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Determination of Certain Hydroxy Compounds with the use of Ce(IV) Reagent

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In the present work, the use of Ce(IV) reagent viz., ammonium hexanitratocerate (IV) in the determination of various hydroxy compounds has been described.

INTRODUCTION

Ammonium hexanitratocerate (IV) is a strong oxidising reagent. As an extension of the use of this reagent[1-4], in the present work, the author describes a general method for determination of all hydroxy compounds.

EXPERIMENTAL

Solution of ammonium hexanitratocetate (IV) reagent (0.1 M) was prepared in 0.5 N nitric acid. Ferrous ammonium sulphate (0.1 M), ferroin (0.001 M) and sulphuric acid (1 M) solutions were also prepared in distilled water. Stock solutions of pure ascorbic acid and other hydroxy compounds were prepared in distilled water. The pharmaceutical preparations of ascorbic acid in the form of tablets were powdered and dissolved in distilled water and the filtrate was kept for estimation. Water base injections were dissolved directly in distilled water. The concentration of sample solutions is 1 mg/ml.

Sample solutions containing 1–5 mg of the compound were taken in a 100 ml conical flask and 10 ml of 0.1 M ammonium hexanitratocerate (IV) reagent was added to it. The reaction mixture was allowed to react for recommended reaction time at room temperature (25–30°C). Now the reaction was quenched by adding 10 ml of 1 M sulphuric acid and contents shaken for 1 minute. The unconsumed Ce(IV) reagent was titrated against 0.1 M Fe(II) reagent using few drops of ferroin indicator. A blank is run under identical conditions and the recovery of the sample is calculated.

$$\text{mg of sample} = M/nN\ (VB - VS)$$

M = mol. wt. of sample, n = molecularity of Ce(IV) reagent, N = normality of Fe(II) solution, VB = Vol. of Fe(II) used for blank, VS = Vol. of Fe(II) used for sample.

RESULT AND DISCUSSION

The recommended procedure has been successfully applied for the determination of samples up to 10 mg., but for simplicity the results are given only upto 5 mg (Table 1). The described reaction condition was

TABLE 1

DETERMINATION OF SOME HYDROXY COMPOUNDS WITH Ce(IV) REAGENT

Sample	X amount taken in (mg)	Reaction time in minutes	Stoich-iometery	Amount obtained by calculation	% Error
1. Ascorbic acid	2.00	30	16	1.9980	−0.10
	4.00			4.0088	+0.22
	6.00			6.0114	+0.19
Celin T	2.00	30	16	2.0128	+0.64
	4.00			4.0088	+0.22
	6.00			6.0078	+0.13
Sorvicin T	2.00	30	16	1.9966	−0.17
	4.00			3.9924	−0.19
	6.00			6.0156	+0.26
Calcium Sandoz T	2.00	30	16	2.0134	+0.67
	4.00			4.0176	+0.46
	6.00			6.0078	+0.13
Rodoxan I	1.00	30	16	1.0016	+0.16
	3.00			3.0093	+0.31
	5.00			4.9880	−0.24
2. Methanol	1.02	10	4	1.0214	−0.13
	2.04			2.0441	+0.20
	3.06			3.0508	−0.30
3. Ethanol	1.02	10	4	1.0258	+0.56
	2.04			1.9937	−0.22
	3.06			3.0692	+0.30
4. *n*-Propanol	1.01	10	4	1.0152	+0.51
	2.02			2.0044	−0.77
	3.03			3.0239	−0.20
5. *n*-Butanol	1.12	10	4	1.1300	+0.44
	2.25			2.2500	+0.20
	3.37			3.3800	+0.35

6. 3-Pentanol	1.05	15	8	1.0533	+0.50
	2.10			2.1089	+0.42
	3.15			3.1595	+0.30
7. Propane-1,2-diol	1.04	20	6	1.6437	+0.35
	2.08			2.0737	−0.30
	3.12			3.1137	−0.20
8. Butane-1,6-diol	1.50	20	12	1.5057	+0.50
	3.00			2.9931	−0.23
	5.00			4.5290	+0.64
9. Butane-2,3-diol	1.03	20	6	1.0352	0.50
	2.06			1.0584	−0.33
	3.09			3.0931	+0.10
10. Triethylene glycol	1.50	20	8	1.5050	+0.33
	3.00			2.9940	−0.20
	4.60			4.4820	−0.40
11. Tetraethylene glycol	1.50	20	8	1.5060	+0.40
	3.00			3.0210	+0.70
	4.50			4.5190	+0.42

X in each case three determination were done, T= tablet, I=Injection

achieved by studying variation in reagent concentration, reaction medium, reaction time and stoichiometry. Based on stoichiometry and the available literature the possible course of reaction was postulated. In simple compounds the violation and identification of final reaction products has also been done.

