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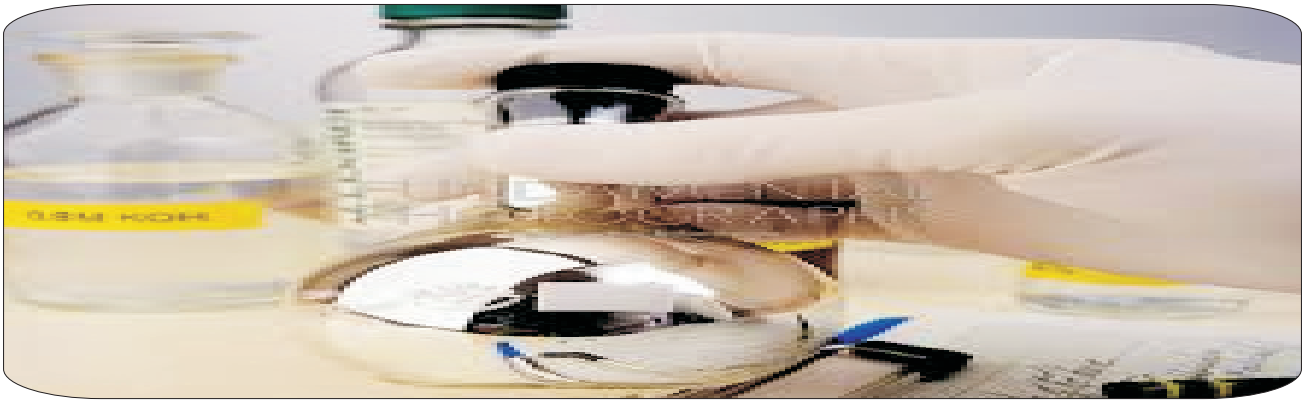

ESTIMATION OF SOME ALDEHYDES USING BrCl REAGENT ON MICRO SCALE

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ABSTRACT

The compounds containing carbonyl grouping 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, the determination of the carbonyl function or of the compounds containing this group is of special significance.

KEYWORDS :Estimation, Aldehydes ,Ketons, Redox reaction, determination, Bromine mono chloride etc.

INTRODUCTION

Estimation of some aldehydes Vaniline, orthonitro benzaldehyde, para nitro-benzaldehyde, meta nito-benzaldehyde, para hydroxyl-benzaldehyde, veratraldehyde, dimethyl amino benzaldehyde, Pyridine 2 aldehyde, thiophene, 2 aldehyde using BrCl reagent in acid medium by micro method has been achieved. Aliquots containing 1-5mg. of the sample are allowed to react with 10ml. of 0.05N BrCl reagent for 15-30 minutes at 5 to 60C on ice bath.

After the completion of reaction, the unconsumed BrCl reagent was titrated with Hypo using Starch as indicator. A blank experiment was also run under identical conditions using all the reagents. Except the sample. The recovery of the sample was calculated with error.

The effect of various variables and interfering substances has been studied, On the basis of Stoichiometry as well as previous available of the reaction. The accuracy of the method is within ±1% most of cases.

Experimental Section

Methods based on oxidation reaction

Methods based on oxidation, can be applied to the carbonyl compounds which are aldehydic in nature and in the course of oxidation, the aldehydic function is oxidised to the carbonyl function. A method for the small scale determination of carbonyl compounds employing Vanadium (v) in sulphuric acid medium as the reagent has been developed and is reported in the present chapter.

Present work

A survey of literature revealed that BrCl has not been utilised for the determination of some aldehydic compounds. This encouraged me to study the reaction of BrCl on aldehydes. A rapid method for the micro determination of aldehydes has thus been evolved. 1-5mg of the sample is taken in a reaction flask and the excess of BrCl is added to it. The contents are allowed to react for a certain reaction time on ice bath. Now the reaction is quenched by adding 10ml of 1m sulphuric acid and the unreacted BrCl is determined by titrating it against Hypo using Starch as indicator.

Material and Methods

Choice of the reagent

In an attempt to develop a quick and convenient method for the small scale determination of aldehydic compounds, BrCl was found to be suitable reagent. The reagent work, at room temperature (in some cases at 50C) and gives quantitative results within shorter time and the accuracy of +1% in most of the cases.

Choice 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 amounts of BrCl reagent at 50C 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-nitro benzaldehyde, M-nitro benzaldehyde P- nitro benzaldehyde, Veratraldehyde, P-Hydroxy benzaldehyde dimethyl aminobenzaldehyde, thiophene-2- aldehyde and pyridine-2-aldehyde was carried out. The effect of interferring substances was also studied.

