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A SIMPLE TITRIMETRIC METHOD FOR DETERMINATION OF ALDEHYDES AND KETONES

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SUMMARY

A simple titrimetric method has been developed for the determination of aldehydes and ketones. The method is based on the reaction of hydroxylamine hydrochloride in alkaline medium with carbonyl group to form the corresponding oxime. Excess hydroxylamine was determined by titration with ferricyanide solution with or without phenolphthalin as indicator. Acetaldehyde, p-nitrobenzaldehyde, salicylaldehyde, benzaldehyde, Anizaldehyde, cyclohexanone, methyl ethyl ketone, ethyl-acetoacetate, acetylacetone and acetophenone give satisfactory results with maximum error 2.67 % and an average recovery of 101.45 %.

The oximation of carbonyl compounds has been used widely for the determination of aldehydes and ketones[1,4]. The reaction rates are normally quite slow in neutral, aqueous media but the reactions are known to be catalysed by both acids and bases[5]. The amount of unreacted hydroxylamine has been determined by acid-base titration[6], redox titration[7], or polarography[8]. The serious limitations of the acid-base titration are that the end point leaves something to be desired and that numerous interferences are obtained from strong inorganic and organic acids and bases.

Polarographic determination of aliphatic aldehydes[9,10] and ketones[9-11] which is recommended by directly polarographic determination suffered from interfering side-reactions such as hydration or acetal formation.

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Potassium hexacyanoferrate (III) is available as a primary standard. Its possible application as a general purpose oxidimetric titarnt has received considerable attention. The indicators which have been used are diphenylamine[12], Fe (II)-dimethylglyoxime[13], methylene blue[14] thionine[14] and phenolphthalin[15]. Potassium ferricyanide possesses other active features such as high purity, high equivalent weight, stability in solution (in absence of light) and applicability to alkaline medium.

The present investigation was directed to study a simple titrimetric method for the determination of carbonyl function (aldehydes and ketones) through the reaction of hydroxylamine-hydrochloride in alkaline medium with carbonyl group to form oxime. Excess hydroxylamine was determined by titration with ferricyanide solution either in presence of phenolphthalin as indicator or without any indicator.

EXPERIMENTAL

All chemicals used were of analytical grade unless otherwise specified and double distilled water was used throughout.

Carbonyl free ethanol was obtained by refluxing absolute ethanol (2 1) with 5 g of 2,4-dinitrophenylhydrazine and 1.5 ml of concentrated hydrochloric acid for 4 hours, and then redistilled twice.

Carbonyl compounds 0.05 M were prepared by dissolving the required calculated weight of carbonyl (aldehyde or ketone) compounds and dissolved in carbonyl free ethanol. Phenolphthalin indicator[16] (0.4 %) The indicator was prepared by mixing phenolphthalein (2 g), sodium hydroxide (10 g), zinc dust (5 g) and water (20 ml) and heating for two hours under reflux. After cooling, the liquid was passed through hardened filter paper and colourless filtrate made up to 50 ml with bidistilled water. This indicator was kept in a dark bottle containing a few granules of zinc. Under this condition it remains colourless for at least one week.

Hydroxylammonium chloride: 0.05 M.

Potassium fericyanide: 0.1 M solution.

Procedure

1–5 ml of aldehyde or ketone solution (0.05 M) was transfered to 100 ml conical flask, 10 ml of hydroxylamine hydrochloride (0.05 M), 3–5 ml of 5 % NaOH solution were added, followed by 2 drops of the indicator. This solution was titrated slowly with standard 0.1 N potassium ferricyanide until solution became red. Volume of potassium ferricyanide equivalent to 10 ml of hydroxylamine hydrochloride (0.05 M) was measured by using the same procedure in absence of ketones and aldehydes.

$$NH_2OH.HCl \equiv 2\ K_3\,[Fe(CN)_6]$$

$$NH_2OH.HCl \equiv \;>C=O$$

$$\text{Molarity of aldehyde or ketone} = \frac{1/2\,(V_0 - V')\,0.1}{V_1}$$

$$= \frac{1/2\,(V_0 - V')\,N}{V_1}$$

where V_0 volume of ferricyanide = total hydroxylamine

V' volume of ferricyanide = remained hydroxylamine

V_1 volume of aldehyde or ketone

N normality of potassium ferricyanide

RESULTS AND DISCUSSION

Aldehydes and ketones react with hydroxylamine hydrochloride to give the corresponding oxime. The presence of sodium hydroxide in essential to insure the conversion of hydroxylamine hydrochloride to free hydroxylamine and to catalyse the reaction[5].

Sant[17] described a method for determining hydroxylamine with potassium ferricyanide at pH 8—10 and the only product of oxidation is elemental nitrogen. Recently, potassium ferricyanide was used as a titrant for hydroxylamine in presence of sodium hydroxide[15]. Therefore, the excess of hydroxylamine after the formation of oxime could be determined according to the equation:

$$2\,NH_2OH + 4\,[Fe(CN)_6]^{3-} + 4\,OH^- \rightarrow N_2O + 4\,[Fe(CN)_6]^{4-} + 5\,H_2O$$

The titration of hydroxylamine in presence and in absence of oxime (e.g., dimethylglyoxime) gave the same results. So the formed oxime has no effect on the titration.

