

Quantitative oxidation of Thiourea and Some of Its Derivatives with Ammonium Hexanitratocerate(IV) Reagent in Nitric Acid Medium at Micro Scale

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An accurate method has been described for the determination of thiourea, phenylthiourea, allylthiourea and *o*-ditolylthiourea at the mg level with the use of ammonium hexanitratocerate(IV) as the oxidant. The sample is reacted with an excess of Ce(IV) solution at room temperature (25°C) for about 30 min, the unreacted Ce(IV) reagent is then determined by titrating against Fe(II), using ferroin indicator. The precision and accuracy are within $\pm 1\%$.

INTRODUCTION

Thiourea is quantitatively oxidised by some organic and inorganic reagents. Depending upon this property procedures have been developed for the determination of thiourea and its derivatives.

Singh *et al.*¹⁻³ determined thiourea and its derivatives using reagents like iodine-monochloride, iodine monobromide and potassium bromate. Sarwar *et al.*⁴ determined thiourea and thioacetamide by oxidation with N-bromosuccinimide. The final oxidation product of sulphur function was reported to be sulphate. Tiwari *et al.*⁵ have also reported a similar method for the milligram determination of thiourea and claimed the final oxidation product to be sulphur and urea. Cheronis *et al.*⁶ have reviewed several methods for the determination of thiourea with the halogens as oxidant. Shukla⁷ developed a method for the milligram determination of thiourea and its derivatives using BrCl as a reagent.

In the present paper a simple and quick method has been developed for the milligram determination of thiourea and its derivatives by oxidation with Ce(IV). The samples were reacted with excess of Ce(IV) at room temperature for 30 minutes, and the unreacted Ce(IV) was determined with ferrous ammonium sulphate using ferroin as indicator.

EXPERIMENTAL

0.1 M Ammonium hexanitratocerate(IV): 13.70 g of ammonium hexa-

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nitratocerate(IV) (AnalaR, BDH) was exactly weighed and dissolved in minimum amount of 0.5 N nitric acid in a 250 mL volumetric flask and made up to the mark with the same solvent.

0.025 M Ferrous ammonium sulphate: 2.4508 g of ferrous ammonium sulphate (AnlaR, BDH) was accurately weighed and dissolved in minimum amount of distilled water in a 250 mL volumetric flask. 10 mL of 4 M sulphuric acid was added to it and the solution was made up to the mark with distilled water.

0.001 M Ferroin: 0.001 M ferrion solution (v/v) was prepared in distilled water, Two drops of the solution were used as indicator.

1 M Sulphuric acid: 1 M solution of sulphuric acid (v/v) was prepared by diluting AR, BDH sample in distilled water.

Sample solution: A stock solution of thiourea and allyl thiourea was prepared by dissolving accurately weighed 30–50 mg of the sample in distilled water and phenyl thiourea and *o*-ditolyl thiourea in acetic acid in a 100 mL volumetric flask. All the samples were of AnalaR, BDH grade.

General procedure: An aliquot containing 1–5 mg of the sample was taken in a 100 mL conical flask and 10 mL of 0.1 M ammonium hexanitratocerate(IV) was added to it. The flask was stoppered and shaken well. The contents were allowed to react for 30 min at room temperature. After the reaction was over, the stopper was rinsed with 5 mL of distilled water and 10 mL of 1 M sulphuric acid was added. The unreacted Ce(IV) was titrated against standard ferrous ammonium sulphate using ferroin as indicator. A blank was also run under identical conditions.

Calculation:

$$\frac{M \times N \times V_B \times V_S}{n}$$

M = Molecular weight of the sample

N = Normality of ferrous ammonium sulphate

V_B = Volume of Fe(II) required to titrate blank (mL)

V_S = Volume of Fe(II) required to titrate sample (mL)

n = moles of Ce(IV) required per mole of the sample for complete reaction

RESULTS AND DISCUSSION

The present method is quick, convenient and easy in operation. The accuracy of the method is within $\pm 1\%$ error and the whole estimation may be completed within 15–30 min.