Effect of variables

Effect of reaction time

Keeping amount of salicylaldehyde, concetration of BrCl and concentration as constant, the reaction time was varied from 1-45 minutes.

Aliquots containing 1-2mg of the sample were allowed to react with 10ml of 0.05N BrCl reagent at room temperature for different intervals of time and the consumption of Hypo was noted. It was found that the consumption of Hypo becomes constant within 20 minutes only. The value does not change by giving more reaction time Similar experiments were performed with vanillin, O-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde and P-hydroxy benzaldehyde. It was

observed that the reaction was completed within 20 minutes only in all these samples, except dimethyl amino benzaldehyde, vertraldehyde, pyridine-2-aldehyde and thiophine-2-aldehyde in 30 minutes. Thus for the general procedure of estimation, a reaction time of 20 minutes (in some of cases 30 minutes) was recommended.

Stiochiometry of the reaction

The stiochiometry of the reaction for salicylaldehyde was established in the following way.Aliquots containing 1.5 mg of salicylaldehyde were taken in a 150ml conical flask and 10ml of 0.05 N BrCl reagent was added to it. Contents were shaken well and allowed to react for twenty minutes at 50C on ice bath. The contents shaken for a minute. The unreacted BrCl reagent and the salicylaldehyde was calculated with the amount of the BrCl reagent consumed for the sample, similar procedure was applied for other aldehydes sample also and the molar ration was calculated

Table-1: Stoichiometric ration between salicylaldehyde and BrCl in Acetic acid medium

Aliquots taken (ml)	Molar ration of BrCl Per mole of thecompound		
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
p-hydroxybenzaldehyde	2.007	2.001	2.003
Vertraldehyde	1.999	2.006	2.008
Dimethylaminobenzaldehyde	2.007	2.001	1.997
Pyridine-2-aldehyde	2.003	2.007	1.996
Thiophine-2-aldehyde	2.007	2.003	1.998

Effect of concentration of BrCl

The most important variable to be studied was the concentration BrCl 1 to 5 mg. of the sample was allowed to react with 10ml. of BrCl reagent of different concentration. The concentration was varied from 0.10 N to 0.40 N and the recovery of the sample was calculated. It was found that the best recovery of the sample was obtained at 0.05 N concentration of BrCl solution. A lower and higher concentration tends to give inaccurate results. Thus the avoid of the wastage of the reagent and to get accurate results 0.05 N concentration of BrCl was recommended for further estimation.

Small scale determination of Aldehydes :

With the recommended procedure, the small scale determination of salicyalaldehyde, vanillin o-nitrobenzal dehyde, m-nitrobenzaldehyde, varatraldehyde, p-hydroxybenzaldehyde, p-nitrobenzaldehyde, dimethylamino benzaldehyde, thiophene-2-aldehyde and pyradine-2-aldehyde was achieved

Table :2 Determination of Pyridine-2-aldehyde with 0.05 N BrCl recommended procedure

Sample	Amount present (ml)	Reaction time (min)	Amount recovered (mg)	Stoichi-ometry	Error %
1	2	3	4	5	6
1. Salicylaldehyde	1.0000	20	0.9910	2	-0.90
	3.0000		3.0005		+0.01
	5.0000		5.0100		+0.20
2. Vanillin	1.0100	20	1.0186	2	+0.84
	3.0300		3.0390		+0.29
	5.0500		5.0740		+0.47
3. O-nitrobenzaldehyde	1.0200	20	1.0246	2	+0.45
	3.0600		3.0644		+0.14
	5.1000		5.1043		+0.08
4. m-nitrobenzaldehyde	1.0300	20	1.0228	2	-0.69
	3.0900		3.0861		-0.12
	5.1500		5.1670		+0.33
5. p-nitrobenzaldehyde	1.0000	20	1.0076	2	+0.75
	3.0000		3.0096		+0.32
	5.0000		5.0249		+0.49
6. p-hydroxybenzaldehyde	1.0500	20	1.0396	50	-0.99
	3.1500		3.1464		-0.11
	5.2500		5.2531		+0.05
7. Dimethyl- aminobenzaldehyde	1.0100	30	1.0140	2	+0.39
	3.0300		3.0320		+0.06
	5.0500		5.0500		0.00
8. Varatraldehyde	1.0400	30	1.0350	2	-0.48
	3.1200		3.1182		-0.05
	5.2000		5.1023		+0.02
9. Thiophene-2-aldehyde	1.0400	30	1.0453	2	+0.50
	3.1200		3.1252		+0.16
	5.2000		5.2106		+0.20
10. Pyridine-2-aldehyde	1.0100	30	1.0039	2	-0.60
	3.0300		3.0219		-0.26
	5.0500		5.0610		+0.20

In each case three determinations were done.

