

Micro Determination of Aromatic Amines With N-Bromosaccharin Reagent

Devendra Kumar Roy¹, Rajni Kumari², Pratibha Singh¹, and R.P. S. Chauhan^{1,*}

¹PG Department of Chemistry, Magadh University, Bodh Gaya 824234, Bihar

²Department of Chemistry, Gaya College (Magadh University), Gaya 823001, Bihar

Abstract: The current study depicts that the advantage of the present procedure using N-bromosaccharin over the other using N-bromosuccinimide is that it gives accurate results and less time consuming in case of p-aminobenzoic acids, diphenylamine and sulphanilic acid. Then there are uniform reaction conditions for all compounds. The only standard solution required is sodium-thiosulphate.

Background: Aromatic amines are widely used in the manufactures of dyes, drugs, explosive, resins, plasticizers, printing materials, accelerators etc. A large number of those 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 aryl amino functions 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.

Materials and Methods: The present study was undertaken with a view to study the possibility of using N-bromosaccharin in place of N-bromosuccinimide for determination of aromatic amines and the results of are incorporated in this work. In order to determine the stoichiometry of reactions aniline were chosen as representative compounds. Different aliquots containing 1-5 mg of samples were taken in glass stoppered conical flasks, followed by addition of a known excess of N-bromosaccharin solution.

Results: Determination of a number of aromatic amino compounds on small scale have been carried out by the general procedure. The relative errors do not exceed $\pm 2.0\%$. Before, applying the reaction for the determination of any amino compound stoichiometry of the reaction has to be determined in each case. The number of bromine atoms entering the molecule depends upon the structure of compound, but it must be known for each determination. Aromatic amines are known to undergo nuclear bromination reactions by using bromination methods. The presence of amino groups in aromatic compounds considerably activates ortho para positions of the benzene ring and allows bromine to enter simultaneously into all these positions.

Conclusion: The current study depicts that the advantage of the present procedure using N-bromosaccharin over the other using N-bromosuccinimide is that it gives accurate results and less time consuming in case of p-aminobenzoic acids, diphenylamine and sulphanilic acid. Then there are uniform reaction conditions for all compounds. The only standard solution required is sodium-thiosulphate.

Key Word: Micro Determination, Aromatic Amines, N-Bromosaccharin

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I. Introduction

Aromatic amines are widely used in the manufactures of dyes, drugs, explosive, resins, plasticizers, printing materials, accelerators etc. A large number of those 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 aryl amino functions 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, diazotisation, 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 special methods. Methods based on spectrophotometry, mass spectrometry, fluorometry 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 scale have been in most cases modified for operations on semimicro and micro scale determinations. Due to basic character of aromatic amines, it is easy to

determine. Based on diazotization reactions of aromatic amines various titrimetric methods have also been developed. Matrka¹⁰ published a review on the use of sodium nitrite as titrating reagent and Goupiand Mangency of titrimetric methods for determination of aromatic amines.

Primary and secondary amines undergo acetylation on treatment with acetic anhydride and liberate acetic acid which forms the basis of determination of amino groups. Hillenbrant et al.¹¹ and Mitchell et al.¹² has developed methods for determination of amines based on titrating liberated acetic acid or residual acetic anhydride respectively.

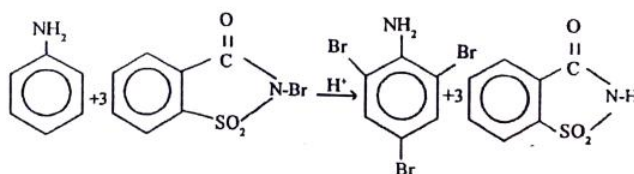
II. Material and Methods

The present study was undertaken with a view to study the possibility of using N-bromosaccharin in place of N-bromosuccinimide for determination of aromatic amines and the results of are incorporated in this work. In order to determine the stoichiometry of reactions aniline were chosen as representative compounds. Different aliquots containing 1-5 mg of samples were taken in glass stoppered conical flasks, followed by addition of a known excess of N-bromosaccharin solution. The reaction was allowed to proceed for 10 minutes at room temperature. After completion of the reaction, excess of N-bromosaccharin was back titrated iodometrically using starch as indicator. A blank experiment was also performed under identical experimental condition but without samples.

