DETERMINATION OF THIOCYANATE AND THIOSULPHATE IONS
BY OXIDATION WITH BIS (TRIFLUOROACETOXY) IODOBENZENE

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Introduction

Several methods have been proposed for the determination of thiocyanate and thiosulphate ions\(^1\). Belcher and co-workers determined thiocyanate and thiosulphate ions by oxidation with iodine in alkaline solution to sulphate ions. In both procedures, the excess of iodine is extracted with chloroform and then determined. Vasatova and Zyka\(^6\) oxidized thiocyanate and thiosulphate ions using cobalt (III). Attempts to utilize these oxidations quantitatively were unsuccessful and only in 9N HCl solutions they stabilized the potential of the reactions in 10 min.

In a previous work the oxidation of a number of inorganic and organic substances with bis (trifluoroacetoxy) iodo benzene has been studied in water - acetonitrile media\(^2\).

In the present paper we report the oxidation of thiocyanate and thiosulphate ions with bis (trifluoroacetoxy) iodo benzene which allows the indirect titrimetric and gravimetric determination of the above two ions.

Experimental

Reagents: Bis (trifluoroacetoxy) iodo benzene was prepared as it has been described previously\(^2\).\(^3\).

Standard solution of bis (trifluoroacetoxy) iodo benzene was prepared by dissolving the appropriate amount of it in acetonitrile.

Potassium thiocyanate: The analytical reagent grade material, was dried under vacuum at 75\(^o\) for 12h, was weighed out and dissolved in 1l of distilled water. This stock solution was stable over a long period.

The standardization of this solution was done by titration with silver nitrate solution conductometrically\(^4\).

Sodium thiosulphate: A 0.100M solution was prepared by a titrisol ampule (Merck AE). This solution is stable for a period of time when kept in dark. A 1.000 \( \times 10^{-3}\)M solution was prepared daily and was used as the stock solution for investigation of the determination of thiosulphate.

This solution was standardized against iodine solution.
Recommended Procedure

a) For the titrimetric determination of thiocyanate: To 5 ml of $5.07 \times 10^{-3}$M KSCN was added 5 ml of $2.19 \times 10^{-2}$M reagent solution in acetonitrile, the mixture was diluted with water to 50 ml allowed for 10 min and titrated with a $1.000 \times 10^{-2}$N Na$_2$S$_2$O$_3$ solution to determine unreacted bis (trifluoroacetoxy) iodobenzene. Back-titration of un consumed bis (trifluoroacetoxy) iodobenzene: An excess of potassium iodide was added to the above solution and the liberated iodine was titrated with standard solution of sodium thiosulphate$^2$.

$$
\text{PhI}(\text{OCOCF}_3)_2 + 2\text{I}^- \rightarrow \text{I}_2 + \text{PhI} + 2\text{CF}_3\text{COO}^-
$$

(1)$^7$

From the difference between the total mmoles of bis (trifluoroacetoxy) iodobenzene added and the un consumed mmoles, we found the amount of the reagent reacted with the thiocyanate ions to sulphate, according to the following equation (2).

$$
\text{SCN}^- + 3\text{PhI}(\text{OCOCF}_3)_2 + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 3\text{PhI} + 6\text{CF}_3\text{COO}^- + 7\text{H}^+ + \text{HCN}
$$

(2)

The above mentioned reaction must take place in a fume hood.

b) For the gravimetric determination of thiocyanate: A 5 to 8 ml aliquot of $5.07 \times 10^{-3}$M KSCN was added 3 to 5 ml $4.38 \times 10^{-2}$M solution of bis (trifluoroacetoxy) iodobenzene in acetonitrile, allowed for 10 min, diluted to 100 ml and warmed for removal of acetonitrile. To the hot solution, a solution of 5 ml $2.5 \times 10^{-1}$M BaCl$_2$•2H$_2$O was added under stirring. The white precipitate of barium sulphate formed settled down on digestion of 30 min on water bath leaving a clear supernatant fluid. The precipitate was filtered after 5 h through a filter paper (Green box, ashless) and was washed throughly with hot water. The precipitate obtained was dried at 110°C ignited and weighed as BaSO$_4$.

c) For the titrimetric determination of thiosulphate: To 8 ml of $1.00 \times 10^{-3}$M Na$_2$S$_2$O$_3$ was added 5 ml of $2.35 \times 10^{-2}$M solution of bis (trifluoroacetoxy) iodobenzene in acetonitrile, the mixture was diluted with water to 40 ml allowed for 5 min and an excess of KI was added to this solution. The liberated iodine was titrated with standard solution of $1.00 \times 10^{-2}$N Na$_2$S$_2$O$_3$.