RESULTS AND DISCUSSION

With the recommended procedure the milligram determination of salicylaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitro- benzaldehyde, p-hydroxy benzaldehyde, valraldehyde, vanillin, dimethyl amino, benzaldeyde, pyridine-2-aldehyde and thiophine-2-aldehyde was achieved. The results given in the Table-14 show that the percentage recovery of the sample is fairly constant with the varying sample amount from 1-5 mg.

Taking salicylaldehyde as the test sample the recommended experimental condition were obtained by carrying out the reaction of the sample with BrCl under different conditions by varying reaction time, temperature sand the amount of BrCl reagent and calculating the percentage recovery of the sample.

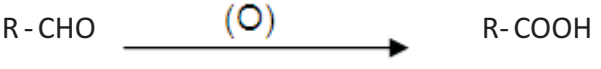
It was found that the reaction was very slow at ice bath and an increase in the reaction time upto 60 minutes does not give quantitative results (70-80% recovery). To make reaction quantitative and save the reaction time the reaction mixture was heated on a water bath. In this case the reaction mixture becomes turbid creates difficulty in locating the end point and gives inaccurate results. The reaction is completed within 30 minutes.

The effect of amount of the sample and the amount of BrCl reagent was also studied. The method is operable even with larger amount of the sample, but increase the consumption of large amount of the reagent. For an accurate determination 10 to 15 times excess of the BrCl reagent was always needed. A large excess leads to inaccurate results.

The stoichiometry of the reaction was also established for each compound, salicyladehyde, vanillin, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, veratraldehyde, p-hydroxyaldehyde, dimethyl aminobenzaldehyde, thiophene-2-aldehyde and pyridine-2-aldehyde consumes 2, 2, 2, 2, 2, 2, 2, 2, 2 and 2 equivalents of BrCl respectively. The stoichimetry does not change by increasing reaction time, reaction temperature and the reagent concentration.

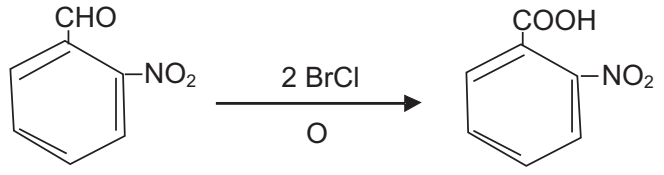
The survey of literature reveals that the oxidation of aldehydic compounds has been of interesting. The compounds which are aldehydic in nature and in the course of oxidation, the aldehydic function is oxidised to the carboxylic function.

It is well known that the aldehydic function is oxidised with any oxidising reagent to from corresponding carboxylic compound.

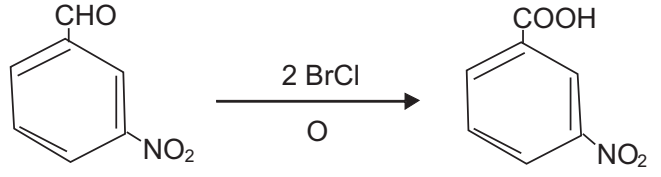


(Aldehydic function) (Carboxylic function)

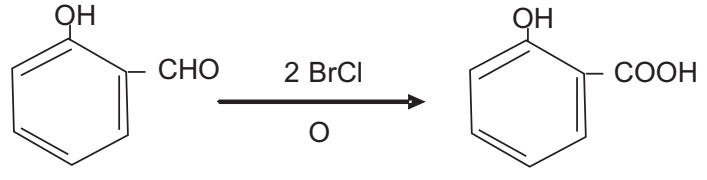
It has been reported earlier by several scientists using different types of oxidising reagent for the determination of aldehydes. In view of above oxidation reaction and considering the amount of BrCl consumed per moles of the aldehyde sample, the following course of reaction may be proposed for the oxidation of aldehyde with the use of BrCl reagent.In the present experiment salicylaldehyde, vanilline, o-nitrobenzaldehyde, p-nitrobenzaldehyde, m-nitrobenzaldehyde, p-hydroxybenzaldehyde, varatraldehyde, dimethyl amino benzaldehyde, thiophene-2-aldehyde and pyridine-2-aldehyde consumes 2, 2, 2, 2, 2, 2, 2, 2, 2 and 2 moles of BrCl respectively. All the aldehyde may get oxidised to corresponding carboxylic acid.The overall reaction for the oxidation of aldehydes may be represented in the following form. The reaction finds support from previous mechanism.55-63