In case of ascorbic acid it is found that carbon dioxide, water and formic acid are evolved as final reaction products. The detection of formic acid has been done by the development of colour with neutral ferric chloride. The liberation of carbon dioxide has been proved qualitatively and quantitatively by absorption in lime water. On this basis it is proposed that ascorbic acid gives following reaction path.

$$C_6H_8O_6 \xrightarrow[8[O]]{16Ce(IV)} 2HCOOH + 4CO_2 + 2H_2O$$

The recommended procedure is applicable to pharmaceutical products as well. The excepients present in tablets do not interfere in the estimation.

In case of primary alcohols it was noted that the final oxidation product is corresponding carboxylic acids. Since aliphatic carboxylic acids are not oxidised with Ce(IV) reagent under present reaction conditions, their presence is detected in the reaction mixture. Methanol, ethanol, *n*-propanol, and *n*-butanols give formic, acetic, propionic and butyric acids respectively. A general reaction may be expressed below.

$$R-CH_2OH \xrightarrow[2[O]]{4Ce(IV)} R-COOH + H_2O$$

where R = H, CH_3 C_2H_5, C_3H_7

Secondary alcohol (3-pentanol) on oxidation gives aliphatic acids having less number of carbon atoms.

$$CH_3CH_2\ CH(OH)\ CH_2CH_3 \xrightarrow[4[O]]{8Ce(IV)} C_2H_5COOH + CH_3COOH + H_2O$$

In a case of vicinal dihydroxy alcohols the final reaction products are aliphatic carboxylic acids corresponding to degradation product ofthe alcohols. Propane 1,2-diol and butane 2,3-diols give similar reaction.

Propane 1,2-diol gives formic acid and acetic acids

$$CH_3CHOH.CH_2OH \xrightarrow[3[O]]{6Ce(IV)} CH_3COOH + HCOOH + H_2O$$

while butane 2,3-diol

$$CH_3CHOH.CHOH.CH_3 \xrightarrow[3[O]]{6Ce(IV)} 2CH_3COOH + H_2O$$

gives acetic acid alone. However, if the hydroxyl groups are separated by one methylene group, then the liberation of carbon dioxide is noticed.

$$CH_3CHOH\ CH_2CH_2OH \xrightarrow[6[O]]{12Ce(IV)} CH_3COOH+HCOOH+2H_2O+CO_2$$

Polymers of ethylene glycol are oxidised only at the ends having hydroxyl groups. The oxide linkage is not broken by the present reagent. Triethylene glycol is oxidised to corresponding dicarboxylic acid.

$$HOCH_2(CH_2OCH_2)_2CH_2OH \xrightarrow[4[O]]{8Ce(IV)} HOOC(CH_2OCH_2)_2COOH+2H_2O$$

A similar course of reaction is adopted by tetraethylene glycol to give corresponding dicarboxylic acid. With the present reagent the determination of trihydroxy compounds like glycerol and tetrahydroxy compounds like pentarythitol could not be done. These compounds show a continuous consumption of the reagent and do not give reproducible and static stoichiometry.

REFERENCES

1. I. C. Shukla, S. Ahmad and R. P. S. Chauhan, *Proc. Nat. Acad. Sci.* (India), 55, 21 (1984).
2. M. M. Beg, Q. S. Usmani and I. C. Shukla, *Mikrochimica Acta* (Wein), 221, (1977).
3. G. S. Usmani, M. M. Beg and I. C. Shukla, *J. Indian Chem. Soc.*, 55, 295 (1978).
4. I. C. Shukla and M. M. Beg, *J. Indian Chem. Soc.*, 56, 637 (1979).

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29th INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (29th ICCC)

The 29th International Conference on Coordination Chemistry (29th ICCC) will be held at Lausanne, Switzerland during 19-24 July 1992. Further information may be obtained from Prof. D. Banerjea, Department of Chemistry, University College of Science, 92, A.P.C. Road, Calcutta-700 009, India.

Seminar on Photochemistry, Laser Chemistry and Photobiology; Fundamentals and Applications

The above seminar is being organized by the Indian Photobiology Society, in collaboration with the University of Madras and University Commission, New Delhi and will be held from January 7 to 9, 1991 at the University of Madras, Guindy Campus, Madras.

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