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A Titrimetric Estimation of Ammonium Thiocyanate, Thiourea, N-Phenylthiourea, N, N′-Diphenylthiourea and Thiosemicarbazide with Ammonium Hexanitratocerate(IV) in Perchloric Acid Medium

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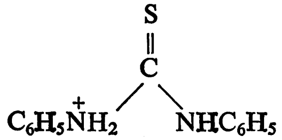
By applying suitable conditions *viz.*, slightly elevated temperatures (45° to 55°C) for different intervals of time in 1.0M perchloric acid medium, the indirect titrimetric estimations of ammonium thiocyanate, thiourea, N-phenylthiourea, N,N′-diphenylthiourea and thiosemicarbazide with cerium(IV) as an oxidant can be achieved. These estimations are fundamentally based on the established stoichiometries of the oxidation reactions of the aforementioned organic substrates. The technique adopted in all the cases is the addition of a known excess of cerium(IV) to a requisite volume of an aqueous solution of the organic substrate and back-titration of the unreacted cerium(IV) with iron(II) solution to a potentiometric end-point or by employing a suitable redox indicator *e.g.*, ferroin.

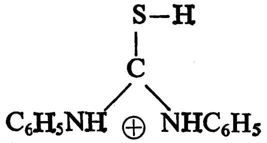
INTRODUCTION

Davies[1] studied the oxidation of thiourea and symmetrical alkyl thioureas with Mn(III) in perchloric acid medium and observed that the oxidation of these substrates takes place through the formation of S-S bonded products, in each case and finally concluded that the oxidation proceeds through an inner sphere mechanism with substitution at the Mn(III) centre as the rate determining process. Turkevich and Dmitrishin[2] carried out analytical estimations of thiourea and symmetrical phenyl thioureas with cerium(IV) in sulphuric acid medium at 20°C and separately at 50°C for different intervals of time. However, these oxidations have not led to the complete oxidations of these substrates but determinations are based on some empirical factors indicating intermediate stages of oxidation. Spectrophotometric kinetics of oxidation of some α-mercapto carboxylic acids, thioureas and its N-substituted derivatives by cerium(IV) in sulphuric acid was undertaken by McAuley and his coworkers[3,4] and they have concluded that the kinetics of oxidations are consistent with a free radical formation, radical dimerisation and subsequent oxidation to the sulphones and further the reaction rates were compared with the reactions of the corresponding oxygen analogues.

In acid solutions, thiourea and symmetrical phenyl thiourea molecules are believed to be monoprotonated[5]. For example the tautomeric forms of the monoprotonated N, N'-diphenyl thiourea species may be written as—



(A)



(B)

Thiourea and symmetrical alkyl thioureas are converted into the corresponding disulfides in the analogous reactions with cerium(IV)[6] and cobalt(III)[7]. In a review paper, Mahanti[8] stated that the oxidation of sulphur compounds proceeds through a radical intermediate e.g. C_6H_5S. The greater stability of these S containing radicals was demonstrated by the experimental observations that α-mercapto acids yield a disulfide as an oxidation product[3]. A detailed oxidation of hydrazine by cerium(IV) in perchloric acid medium at different pH conditions was undertaken by Morrow and Sheeres[9] and they have concluded that initially a molecule of hydrazine undergoes protonation and subsequently disproportionation of the protonated species takes place yielding N_2 and an ammonium salt. These findings are of much relevance in the present study particularly in the oxidation of thiosemicarbazide by cerium(IV).

EXPERIMENTAL

1. Cerium(IV) Solution :

A 0.1 M solution of cerium(IV) in 1.0 M perchloric acid and prepared by dissolving a requisite amount of AnalaR grade ceric ammonium nitrate in 1.0 M perchloric acid solution which was already prepared with conductivity water. Further this cerium(IV) solution was standardised with a standard iron(II) solution to a potentiometric end-point and separately by a visual titration using ferroin as an indicator. Cerium(IV) solution, thus prepared, was stored in an amber coloured Jena glass bottle and its normality was checked from time to time.

2. Perchloric acid solution :

Perchloric acid was proportionately diluted with conductivity water to have perchloric acid solutions of desired strength.

3. The 0.01 M solutions of ammonium thiocyanate, thiourea, N-phenylthiourea and thiosemicarbazide were prepared in condctivity water

by dissolving a requisite amount of organic substrate after duly checking the purity of each substrate[10]. A 0.01 M solution of N, N′-diphenylthiourea was prepared in glacial acetic acid as it is sparingly soluble in water.

