

Determination of Carbonyl Compounds with Ammonium Hexanitratocerate (IV) Reagent in Nitric Acid Medium at Micro Scale

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Abstract – The use of Ce (iv) is volumetric analysis upto the 1942. Ammonium hexanitratocerate rate (iv) has been described as proposed reference standard and as a primary standard in oxidimetry. It consists of oxidizable cation 2NH_4^+ and complex anion $\text{Ce}(\text{NO}_3)_6$. Which is known to be powerful oxidizing material solutions of hexanitratoceric acid $\text{H}_2\text{Ce}(\text{NO}_3)_6$ in nitric acid are known to be unstable to a minute but measurable extent. A survey of literature revealed that ammonium hexanitratocerate (iv) reagent has not been for carbonyl compounds, polyhydric alcohols and sugar. This encourages me to study the reactions of ammonium hexanitratocerate (iv) on carbonyl compounds. Polyhydric alcohols and sugars.

Key Words: Ammonium Hexanitratocerate, volumetric analysis, carbonyl compounds.

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INTRODUCTION

The compounds containing carbonyl group may be either aldehydic or ketonic and both of these could be determined by applying some important reactions of the carbonyl function like oxidation, reduction and condensation with the help of the reagents. In view of the fact that a large number of naturally occurring compounds contain this carbonyl function and quite a few synthetic or naturally occurring compounds are of practical and industrial importance.

A detail survey of literature reveals that earlier analytical methods developed for the propose were mostly directed towards the determination of individual compounds like acetone or formaldehyde. One such survey was published by Mitchell who covers references upto 1951. Although some of the methods are gravimetric. It has been found that volumetric or colorimetric methods are better and these frequently form the basis of the specific methods.

Methods based on chromatography, spectrometry photometry or Polarography or mass spectrometry has been proposed from time to time and are frequently employed. Whereas most of the methods originally developed were available on macroscale. They have been modified for operations on the semi-micro and micro-scale determinations.

Singgia and maxey introduced a specific sulphitesulphuric acid reagent which was found to be better and was employed for several aldehydes in my

experiment; I'm using potentiometric titration against alkali:

METHODS BASED ON OXIDATION REACTION

Methods based on oxidation can be applied to be carbonyl compounds which are aldehydic in nature and in the course of oxidation, the aldehydic function is oxidised to the carbonyl function silver oxide has been employed as an oxidant by several workers like Bailey and kaux, Mitchell and smith, Rush and Johnson where in precipitated mercury redissolved in iodine after the acidification with acetic acid followed by determination of the excess iodine by titration against thiosulphate. Yaneagishi, Yokoo and Inoue also employed Nessler's reagent indirectly by adding hydrazine and measuring the liberated nitrogen gas.

Acid or alkaline potassium Permanganate was first employed for the determination of chloral and was subsequently employed in other cases. Peroxytrifluoroacetic acid in ethylene chloride was subsequently applied for the determination by Howthorne Bag, Chauhan and Shukla. They first used ceric ammonium nitrate for the determination of few aldehydic compounds. Ammonium hexanitratocerate (iv) in 0.5 N nitric acid has also been used for the determination of certain organic compounds.

A method for the small scale determination of carbonyl compounds employing ammonium hexanitratocerate (iv) in nitric acid medium as the

reagent has been developed and is reported in this article.

PRESENT WORK

A survey of literature revealed that ammonium hexanitratocerate (iv) has not been utilized for the determination of some aldehydic compounds. This encouraged me to study the reaction of ammonium hexanitratocerate (iv) on aldehydes a rapid method for the milligram determination of aldehydes has thus been evolved.

1-5 mg of the sample is taken in a reaction flask and the excess of ammonium hexanitratocerate (iv) is added to it. The contents are allowed to react for a certain reaction time at 50° on were bath 1-2 mg of solid Salicylaldehyde were taken in 150 ml conical flask, and 10 ml of 0.15 M ca (iv) reagent was added to it. Contents were shaken wall and allowed to react for twenty minutes at 50°C on water bath. The reaction was quenched by adding 10 ml of 1 M sulphuric acid and contents shaken for a minute. The unreacted Ce (iv) was titrated against 0.025 M ferrous ammonium sulphate using ferron indicator. A blank experiment was also run under identical condition. The molar ratio of Ce (IV) reagent and the salicylaldehyde was calculated with the amount of the Ce (IV) reagent consumed for the sample, also and the molar ratio was calculated. (Table-1)

Stoichiometric ratio between salicylaldehyde and Ce (IV) in nitric acid medium.

