

Analytical Studies on the Oxidation of Nitroanilines using Potassium Dipertellurato Cuprate (III)

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An accurate method has been described for the determination of *o*, *m* and *p*-nitroaniline with the use of potassium dipertellurato cuprate(III) as the oxidant. The sample is reacted with excess of Cu(III) solution at hot plate under refluxing condition for about 10 min. After the reaction was over, the contents were cooled to room temperature. The unreacted Cu(III) reagent was estimated by the Arsenite method. A blank was also run under identical conditions using all reagents except the sample. The precision and accuracy are within $\pm 1\%$.

INTRODUCTION

Aromatic amines are great industrial importance. They are widely used in the manufacture of dyes, drugs, explosive, resin, printing material, etc. Because of their great industrial and chemical importance, a large number of procedures have been developed for the determination of aromatic amines.¹⁻⁶ In the present paper we describe a method for the determination of *o*, *m* and *p*-nitroaniline at the mg level using potassium dipertellurato cuprate(III) as the oxidising agent. The sample was allowed to react with a calculated excess of Cu(III) solution for about 10 min at hot plate to reflux. After the reaction was over, the unreacted Cu(III) was determined by the arsenite method.⁷ A blank was also run under identical conditions and the recovery of the aromatic amines sample was calculated. The method is convenient, specific and operable at ordinary laboratory conditions. It does not involve sophisticated instruments and rigorous reaction conditions. The Cu(III) reagent is easy to use and does not decompose on storage. The precision and accuracy are $\pm 1\%$.

EXPERIMENTAL

Potassium dipertellurato cuprate(III) reagent (0.035 M)

Copper sulphate (7.0805 g, E. Merck), potassium tellurite (15.8630 g, BDH), potassium persulphate (21.1010 g, AnalaR/BDH) and potassium hydroxide (40 g, E. Merck) were added to 400 mL of distilled water in a 500 mL Corning glass conical flask. The mixture was shaken thoroughly and then heated on a hot plate for about 40 min. It was then cooled to room temperature and filtered through G-4 Jena sintered crucible. The solution was raised to the mark with distilled water in a 500 mL volumetric flask.⁷

About 2 g starch (BDH) was dropped in 100 mL of boiling distilled water for

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2% starch solution. KI (25 g, E. Merck) was dissolved in distilled water and the solution was raised to the mark in a 250 mL measuring flask. Sodium thiosulphate (0.01 M) (2.48 g, AnalaR/BDH) was weighed and dissolved in distilled water in a one litre volumetric flask and the solution was standardised with 0.01 M CuSO_4 solution iodometrically. CuSO_4 (0.01 M) (0.6242 g, AnalaR/BDH) was accurately weighed and dissolved in minimum quantity of distilled water in a 250 mL volumetric flask containing a small amount of acetic acid. For 0.01 N solution of iodine a saturated solution of KI (4 g, E. Merck) was prepared and 1.27 g of iodine (E. Merck) was introduced into the saturated solution of KI and it was standardised against hypo solution and kept in an amber glass bottle. Sodium arsenite (0.02 M) (1.299 g, AnalaR/BDH) was dissolved in distilled water in a 500 mL flask. It was then standardised against the standard solution of iodine.

Stock solutions of each of the *o*, *m* and *p*-nitroaniline were prepared in hot distilled water. 100 mg of the sample was taken in 100 mL of measuring flask and the solution was made up to the mark with distilled water.

General procedure

Aliquots containing 1–5 mg of the sample were taken in a 150 mL Erlenmeyer flask fitted with an air-condenser. 10 mL of Cu(III) reagent was added to the sample in the flask and the contents were shaken and kept on a hot plate for reflux for the prescribed reaction time maintaining the volume of reaction-mixture constant by adding distilled water from the top of the condenser. After the reaction was over, the contents were cooled to room temperature. The unused Cu(III) reagent was estimated by the Arsenite method.⁷ A blank was also run simultaneously using all reagents omitting the sample.

$$\text{Mass of sample (mg)} = \frac{M \cdot N(S - B)}{n}$$

where M = relative molecular mass of sample,

N = normality of iodine solution,

S = volume of iodine for the sample experiments,

B = volume of iodine for the blank experiments,

and n = number of moles of Cu(III) per mole of sample.