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometries of the reactions between each of the aforementioned substrates and cerium(IV) has been established for the experimental conditions employed at 45° to 55°C for different intervals of time i.e. 15 min to 30 min. in case of ammonium thiocyanate, thiourea and thiosemicarbazide, while 90 min. to 120 min. in the case of N-phenylthiourea upto formic acid stage and 240 min. to 300 min. for N,N′-diphenylthiourea upto the end-product formic acid stage. Under the aforementioned conditions, it is observed that N-phenylthiourea consumes 24.0 equivalents of cerium(IV) while N,N′-diphenylthiourea consumes 40.0 equivalents.

One of the oxidation products viz., formic acid in case of N-phenylthiourea and N,N′-diphenylthiourea is not further oxidised under the experimental conditions employed. It is also observed that the factors of stoichiometries of oxidation remained constant even with the change of stipulated reaction times.

The end-products *viz.*, urea formed in some of these oxidation reactions was tested through a well known biuret test. The other end-product formic acid responded positively with (a) acidified $KMnO_4$ solution, (b) Fehling's solution, (c) Tollen's Reagent[11]. One of the oxidation products viz., p-hydroxyphenylurea in case of N-phenylthiourea and di(p-hydroxyphenyl) urea in case of N,N′-diphenylthiourea was tested with neutral $FeCl_3$[11]. Quinones which have formed as intermediate oxidation products were also tested after duly converting them into hydroquinones through reduction with Zn dust and a few drops of conc. HCl followed by the test with neutral $FeCl_3$[11]. The presence of other end-products viz., SO_4^{2-} and HCN were also tested by standard methods. Free radical intermediates were also tested through acrylonitrile polymerisation in the absence of air. Sulphones[12] which are formed as intermediate oxidation products in some of these oxidation reactions were also tested.

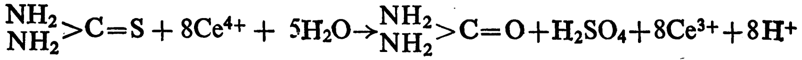
The following patterns of oxidation are consistent with the observed stoichiometries i.e., 1.0 ammonium thiocyanate : 6 Ce(IV); 1.0 thiourea : 8 Ce(IV); 1.0 N-phenylthiourea : 12 Ce(IV) upto p-benzoquinone stage, while 24.0 Ce(IV) are required for complete oxidation upto formic acid stage. In a similar manner 1.0 N, N′-diphenylthiourea : 16 Ce(IV) upto p-benzoquinone stage, while 40.0 Ce(IV) are required for complete oxidation upto formic acid stage; 1.0 thiosemicarbazide : 9 Ce(IV).

The oxidation reactions basing on the aforementioned stoichiometries can be written as follows.

1. $NH_4SCN \rightleftharpoons NH_4^+ + SCN^-$

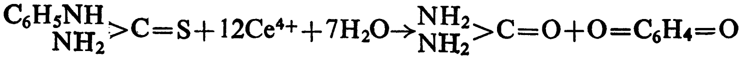
Ammonium
thiocyanate

$$SCN^- + 6Ce^{4+} + 4H_2O \rightarrow SO_4^{2-} + 6Ce^{3+} + 7H^+ + HCN$$

2.


$$\begin{matrix}NH_2\\NH_2\end{matrix}\!>C=S + 8Ce^{4+} + 5H_2O \rightarrow \begin{matrix}NH_2\\NH_2\end{matrix}\!>C=O + H_2SO_4 + 8Ce^{3+} + 8H^+$$

Thiourea

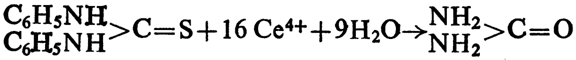
3. (a)


$$\begin{matrix}C_6H_5NH\\NH_2\end{matrix}\!>C=S + 12Ce^{4+} + 7H_2O \rightarrow \begin{matrix}NH_2\\NH_2\end{matrix}\!>C=O + O=C_6H_4=O + 12Ce^{3+} + 12H^+ + H_2SO_4$$