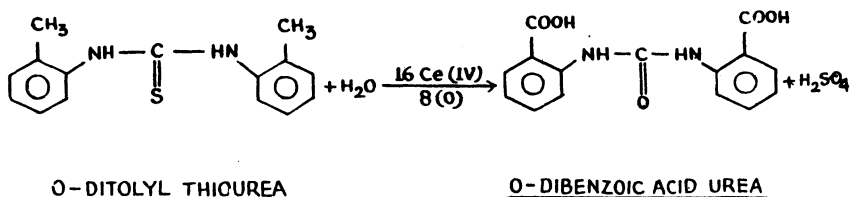
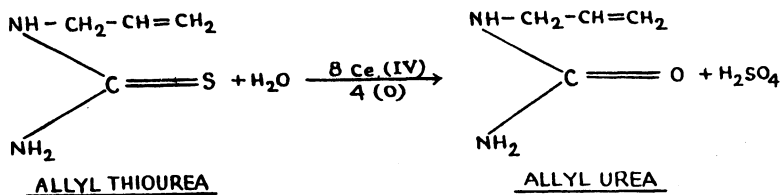
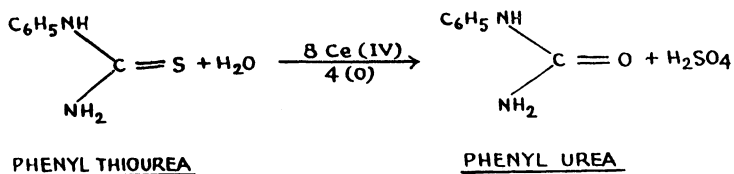
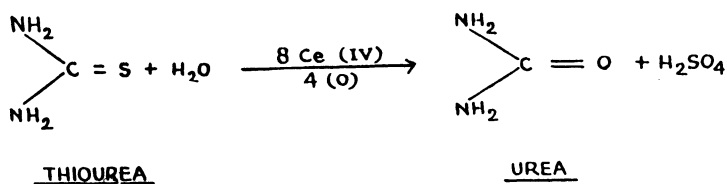
We have tried to trace the course of reaction with Ce(IV) for the oxidation of thiourea on the basis of the following experiments: 20–30 mg of the sample dissolved in cold distilled water was taken in a 100 mL conical flask. A known excess of 0.1 M Ce(IV) solution was added to it and the contents were allowed to react for 30 min. After the reaction was over the flask was taken out and 10 mL

of 1 M H_2SO_4 added to it. The contents were acidified with 1 mL of hydrochloric acid (MAR grade). To this solution a few drops of 1% aqueous BaCl_2 were added. On shaking a white precipitate of BaSO_4 was obtained. Now the reaction mixture was filtered and precipitated BaSO_4 was eliminated.

The filtrate was evaporated to dryness on a water bath and the solid mass obtained in this way on purification was found to be urea.

On the basis of stoichiometry and above experiment, a possible course for the oxidation of thiourea, phenyl thiourea, allyl thiourea, *o*-ditolyl thiourea may be represented as shown in Scheme -I

It was observed that the presence of urea and its derivatives does not interfere in the determinations. The above mechanism finds support from previous work^{4, 5, 7}.



Scheme-I

TABLE-I
SMALL SCALE DETERMINATION OF THIOUREA AND ITS DERIVATIVES WITH
THE RECOMMENDED PROCEDURES:

Sample	Amount taken (mg)	Reaction time (min)	Amount recovered (mg)	Stoichiometry	Error (%)
Thiourea	1.0000	30	1.0038	8	+0.38
	3.0000		3.0067		+0.22
	5.0000		5.0096		+0.19
Phenyl thiourea	1.0200	15	1.0179	8	-0.20
	3.0600		3.0824		+0.73
	5.1000		5.1279		+0.54
Allyl thiourea	1.0100	30	2.0095	8	-0.05
	3.0300		3.0427		+0.41
	5.0500		5.0833		+0.65
<i>o</i> -Ditolyl thiourea	1.0000	15	1.0004	16	+0.04
	3.0000		3.0094		+0.31
	5.0000		4.9863		-0.27

In each case three determinations were done.

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