

Recent Approach for Micro Determination of Phenols: A Study using N-Bromosaccharin Reagent

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Abstract: The current study depicts that in case of *o*-hydroxybenzoic acid, hydrogen bonding present between *o*-hydroxyl and carboxyl groups, whereas in case of resorcinol, pyrogallol, and phloroglucinol steric hindrance play as important role, responsible for slow reactivity of these compounds.

Background: Aromatic phenols are widely used in the manufacture of dyes, drugs explosive, resins, Plasticizers, printing materials, accelerators etc. A large number of polyphenolic compounds present in nature are responsible for their color and taste. In view of the fact that a large number of naturally occurring compounds containing phenolic function are of great practical and industrial importance, suitable methods for determination of these functions or of the compounds containing these functions would be of special significance to analytical chemists. A detailed survey of literature reveals that a large number of procedures for determination of organic compounds containing these functions are available.

Materials and Methods: The number of bromine atoms entering the molecule depends upon the structure of compound, but it must be known for each determination. Phenols are known to undergo nuclear bromination reactions. The presence of phenolic groups in aromatic compounds activates ortho para positions of the benzene ring and allows bromine to enter simultaneously into all these positions. The mechanism of reactions in case of phenol was verified by separating tribromophenol from the reaction mixture.

Results: In case of *m*-nitrophenol the observed stoichiometry of two be explained by the formation of a dibromo product as: (ortho positions remains unsubstituted due to steric hindrance Phenol having carboxyl group in ortho or para positions undergo decarboxylation followed by substitution with bromine atoms in the same way as in the case of *N*-bromosuccinimide and the reaction may be represented. Similarly, the observed stoichiometry in all cases may be explained by assuming the formation of corresponding Bromo derivatives.

Conclusion: The current study depicts that in case of *o*-hydroxybenzoic acid, hydrogen bonding present between *o*-hydroxyl and carboxyl groups, whereas in case of resorcinol, pyrogallol, and phloroglucinol steric hindrance play as important role, responsible for slow reactivity of these compounds.

Key Word: Micro Determination, Phenol, N-Bromosaccharin

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I. Introduction

Aromatic phenols are widely used in the manufacture of dyes, drugs explosive, resins, Plasticizers, printing materials, accelerators etc. A large number of polyphenolic compounds present in nature are responsible for their color and taste. In view of the fact that a large number of naturally occurring compounds containing phenolic function are of great practical and industrial importance, suitable methods for determination of these functions or of the compounds containing these functions would be of special significance to analytical chemists. A detailed survey of literature reveals that a large number of procedures for determination of organic compounds containing these functions are available. These procedures are based on application of important reactions of such functions, like esterification, oxidation, diazotization, nitrosation and bromination of the phenyl ring. Although some of these methods are gravimetric, it has been found that volumetric or colorimetric methods are better and these frequently form the basis of specific methods. Methods based on spectrophotometry, mass spectrometry, fluometry or chromatography have also been proposed from time to time and are frequently employed.

It should be noted that most of the methods are applicable for determination of individual known compounds and cannot be used to determine these functions in a compound of unknown structure. The methods originally developed on macro scales have been in most cases modified for operations on semimicro and micro scale determinations.

Due to weakly acidic and basic character of phenols. As a rule, phenols cannot be determined by acidimetry in aqueous medium. Fritz and Keen' evolved a method for determination of phenol by carrying out dilutions in nonaqueous solvents. Matrk⁸ published a review on the use of sodium nitrite as titrating reagent and Goupil and Mungency⁹ of titrimetric methods for determination of phenols.

Phenolic compounds containing two or more hydroxyl groups have been determined by oxidation methods. Mikhk¹⁰ used ferricyanide as oxidant for determination of p-dihydroxy benzene; Rad and Shastri' used 0.05 N sodium vanadate as oxidant for determination of hydroquinone and metol in presence of sulphuric acid and oxalic acid respectively, and other workers used eerie sulphate' and potassium permanganate solution as oxidants for determination of phenols. Mori et al.' developed an anodic oxidation method for determination of phenols. Reis' used sodium hypobromite as oxidant for amino groups, while shastri and Rao¹⁰ used eerie sulphate for oxidation of p-methylaminophenols. Matrk¹¹ determined a-naphthol by nitrosation volumetrically. Due to acidic nature of phenols, they can be determined by esterification. Esterification of phenols does not take place as rapidly as that of alcohols. Schenk and Fritz¹² devised a method for determination of phenol by acetylation using perchloric acid as catalyst, this method has also been extended to microscale.