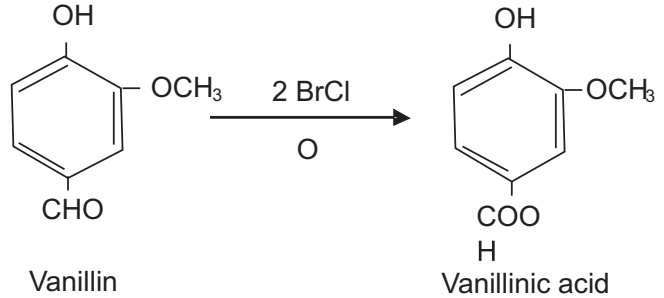
o-nitrobenzaldehyde o-nitrobenzoic acid



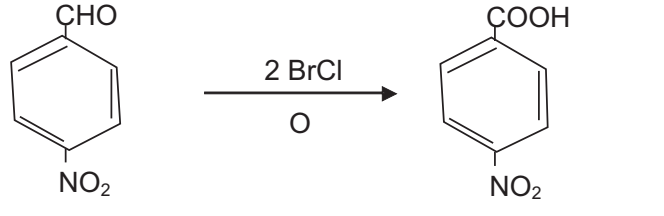
m-nitrobenzaldehyde m-nitrobenzoic acid



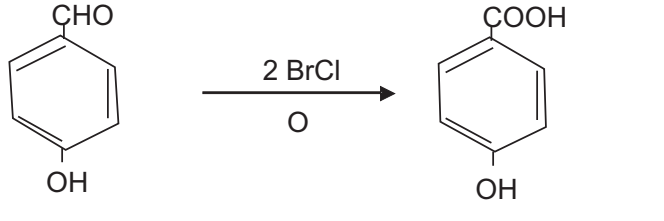
Salicylaldehyde Salicylic acid



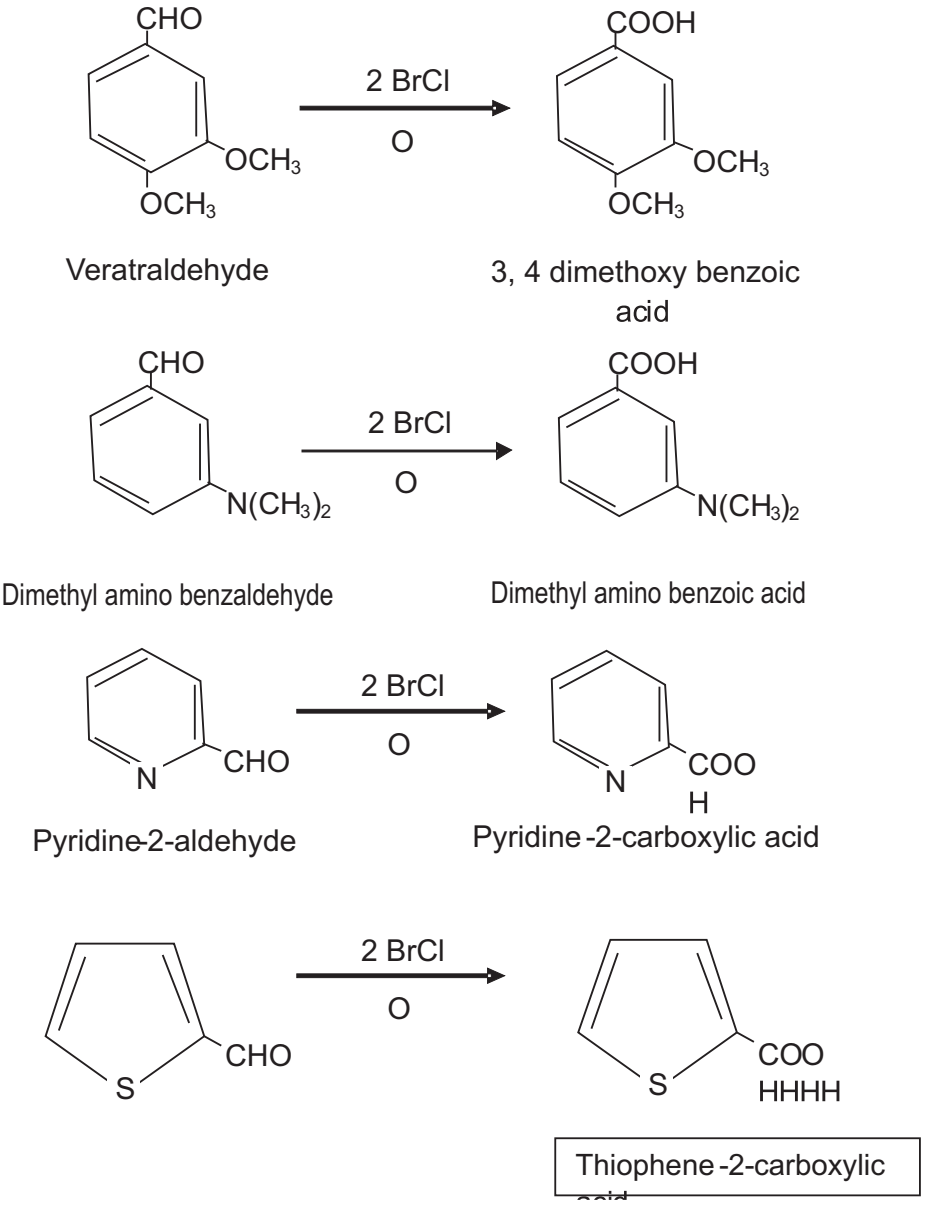
Vanillin Vanillinic acid



p-nitrobenzaldehyde p-nitrobenzoic acid



p-hydroxybenzaldehyde p-hydroxybenzoic acid



On the basis of above observations it can be summarized that generally all aldehydic compounds gets oxidises to corresponding carboxylic acid.

EXPERIMENTAL

REAGENTS AND SOLUTIONS

Bromine monochloride 0.05N solution

0.6958 g. potassium bromate (AnalaR, B.D.H.) and 0.9917 g. potassium bromide (AnalaN, B.D.H.) were dissolved in 125 ml. of distilled water in 500 ml. volumetric flask. The solution was cooled in ice, 50 ml. of concentrated hydrochloric acid (M.A.R., grade) was added and the solution was made up to the mark with distilled water. The solution was standardised with 0.02 N. Sodium thiosulphate solution and stored in an ice and salt mixture.

Glacial acetic acid (AnalaR, B.D.H.)

Sodium thiosulphate - A stock solution of sodium thiosulphate was prepared by disolving 4.9604 g. of sodium thiosulphate in distilled water in a one litre volumetric flask. The solution was standardised with 0.02 N copper sulphate iodometrically.

Potassium iodide- 15% (w/v) aqueous solution was prepared.

Starch solution- 1% (w/v) aqueous solution

PREPARATION OF SAMPLE SOLUTION

The samples were weighed accurately and dissolved in minimum amount of acetic acid and made up to the volume with cold distilled water in volumetric flask to give a concentration of 1 Mg./ml.