Table – 1

Compound	Molar ratio of Ce (IV) per mole of the compound		
Salicylaldehyde	2.007	2.003	1.996
Vanillin	2.001	2.007	1.998
O- nitrobenzaldehyde	2.050	2.050	2.050
m-nitrobenzaldehyde	2.020	2.080	2.020
P- nitrobenzaldehyde	2.003	1.996	2.007

SMALL SCALE DETERMINATION OF ALDEHYDES

With the recommended procedure, the small scale determination of salicylaldehyde, vanillin, O-nitrobenzaldehyde, m- nitrobenzaldehyde, and p-nitrobenzaldehyde in Table 2,3,4,5 and 6 respectively.

Now the reaction is quenched by adding 10 ml of 1M sulphuric acid and the unreacted Ce (IV) is determined by titrating it against ferrous ammonium sulphate using ferroin as indicator.

CHOICE OF REAGENT

In an attempt to develop a quick and convenient method for the small scale determination of aldehydic

compound, ammonium hexanitratocerate (IV) was found temperature (in some case at 50° C) and gives quantitative results within shorter time and the accuracy of ± 1 in most of the cases.

APPROACH OF THE REACTION

For testing the quantitative validity of the reaction salicylaldehyde was taken as test sample. Different amount of the sample were allowed to react with varying amount of Ce (IV) reagent at 50° C for different intervals of reaction time. The stoichiometry of the reaction was established for each samples and a possible course of reaction was suggested.

On the basis of the reaction conditions developed for salicylaldehyde the estimation of other aldehydes derivative like vanillin, O- nitrobenzaldehyde, m-nitrobenzaldehyde and P- nitrobenzaldehyde.

STOICHIOMETRY OF THE REACTION

The stoichiometry of the reaction for salicylaldehyde was established in the following ways:-

Milligram determination of salicylaldehyde with 0.15 M Ammonium hexanitratocerate (IV) in 0.5 N nitric acid.

TABLE-2

Allquots taken (ml)	Sample size (mg)	Reaction Time (min)	Recovery (mg)	Stoichiometry	Error %
1	1.0000	20	0.9908	2	-0.92
			0.9908		-0.91
			0.9910		-0.90
2	2.0000	20	2.0095	2	+0.42
			1.9819		+0.90
			2.0095		+0.42
3	3.0000	20	3.0005	2	+0.01
			3.0281		+0.90
			3.0280		+0.90
4	4.0000	20	4.0192	2	+0.40
			3.9914		-0.24
			4.0190		+0.35
5	5.0000	20	5.0100	2	+0.20
			4.9549		-0.90
			5.0100		+0.20

Milligram determination of Vanillin with 0.15 M Ammonium hexanitratocerate(IV) in 0.5 N nitric acid.

TABLE-3

Allquots taken (ml)	Sample size (mg)	Reaction Time (min)	Recovery (mg)	Stoichiometry	Error %
1	1.0000	20	1.0186	2	+0.89
			1.0158		+0.56
			1.0158		+0.56
2	2.0000	20	2.0342	2	+0.70
			2.0288		+0.42
			2.0342		+0.70
3	3.0000	20	3.0446	2	+0.47
			3.0390		+0.29
			3.0390		+0.29
4	4.0000	20	4.0576	2	+0.43
			4.0520		+0.29
			4.0576		+0.43
5	5.0000	20	5.0790	2	+0.58
			5.0740		+0.47
			5.0740		+0.47

Milligram determination of O-nitrobenzaldehyde with 0.15 M Ammonium hexanitratocerate (IV) in 0.5 N nitric acid.

TABLE-4

Aliquots taken (ml)	Sample size (mg)	Reaction Time (min)	Recovery (mg)	Stoichiometry	Error %
1	1.0200	20	1.0246 1.0214 1.0214	2	+0.45 +0.13 +0.13
2	2.0400	20	2.0461 2.0398 2.0461	2	+0.29 -0.01 +0.29
3	3.0600	20	3.0644 3.0613 3.0581	2	+0.14 +0.04 -0.06
4	4.0800	20	4.0922 4.0891 4.0891	2	+0.29 +0.22 +0.22
5	5.1000	20	5.1043 5.1011 5.0979	2	+0.08 +0.02 -0.40

Milligram determination of m-nitrobenzaldehyde with 0.15 M ammonium hexanitratocerate (IV) in 0.05 N nitric acid.

