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Quantitative estimation of purity of N-phenyl-β-naphthylamine (Nonox-D) by electrophilic bromination method

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ABSTRACT

N-Phenyl-β-naphthylamine (Nonox-D) is used as an antioxidant in composite propellant formulations based on hydroxyl terminated polybutadiene (HTPB). The service performance of a composite propellant over a long storage period depends on the nature, effective concentration and purity of antioxidants added. Therefore, a new method has been developed to determine the quantitative estimation of purity of Nonox-D using bromate and bromide in acidic medium. The determination of quantitative estimation of purity involves treating Nonox-D with an excess of potassium bromate and potassium bromide in the presence hydrochloric acid using acetic acid as medium .After bromination of Nonox-D, the excess bromine is quantitatively determined by addition of potassium iodide solution followed by back-titration of the liberated iodine with standard sodium thiosulphate solution. The data obtained by analyzing different sources of Nonox-D indicate that the developed method is much reliable, fast and accuracy tolerance is in the range of ±0.5% and more safe in comparision to toluene diisocyanate method reported earlier.

KEYWORDS

Nonox-D;
Bromination;
Bromate-bromide;
Antioxidant;
Composite propellant.

INTRODUCTION

Hydroxyl terminated polybutadiene (HTPB) is the workhorse binder for composite propellants currently being used in space as well as missile programmes[1] all over the globe. The basic ingredients of composite propellants are an oxidizer such as ammonium perchlorate, a metallic fuel like aluminium powder along with HTPB as binder. Due to the presence of double bonds in the polymeric backbone of HTPB, it undergoes degradation due to oxidation by atmospheric oxygen, high temperature, high shear associated with high energy radiation. The degradation results in loss of mechanical properties, change in color which ultimately affects the shelf life of the propellant[2,3]. Hence to increase the shelf life as well as to preserve the mechanical properties throughout the service life of the propellant, antioxidants are added to prevent the formation of free radical that otherwise lead to the degradation of polymeric network. In literature, a number of antioxidants, like butylated hydroxyl toluene(BHT), diphenyl amine(Accinox-B), N-Phenyl-β-naphthylamine(Nonox-D), 2,2-methylene bis-(4-methyl-6-tertiarybutylphenol) (Vulcanox-BKF) and polymerized 1,2-dihydro-2,2,4-trimethylquinoline (Accinox-TQ) have been reported and used for HTPB systems[4]. However, commonly used antioxidant for HTPB based composite propellants is Nonox-D[5] and to be effective even at 0.1 % level. Furthermore, the

service performance over a long storage period depends on the nature, effective concentration and purity of the antioxidants added.

In view of better performance and commercial interest in different grades of Nonox-D, there is a need for rapid and simple method for the estimation of the purity of Nonox-D. The most commonly used method to determine purity of organic nitrogen is Kjeldahl method[6]. However, this method is highly laborious and time consuming as it requires several hours of digestion, distillation followed by titration. This method is non reproducible and non specific for Nonox-D as nitrogen in any form also contributes and thus producing erratic results. Further, gas/liquid chromatography has also been reported as a powerful analytical technique for the quantitative estimation of purity of Nonox-D. However, this technique always needs a reference sample of the purity of more than 99.99%.

In continuation to this work further, the determination of quantitative estimation of purity of Nonox-D using toluene diisocyanate, has been reported elsewhere[7]. Though the developed method using toluene diiso cyanate is rapid and accurate, yet it suffers from the fact that toluene diisocyanate is a carcinogenic in nature which poses health and handling problem. Therefore, there is a need to develop such a method for quantitative estimation of purity of Nonox-D, which avoids handling of dangerous chemicals. In view of this, a successful attempt has been carried out for quantitative estimation of purity of Nonox-D by aromatic electrophilic bromination method.

In the following section, we report the quantitative estimation of purity of Nonox-D using potassium bromate and potassium bromide in acidic medium.

EXPERIMENTAL

Material

N-Phenyl-β-naphthylamine (Nonox-D), procured from Aldrich, USA, ABR organics Hyderabad & Surbhi chemicals industries, Pune, were used as such for the determination of purity. Potassium bromide, potassium bromate, sodium thiosulfate, potassium iodide, glacial acetic acid and hydrochloric acid were of AR grade and procured from Merck-India.

Procedure

To a dry iodine flask (capacity 250 mL) accurately weighed 0.2 g of Nonox D and added 50 mL of glacial acetic acid to it. After this, pipetted out 25 mL of 0.5 N bromated-bromide solutions and added into flask followed by 10 mL of conc. hydrochloric acid. The stopcock was tightly closed, swirled and kept for 15 minutes at room temperature. To this, 10 mL of 15 % potassium iodide solution, freshly prepared, was rapidly added to flask, immediately re-stoppered and swirled the contents for a moment. Titrated the liberated iodine with standard 0.5 N sodium thiosulphate solution until the solution became slightly yellow, then added 5 mL of starch as an indicator and continued the titration until the blue color disappeared. A blank titration was also carried out without Nonox-D.

