stoichiometry in the case of thioglycollic acid is

10 moles of cerium(IV) per 2 moles of thioglycollic acid to yield stable sulphone product. The formation of these end-products in the above said oxidation reactions was established through different tests[7]. The oxidation reaction basing on the above said stoichiometrics can be written as follows:

$$\underset{\text{Malic acid}}{CH_2COOH{\cdot}CH(OH){\cdot}COOH} + 8\,Ce^{4+} + 3H_2O \rightarrow 8Ce^{3+} + 8H^+ + 2HCOOH + 2CO_2\uparrow \quad (1)$$

$$\underset{\text{Tartaric Acid}}{CH(OH)COOH{\cdot}CH(OH){\cdot}COOH} + 6\,Ce^{4+} + 2H_2O \rightarrow 6Ce^{3+} + 6H^+ + 2HCOOH + 2CO_2\uparrow \quad (2)$$

$$\underset{\text{Thioglycollic acid}}{2CH_2SH{\cdot}COOH} + 10\,Ce^{4+} + 4H_2O \rightarrow \underset{\text{sulphone}}{CH_2COOH{\cdot}SO_2{\cdot}SO_2{\cdot}COOH{\cdot}CH_2} + 10Ce^{3+} + 10H^+ \quad (3)$$

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