From the difference between the total mmoles of the reagent added and un consumed mmoles we found the amount of the reagent consumed for the oxidation of thiosulphate ions to sulphate (3)$^1$.

$$
\text{S}_2\text{O}_3^{2-} + 4\text{PhI}(\text{OCOCF}_3)_2 + 5\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 4\text{PhI} + 8\text{CF}_3\text{COO}^- + 10\text{H}(3)
$$

d) For the gravimetric determination of thiosulphate: A 20 to 32 ml aliquot of $2.50 \times 10^{-4}$M Na$_2$S$_2$O$_3$ was added 5 ml $2.35 \times 10^{-2}$ solution of bis (trifluoroacetoxy) iodobenzene in acetonitrile allowed for 5 min and diluted with water to 50 ml and warmed for evaporation of acetonitrile. Then the sulphate ions were determined as in procedure (b).

Results and discussion

Analysis of aqueous thiocyanate and thiosulphate ions gave the experimental
results shown in tables I and II. Each mmol, as we can see from the reactions given, of thiosulphate and thiocyanate ions needs 4 and 3 mol of bis (trifluoroacetoxy) iodosobenzene respectively.

TABLE I: Experimental results from titrimetric and gravimetric determination of aqueous thiocyanate solutions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Added (mmol)</th>
<th>No of expts done</th>
<th>Found(^a) (mmol)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>By titration</td>
<td>Gravimetrically</td>
<td></td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>0.0253</td>
<td>8</td>
<td>0.0233±0.8×10(^{-3})</td>
<td>0.0249±0.6×10(^{-3})</td>
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<tr>
<td></td>
<td>0.0304</td>
<td>8</td>
<td>0.0311±1.1×10(^{-3})</td>
<td>0.0301±0.7×10(^{-3})</td>
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<tr>
<td></td>
<td>0.0355</td>
<td>8</td>
<td>0.0361±0.9×10(^{-3})</td>
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<tr>
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<td>0.0405</td>
<td>8</td>
<td>0.0391±1.2×10(^{-3})</td>
<td>0.0409±1.1×10(^{-3})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Average value of eight determinations ± standard deviation.

TABLE II: Experimental results from titrimetric and gravimetric determination of aqueous thiosulphate solutions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Added (mmol)</th>
<th>No of expts done</th>
<th>Found(^a) (mmol)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>By titration</td>
<td>Gravimetrically</td>
<td></td>
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<tr>
<td>Thiosulphate</td>
<td>0.0050</td>
<td>8</td>
<td>0.0052±1.2×10(^{-4})</td>
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<td>0.0060</td>
<td>8</td>
<td>0.0058±2.1×10(^{-4})</td>
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<td>0.0070</td>
<td>8</td>
<td>0.0073±1.8×10(^{-4})</td>
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<tr>
<td></td>
<td>0.0080</td>
<td>8</td>
<td>0.0077±2.5×10(^{-4})</td>
<td>0.0081±1.3×10(^{-4})</td>
<td></td>
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</tbody>
</table>

\(^a\) Average value of eight determinations ± standard deviation.

The successful titrations and gravimetric determinations of these compounds is due to the fast oxidation at room temperature.

We had not interferences from the common ions such as Ca\(^{++}\), Mg\(^{++}\), Al\(^{+++}\), Ni\(^{++}\), Co\(^{++}\), Zn\(^{++}\), Cd\(^{++}\), NO\(_3\)\(^-\), PO\(_4\)\(^{3-}\), CH\(_3\)COO\(^-\) etc.
We had interference from ions which participated in redox reactions with bis (trifluoroacetoxy) iodosobenzene\(^{2,8}\).

The authors wish to thank Dr. S. Spyroudis, Laboratory of Organic Chemistry, for a gift of the bis (trifluoroacetoxy) iodosobenzene sample.

Summary

Thiocyanate and thiosulphate ions are oxidized by bis (trifluoroacetoxy) iodosobenzene to sulphates which enable the indirect determination of these ions by back-titration or gravimetrically. Each mmol of thiocyanate and thiosulphate ions needs 3 and 4 mmoles of the reagent respectively to give sulphate ions.
Περίληψη

Προσδιορισμός θειοκυανιούχων και θειοθειικών ιόντων κατόπιν οξείδωσης με διτριθυροακετοξυμοβενζόλιο

Στην εργασία αυτή περιγράφεται μια μέθοδος οξείδωσης των θειοκυανιούχων και θειοθειικών ιόντων με ακετονιτρυλικό διάλυμα διτριθυροακετοξυμοβενζόλιου. Τα θεοκυανιούχα και θειοθειικά ιόντα οξειδώνονται προς θειικά και προσδιορίζονται με επανογκομέτρηση και σταθμικά. Βρέθηκε πειραματικά, ότι κάθε mmol θειοκυανιούχων και θειοθειικών ιόντων χρειάζεται 3 και 4 mmoles από το αντιδραστήριο αντίστοιχα για να οξειδωθεί προς θειικά ιόντα. Με βάση τη στοιχειομετρία αυτή δίνονται και οι χημικές εξισώσεις της οξείδωσης.

References