All the sample were of Baker analysed reagent and purity was tested by their melting point determined.

GENERAL PROCEDURE

Aliquots containing 1-9 mg. of the sample was placed in a 100 ml. iodine flask followed by addition of 5 ml. of glacial acetic acid, 10 ml. 0.05 N solution of bromine monochloride was added to it and the contents were shaken thoroughly. The flask was stoppered, placed in ice bath containing ice salt mixture and allowed to react for 5 minutes with occasional shaking. In case of Salicylaldehyde, Vaillin, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p- nitrobenzaldehyde, p-hydroxybenzaldehyde were allowed to proceed for 20 minutes. But in case of Dimethyl-aminobenzaldehyde, Varatraldehyde, Thiophene-2-aldehyde- Pyridine-2-aldehyde reactions were allowed to proceed for 30 minutes. After the reaction was over the stopper was washed with 5 ml. of distilled water and 10 ml. of potassium iodide (15% was added to it. Contents were shaken thoroughly and kept for a minute. The liberated iodine was titrated with standardised 0.02 N sodium thiosulphate solution using starch as indicator. A blank experiment was also performed under identical conditions using all the re-agent except the sample.

CALCULATION

$$\text{mg. of sample} = \frac{(B-A) \times M \times N}{2 \times n}$$

A = ml. sodium thiosulphate for sample.
B = ml. sodium thiosulphate for blank.
N = Normality of sodium thiosulphate solution
M = Molecular weight of the sample
n = Moles of brominemonochloride for the sample.

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