Reaction temperature 50° C

TABLE- 5

Aliquots taken (ml)	Sample size (mg)	Reaction Time (min)	Recovery (mg)	Stoichiometry	Error %
1	1.0300	20	1.0028 1.0298 1.0228	2	-0.09 -0.01 -0.09
2	2.0600	20	2.0527 2.0562 2.0562	2	-0.35 -0.18 -0.18
3	3.0900	20	3.0861 3.0931 3.0931	2	-0.12 +0.10 +0.10
4	4.1200	20	4.1055 4.1125 4.1160	2	-0.35 -0.18 -0.09
5	5.1500	20	5.1670 5.1740 5.1670	2	+0.33 +0.46 +0.33

Milligram determination of p-nitrobenzaldehyde with 0.15 M ammonium hexanitratocerate (IV) in 0.05 N nitric acid.

Reaction temperature 50° C

TABLE- 6

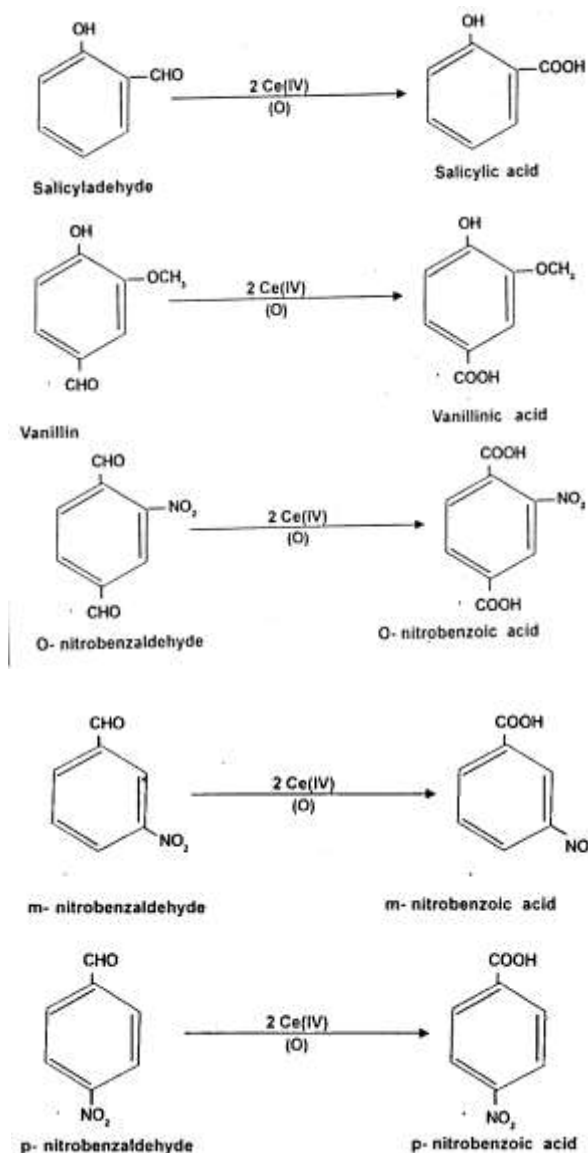
Aliquots taken (ml)	Sample size (mg)	Reach Time (min)	Recovery (mg)	Stoichiometry	Error %
1	1.0000	20	1.0076 0.9943 0.9943	2	+0.76 -0.57 -0.57
2	2.0000	20	2.0152 2.0020 2.0152	2	+0.76 +0.10 +0.76
3	3.1000	20	3.0096 3.0229 3.0096	2	+0.32 +0.76 +0.32
4	4.0000	20	4.0438 4.0305 4.0305	2	+1.09 +0.76 +0.76
5	5.10076	20	5.0249 5.0382 5.0249	2	+0.49 +0.76 +0.49

RESULT AND DISCUSSION

With the recommended procedure the milligram determination of salicylaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p- nitrobenzaldehyde & vanillia were achieved. The results given in the Table to were achieved. The results given in the Table to show that the percentage recovery of the sample is fairly constant with the varying sample amount.

Taking salicylaldehyde as the test sample the recommended experimental conditions were obtained by carrying out the reaction of the sample with Ce (IV) under different condition by varying reaction time, temp. And the amount of Ce (IV) agent and calculated the % recovery of the sample.

The overall reaction for the oxidation of aldehydes may be represented in the following form. The reaction finds support from previous mechanism.



On the basis of above observations it can be summarized that generally all aldehydic compound get oxidised to corresponding carboxylic acid.

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