RESULTS AND DISCUSSION

With the recommended procedure the determination of aromatic amines has successfully been achieved on 1–5 mg of sample size within the accuracy of $\pm 1\%$ (Table-1) in most of the cases.

The reaction proceeded quantitatively and the oxidation was completed within the prescribed reaction time. For accurate results a two-time excess of Cu(III) reagent needed theoretically for the oxidation of a particular compound was always necessary, while very large excess gave lower results.

The stoichiometry of the reaction was established with every compound by reacting 1–2 mg of the sample for different intervals of the reaction time with a calculated excess of Cu(III) reagent at hot plate. The reaction was carried out at

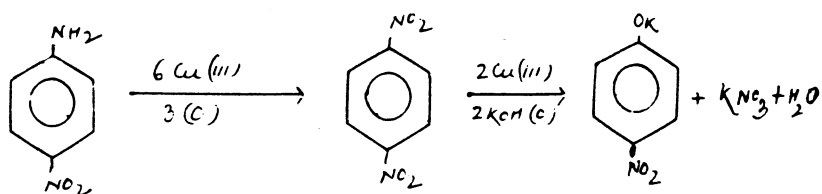
1, 2, 5 and 10 min and the recovery of the sample was calculated. It was found that the consumption of Cu(III) goes on increasing with increase of reaction time and attains a constant value at 10 min. In this way it was found that the consumption of Cu(III) for *o*-nitroaniline, *m*-nitroaniline and *p*-nitroaniline was 8, 6 and 8 mol respectively.

TABLE-1
DETERMINATION OF AROMATIC AMINES WITH 0.035 M Cu(III).

S. No.	Sample	Amount taken (mg)	Reaction time (min)	Amount recovered (mg)	Molarity	Error*%
1.	<i>o</i> -nitroaniline	1.0000	10	1.0013	8	+0.13
		3.0000		3.0063		+0.21
		5.0000		4.9870		-0.26
2.	<i>m</i> -nitroaniline	1.0000	10	1.0016	6	+0.16
		3.0000		3.0048		+0.16
		5.0000		5.0110		+0.22
3.	<i>p</i> -nitroaniline	1.0000	10	1.0025	8	+0.25
		3.0000		2.9969		-0.10
		5.0000		5.0090		+0.18

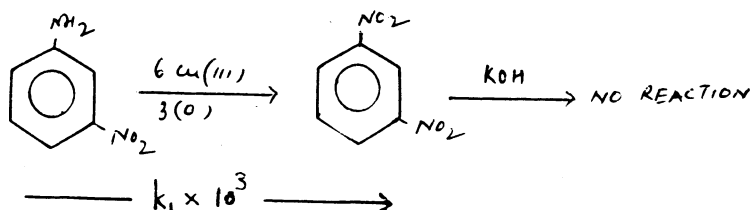
*Average of 3 determinations.

Considering the oxidation reaction of aromatic amines and the number of equivalents of Cu(III) consumed for a particular sample, the following course of reaction may be suggested for the oxidation of *o*, *m* and *p*-nitroaniline. *p* and *o*-nitroaniline consumes 8 equivalents of Cu(III) reagent while *m*-derivative consumes only 6 equivalents. The oxidation of *p*-nitroaniline may be shown below:



Replacement of one of the nitro groups in *o* and *p*-dinitrobenzenes by a strong nucleophile is a well established fact.⁸ Here the basic medium of Cu(III) reagent provides the strong nucleophile —OH which replaces a —NO₂ group.

m-Nitroaniline gives *m*-dinitrobenzene as the final product.



Due to electron withdrawing group $-\text{NO}_2$, electron density at *o*- and *p*-positions is lowered, but *m*-position remains practically unaffected. Hence the nucleophile $-\text{OH}$ replaces $-\text{NO}_2$ group from *o*- and *p*- positions only and not from the *m*- position.

The above course of reaction was found to support the previous mechanism.⁹ Reducing substances like sugar, alcohols, phenols etc. interfere in the determination, hence their presence should be avoided.

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