Stoichiometry of reaction was found to be one mole of hydroxylamine required 2 moles of ferricyanide whereas carbonyl group reacted with only one mole of hydroxylamine.

Table 1: Determination of Aldehydes and Ketones by Hydroxylamine and Potassium ferricyanide[+]

Substance	Vol. of 0.05M soln.	Vol. of potassium ferricyanide 0.1M (Vo)	Recovery %
Hydroxylamine	10	10	
p-Nitrobenzaldehyde	5	5	100
	3	7	100
	2	7.95	102.5
	1	8.975	102.5
m-Chlorobenzaldehyde	5	4.95	101.00
	3	6.95	101.70
	2	7.975	101.25
	1	8.988	110.20
Salicylaldehyde	5	4.9	102.0
	3	6.92	102.67
	2	7.95	102.50
	1	8.975	102.50
Benzaldehyde	5	4.9	102.0
	3	6.95	101.70
	2	7.95	102.50
	1	8.98	102.00
Anisaldehyde	5	4.90	102.0
	3	6.92	102.67
	2	7.90	102.50
	1	8.975	102.50
Acetaldehyde	5	5	100
	3	7	100
	2	8	100
	1	9	100
Cyclohexanone	5	5	100
	3	7	100
	2	8	100
	1	9	100
Methyl ethyl ketone	5	4.95	101.0
	3	6.95	101.7
	2	7.95	102.5
	1	9.025	102.5
Etyl acetoacetate	5	4.95	101.0
	3	7	100.0
	2	7.97	101.5
	1	9	100.0
Acetyl acetone	5	4.95	101.0
	3	6.95	101.7
	2	7.95	102.5
	1	9	100
Acetophenone	5	4.95	101.0
	3	6.95	101.7
	2	7.95	102.5
	1	8.975	102.5

[+] Mean of 4 titrations

Main 101.45

The sequence of addition of aldehyde, hydroxylamine and sodium hydroxide has no effect.

Phenolphthalein is an acid-base indicator whereas reduced phenolphthalien (phenolphthalin) has been used as redox indicator. It is oxidised by potassium ferricyanide to give a distinct red colour. So it is used as indicator in this work. Some trials were carried out for the use ferricyanide as selfindicator. It succeeded in the case of hydroxylamine alone and in presence of some carbonyl compounds. The produced coloured eximes required phenolphthalin indicator to get a distinct end point.

The results are tabulated in Table (1). It is clear that all aldehydes and ketones give good results with maximum error 2.67 % and an average recovery of 101.45 %.

Acetyl acetone which contains two carbonyl groups was found to react as containing one carbonyl group only, this may be due to the conversion to enol form. Mixture of two ketones, two aldehydes or aldehydes and ketones gives the total carbonyl groups, i.e., this method can be applied for determination of carbonyl function.

Carboxylic acids and amides do not interfer. In contrast, acid chlorides and anhydrides make interference in oximation and must be absence.

REFERENCES

1- S. SIGGIA, "Quantitative Organic Analysis via Function Groups", Wiley, New York, 1954, p. 21.

2- F.E. CRITCHFIELD, "Organic Function Group Analysis", Pergamon Press, Oxford (1963).

3- J.E. RUCH, J.B. JAHNSON AND F.E. CRITCHFIELD, Anal. Chem., 1961, **33**, 1966.

4- J.S. FRITS AND G.S. HAMMOND, "Quantitative Organic Analysis, John Wiley — Sons, Inc. N.Y., 1957.

5- L.P. HAMMETT, "Physical Organic Chemistry", McGrawHill Book Co., N.Y., 1940, Chapter 11.

6- Ref. 1, p. 7.

7- R. JACQUEMAIN AND P. GALLIOT, Ann. Chim., 1955, **1** (12), 262.

8- M.A. AL-HAJAJJI AND I.Z. AL-ZAMIL, accepted for publication in J. Chem. Soc. pak. 1981

9- G.M. GAL'PERN, V.A. IL'INA, L.A. SIGUNOVA, N.N. FILATOVA AND V.I. ORCHINNIKOV, Zh. Analit. Khim., 1971, **26**, 1206.

10– G.W.C. MILNER, "ThePrinciples and Application of Polarography and Other Electroanalytical Processes", Longman London, 1957.

11– S.A.K. HSIEH AND T.S. MA, Mikrochim. Acta, 1977, **1**, 325.

12– K. SOMEYA, Z. Anorg. Chim., 1926, **152**, 386.

13– K. KOMAREK, Coll. Cezch. Chem. Comm., 1938, **9**, 246.

14– O. TOMICEK, "Chemical Indicators", Butterworth, London, 1951.

15– S. SHAHINE AND S. EL-MEDANY, Ind. J. Chem., 1978, **16A**, 726.

16– S. SHAHINE AND M.F. EL-SHAHAT AND R. MAHMOOD, Ind. J. Chem., 1975, **13** (6), 626.

17– B.R. SANT, Z. Anal. Chem., 1955, **145**, 257; 1957, **158**, 116.