N-Phenyl thiourea

(b) $O=C_6H_4=O + 12Ce^{4+} + 10H_2O \rightarrow 6HCOOH + 12Ce^{3+} + 12H^+$

p-benzoquinone

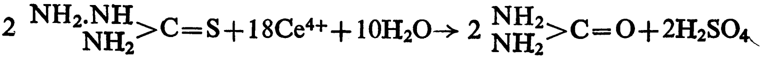
4. (a)


$$\begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}\!>C=S + 16\,Ce^{4+} + 9H_2O \rightarrow \begin{matrix}NH_2\\NH_2\end{matrix}\!>C=O + 2\,O=C_6H_4=O + 16Ce^{3+} + 16H^+ + H_2SO_4$$

N,N′-diphenylthiourea

(b) $2O=C_6H_4=O + 24Ce^{4+} + 20\,H_2O \rightarrow 12HCOOH + 24Ce^{4+} + 24H^+$

p-benzoquinone

5.


$$2\,\begin{matrix}NH_2.NH\\NH_2\end{matrix}\!>C=S + 18Ce^{4+} + 10H_2O \rightarrow 2\,\begin{matrix}NH_2\\NH_2\end{matrix}\!>C=O + 2H_2SO_4 + 18Ce^{3+} + 18H^+ + N_2\uparrow$$

Thiosemicarbazide

Recommended Procedure

Transfer an aliquot of 0.01 M solution (5.00 to 20.00 mg) of one of the organic substrates into an Erlenmeyer flask and add a known excess (two times more than the required stoichiometry) of cerium(IV) solution for oxidation and further add a requisite volume of stock $HClO_4$ (11.55M) to maintain an overall 1.0 M [$HClO_4$]. The mixture should be heated to 45° to 55°C for the above mentioned durations of time so as to achieve a definite stage of oxidation of the organic substrate. Reagent blanks of cerium(IV) in 1.0 M perchloric acid under identical experimental conditions showed no significant decrease in the concentration of cerium(IV).

A large number of determinations were carried out utilising the above recorded stoichiometries at 45° to 55°C. In all these analytical estimations, unused cerium(IV) was back-titrated with a standard iron(II) solution to a potentiometric end-point. Some typical results are furnished in the following Table.

TABLE 1

DETERMINATION OF AMMONIUM THIOCYANATE, THIOUREA, N-PHENYLTHIOUREA, N, N'-DIPHENYLTHIOUREA AND THIOSEMICARBAZIDE BY CERIUM(IV) IN PERCHLORIC ACID MEDIUM (1.0 M) AT 45°–55°C

Ammonium thiocyanate			Thiourea			N-phenyl thiourea		
Taken m moles	Found m moles	Error %	Taken m moles	Found m moles	Error %	Taken m moles	Found m moles	Error %
0.0300	0.0302	+0.66	0.0300	0.0298	−0.67	0.0300	0.0299	−0.33
0.0500	0.0504	+0.80	0.0500	0.0502	+0.40	0.0500	0.0501	+0.20
0.0700	0.0700	0.00	0.0700	0.0701	+0.14	0.0700	0.0703	+0.42
0.0900	0.0899	−0.11	0.0900	0.0902	+0.22	0.0900	0.0901	+0.11
0.1000	0.0994	−0.60	0.1000	0.0995	−0.50	0.1000	0.1000	0.00
0.1200	0.1196	−0.33	0.1200	0.1198	−0.17	0.1200	0.1195	−0.42

N, N'-diphenylthiourea			Thiosemicarbazide			
Taken m moles	Found m moles	Error %	Taken m moles	Found m moles	Error %	Standard Deviation
0.0300	0.0303	+1.0	0.0300	0.0301	+0.33	0.0002
0.0500	0.0506	+1.2	0.0500	0.0503	+0.60	0.0026
0.0700	0.0708	+1.14	0.0700	0.0702	+0.28	0.0004
0.0900	0.0912	+1.33	0.0900	0.0900	0.00	0.0005
0.1000	0.0992	−0.80	0.1000	0.0996	−0.40	0.0003
0.1200	0.1192	−0.67	0.1200	0.1197	−0.25	0.0023

Further the factors worked out on the basis of the aforementioned stoichiometries are as follows—

1 ml of 0.1 M Ce(IV) ≡ 1.269 mg of ammonium thiocyanate
≡ 0.9515 mg of thiourea
≡ 0.6333 mg of N-phenylthiourea (on the basis of 1 : 24 Ce(IV))
≡ 0.5700 mg of N, N′-diphenylthiourea (on the basis of 1 : 40 Ce(IV)
≡ 1.011 mg of thiosemicarbazide

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