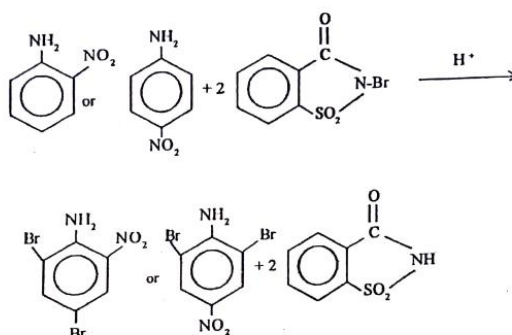
III. Result and Discussion

Determination of a number of aromatic amino compounds on small scale have been carried out by the general procedure. The relative errors do not exceed $\pm 2.0\%$. Before, applying the reaction for the determination of any amino compound stoichiometry of the reaction has to be determined in each case. The number of bromine atoms entering the molecule depends upon the structure of compound, but it must be known for each determination. Aromatic amines are known to undergo nuclear bromination reactions by using bromination methods. The presence of amino groups in aromatic compounds considerably 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 aniline was verified by separating tribromo aniline from the reaction mixture. The compound were identified by their m.p. tribromoaniline (m.p. 117°C).

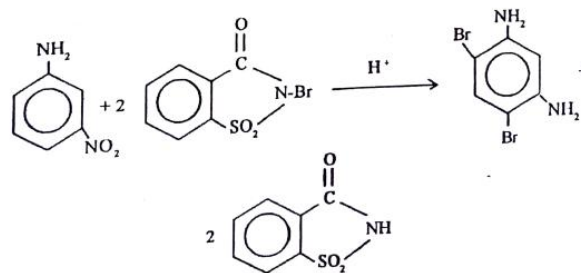
The overall reaction of N-bromosaccharin with aniline (stoichiometry 3) proceeds in the same way as in the case of N-bromosuccinimide²¹ and may be represented as:



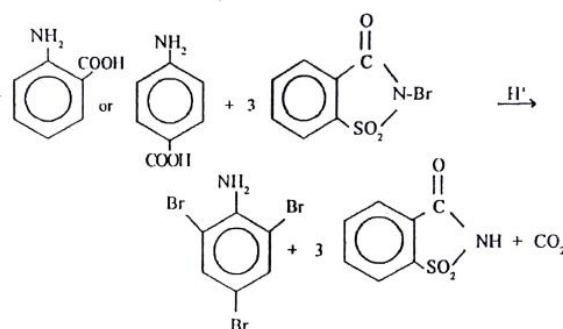
Aniline having a nitro group at ortho or para positions consumes two moles of N-bromosaccharin and gives dibromo product. The reaction may be represented as:



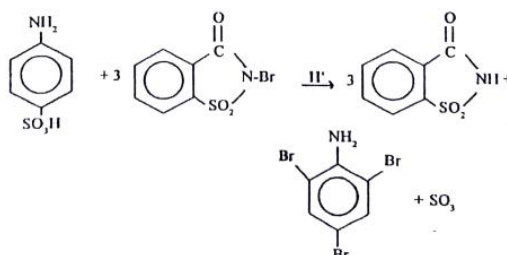
Similarly, in the case of m-nitro aniline the observed stoichiometry two may be explained by assuming the formation of a dibromo product as:



One of the ortho positions remains unsubstituted due to steric hindrance. Aniline having carboxylic 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:



Sulphanilic acid (stoichiometry - 3) undergoes disulphonation followed by substitution with bromine atoms giving tribromoaniline 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 the advantage of the present procedure using N-bromosaccharin over the other using N-bromosuccinimide is that it gives accurate results and less time consuming in case of p-aminobenzoic acids, diphenylamine and sulphanilic acid. Then there are uniform reaction conditions for all compounds. The only standard solution required is sodium-thiosulphate. The method is simple, accurate and quick, since the complete determination including pipetting and titration can be completed in about 20 minutes.

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