II. Material and Methods

An aliquot containing 1-5 mg of sample from the stock solution was transferred to a 100 ml glass stoppered conical flask. 10 ml of N-bromosaccharin solution was added. The flask was stoppered and contents were shaken thoroughly. The reaction was allowed to proceed for 10 minutes at room temperature (25°C) with occasional shaking. The stopper was washed with 5 ml of distilled water followed by addition of 5ml potassium iodide solution. The contents were shaken thoroughly and liberated iodine was titrated against standard sodium thiosulphate solution using starch as indicator. A blank experiment was also run under identical conditions. A blank experiment was also run under identical experimental conditions, but without the samples. Formula for Calculation

$$\text{Recovery of sample (mg)} = \frac{(V_b - V_s) \times N \times W}{2 \times n}$$

Where

V_b = Volume of sodium thiosulphate solution required to titrate blank (ml.)

V_s = Volume of sodium thiosulphate solution required to titrate sample (ml).

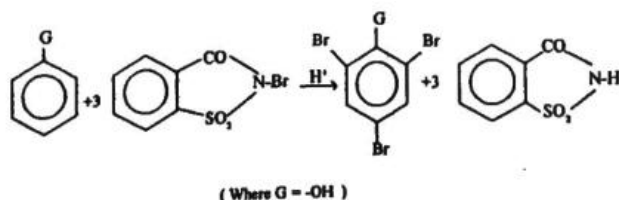
N = Normality of sodium thiosulphate solution

W = molecular weight of sample.

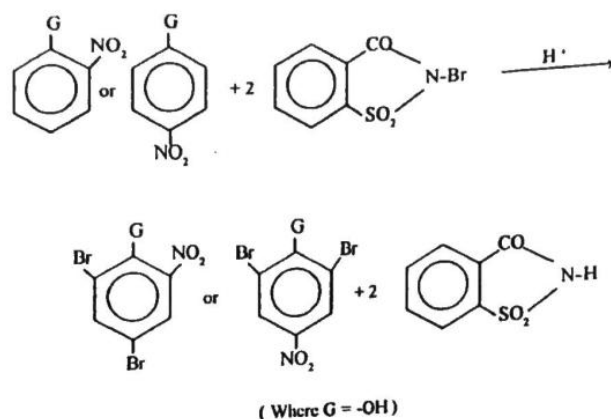
n = Stoichiometry number of moles

III. Result and Discussion

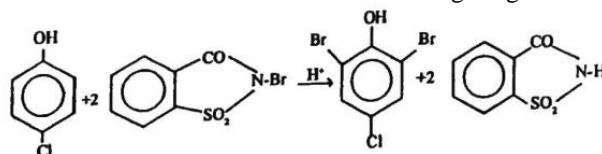
The number of bromine atoms entering the molecule depends upon the structure of compound, but it must be known for each determination. Phenols are known to undergo nuclear bromination reactions. The presence of phenolic groups in aromatic compounds activates ortho and para positions of the benzene ring and allows bromine to enter simultaneously into all these positions. The mechanism of reactions in case of phenol was verified by separating tribromophenol from the reaction mixture. The compounds isolated were identified by their m.p. determinations as tribromophenol (m.p. 94°C). The overall reaction of N-bromosaccharin with phenol (stoichiometry 3) proceeds in the same way as in the case of N-bromosuccinimide and may be represented as:



Phenol having a nitro group at ortho or para positions consumes two moles of N-bromosaccharin and gives dibromo product. The reaction may be represented as:

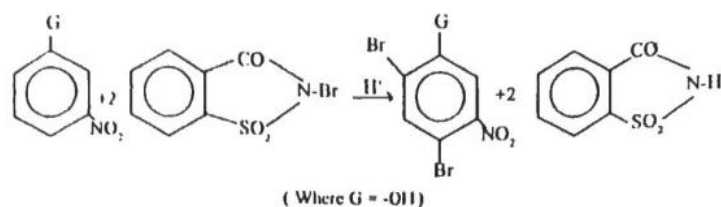


Similarly p-chlorophenol consumes two moles of N- bromosuccinimide giving dibromo derivatives as:



In case of m-nitrophenol the observed stoichiometry of two is explained by the formation of a dibromo product as:

(ortho positions remain unsubstituted due to steric hindrance. Phenol having a carboxyl group in ortho or para positions (stoichiometry 3) undergo decarboxylation followed by substitution with bromine atoms in the same way as in the case of N-bromosuccinimide and the reaction may be represented as:



Similarly, the observed stoichiometry in all cases may be explained by assuming the formation of corresponding bromo derivatives.



IV. Conclusion

The current study depicts that in case of o-hydroxybenzoic acid, hydrogen bonding is present between the hydroxyl and carboxyl groups, whereas in case of resorcinol, pyrogallol, and phloroglucinol steric hindrance plays an important role, responsible for the slow reactivity of these compounds.

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