RESULTS AND DISCUSSION

Electrophilic bromination aspects

Aromatic compounds can be brominated by treatment with bromine in the presence of a catalyst, most often iron. However, the real catalyst is not the iron itself, but its halogenated compound like ferric bromide/ ferric chloride formed in small amounts from the reaction between iron and the reagent. For active substrates, including amines, phenols, naphthalene, and polyalkyl benzenes such as mesitylene and isodurene, no catalyst is needed. Indeed, for amines and phenols the reaction is so rapid that it is carried out with a dilute solution of bromine in water at room temperature. Even so, with amines it is not possible to stop the reaction before all the available ortho and para positions are substituted, because the initially formed bromoamines are weaker bases than the original amines and are less likely to be protonated by the liberated HBr. For this reason, primary amines are often converted to the corresponding anilides if monosubstitution is desired. The rapid room-temperature reaction of bromine with amines is often used as a qualitative and quantitative test for these compounds. Since Nonox-D is N-phenyl-β-naphthylamine, both of its phenyl and naphthyl ring is rich in electron density, due to activation by amino group, it will undergo aromatic bromination reaction quantitatively.

Electrophilic bromination steps

1. Generation of bromine

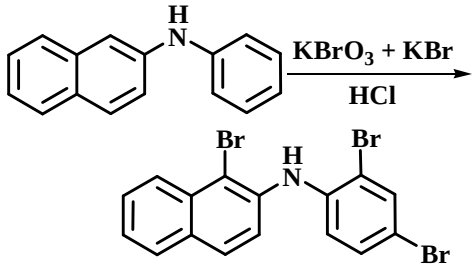
Acid solutions of bromine of exactly known concentration are readily obtainable from a standard potassium bromate solution by adding acid and an excess of bromide.

$$KBrO_3 + 5KBr + 6\,HCl \rightarrow 3\,Br_2 + 3\,H_2O + 6KCl$$

In the above reaction, one mole of bromate yields six atoms of bromine. Bromine is very volatile, and hence all operations should be conducted at low temperature as possible in conical flasks fitted with ground-glass stoppers. Potassium bromate is readily available in a high state of purity; the product has an assay value of at least 99.9 per cent. The substance can be dried at 120-150°C, is anhydrous, and the aqueous solution can be kept indefinitely, therefore, it is employed as a primary standard.

2. Aromatic electrophilic bromination of Nonox-D

The liberated molecular bromine reacts with Nonox-D to form tribromo derivative of Nonox-D. Hence the equivalent weight of Nonox-D is one-sixth of its molecular weight. Further, the tribromo product was separated out after titrimetric analysis and recrystallised with acetone which shows melting point in the range of 147-149ºC. The structure of tribromo derivative was fully characterized using IR, ^{1}H NMR, ^{13}C NMR and mass spectrum and elemental analysis.



3. Reaction of excess bromine with potassium iodide

The excess of bromine is determined iodometrically by the addition of freshly prepared excess of potassium iodide solution and titrated the liberated iodine with standard thiosulphate solution using starch as an indicator.

$$Br_2\ (excess) + KI \rightarrow I_2 + 2\,KBr$$

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6$$

TABLE 1: Data on quantitative estimation of purity of Nonox-D of different sources

Sl.no	Aldrich (%)	ABR Organics (%)	Surbhi (%)
1	99.65	96.40	94.10
2	99.70	96.35	94.40
3	99.55	96.10	93.90
4	99.60	95.90	94.57
5	99.60	95.95	94.50

CALCULATION

$$\%\,Purity\ of\ Nonox-D = \frac{(B-A)\times N_{Thio}\times 36.5}{W\times 1000}\times 100$$

Where, B is volume of sodium thiosulphate solution required for the blank, in mL, A is volume of sodium thiosulphate solution required for the titration, in mL, N_{Thio} is normality of sodium thiosulphate solution, W is the weight of Nonox-D in grams.

Further to this, the quantitative estimation of purity of Nonox-D was ascertained by using Aldrich make Nonox-D of known purity (>99.5%). The developed method was employed to quantify the purity of Nonox-D of Aldrich make along with ABR Organics and Surbhi make. The results obtained are presented in TABLE 1. It is clear from the table-1 that the percentage purity of Aldrich make Nonox-D is >99.5 %. The samples of ABR Organics and Surbhi show the purity of Nonox-D is 96% ±0.5 % and 94% ± 0.5%, respectively, indicating better purity of ABR organics in comparison to that of Surbhi make. The purity determination value of developed method was also cross checked using gas chromatography for the same samples and data obtained are in the agreement of developed method. Furthermore, the developed method has already been included in the text of quality improvement and this method is being used as routine analysis of Nonox-D for its quantitative estimation of purity before use in propellant compositions.

CONCLUSION

A new method for the quantitative estimation of purity of Nonox-D has been developed based on bromination reaction. The developed method is accurate and reliable. The tolerance limit of this method is ±0.5%. Moreover, the developed method does not need reference sample as advanced instrumental methods need.

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The developed method has also been included in the text of routine quality check of Nonox-D for the quantitative estimation of its purity before use in propellant formulations

ACKNOWLEDGMENT

The authors thank Dr. A.Subhananda Rao, Director, High Energy Materials Research Laboratory, Pune for his support and encouragement during the course of the study.

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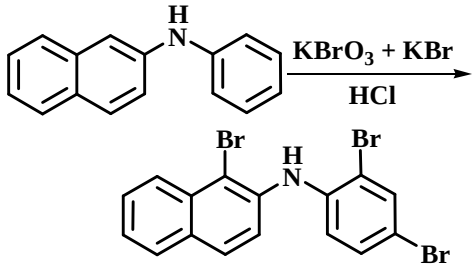

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CONCLUSION

A new method for the quantitative estimation of purity of Nonox-D has been developed based on bromination reaction. The developed method is accurate and reliable. The tolerance limit of this method is ±0.5%. Moreover, the developed method does not need reference sample as advanced instrumental methods need.

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The developed method has also been included in the text of routine quality check of Nonox-D for the quantitative estimation of its purity before use in propellant formulations

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