The Oxidimetric Determination of Thioureas with Potassium Bromate

By Balwant SINGH, Balbir Chand VERMA and M. S. SARAN

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Szebelledy and Madis[1] determined thiourea by titrating it with bromate in a hydrochloric acid medium at 40 to 50°C in the presence of potassium bromide and a little gold chloride. The end-point was marked by the appearance of a yellow colour which persisted only for 5 to 10 sec. On the other hand, Mahr[2] titrated thiourea with a standard bromate-bromide solution in a sulphuric acid medium at 35°C in the presence of potassium iodide and a little starch. The end-point was the appearance of a blue colour when thiourea was oxidised to formamidine disulphide. Rao and Neelakantam[3] found Mahr's method to be erratic and developed a method replacing

1) L. Szebelledy and V. Madis, *Z. anal. Chem.*, **114**, 253 (1938).
2) C. Mahr, ibid., **117**, 91 (1939).
3) K. B. S. R. P. S. P. Appa Rao and K. Neelakantam, *Ind. J. Pharm.*, **14**, 50 (1952).

potassium bromate by potassium permanganate and using a lower concentration of sulphuric acid and double the amount of potassium iodide.

However, no systematic study has so far been made regarding the oxidimetric determination of thiourea and its organic derivatives. In the present work an attempt will be made to use potassium bromate as a redox reagent for the determination of thioureas in a sulphuric acid medium at room temperature. In the presence of potassium iodide, the thiourea and its organic derivatives will be oxidised to their corresponding disulphides with this oxidant.

Experimental

A known weight (10 to 60 mg.) of each compound was taken in a titration flask. In the case of thiourea and its alkyl derivatives, sufficient water and enough sulphuric acid to keep the acid concentration at 2 N were added. Each aryl derivative of thiourea was dissolved in 18 N sulphuric acid (10 to 15 ml.), and sufficient water (50 to 90 ml.) was added to keep the acid concentration between 2.5 to 4.0 N. To the solution of each compound a 0.40 ml. portion of 10% potassium iodide solution was added except in the case of the *p*-tolyl-, *p*-methoxyphenyl- and *p*-ethoxyphenyl thioureas, to which 0.10 ml. portions of 10% potassium iodide solution were added. The solution in each case was cooled to room temperature and titrated with standard (N/20) potassium bromate. The end-point in each case was detected visually as well as potentiometrically. In visual titrations,

Table I. The determination of thiourea and its organic derivatives with standard (N/20) potassium bromate

Compound	Visual method		Potentiometric method	
	Taken g.	Found g.	Taken g.	Found g.
$H_2N{\cdot}CS{\cdot}NH_2$	0.0152 0.0457	0.0152 0.0459	0.0152 0.0457	0.0151 0.0458
$CH_3NH{\cdot}CS{\cdot}NH_2$	0.0099 0.0449	0.0099 0.0451	0.0165 0.0513	0.0165 0.0513
$CH_3CH_2NH{\cdot}CS{\cdot}NH_2$	0.0124 0.0553	0.0124 0.0550	0.0226 0.0543	0.0226 0.0543
$(CH_3)_2CHNH{\cdot}CS{\cdot}NH_2$	0.0112 0.0554	0.0112 0.0556	0.0178 0.0488	0.0178 0.0490
$n\text{-}CH_3CH_2CH_2{\cdot}CH_2NH{\cdot}CS{\cdot}NH_2$	0.0105 0.0553	0.0105 0.0550	0.0263 0.0560	0.0262 0.0561
$(CH_3)_2CHCH_2NH{\cdot}CS{\cdot}NH_2$	0.0103 0.0502	0.0103 0.0501	0.0203 0.0555	0.0202 0.0553
$n\text{-}CH_3CH_2CH_2CH_2CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$	0.0102 0.0525	0.0102 0.0522	0.0147 0.0573	0.0147 0.0572
$o\text{-}(CH_3)C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH_2$	0.0155 0.0500	0.0155 0.0499	0.0126 0.0608	0.0126 0.0609
$p\text{-}(CH_3)C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH_2$	0.0103 0.0532	0.0103 0.0530	— —	— —
$o\text{-}(OCH_3)C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH_2$	0.0165 0.0535	0.0166 0.0536	0.0184 0.0541	0.0184 0.0544
$p\text{-}(OCH_3)C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH_2$	0.0202 0.0500	0.0201 0.0497	— —	— —
$o\text{-}(OC_2H_5)C_6H_4NH{\cdot}CS{\cdot}NH_2$	0.0142 0.0496	0.0142 0.0493	0.0096 0.0519	0.0096 0.0517
$p\text{-}(OC_2H_5)C_6H_4NH{\cdot}CS{\cdot}NH_2$	0.0107 0.0501	0.0107 0.0498	— —	— —

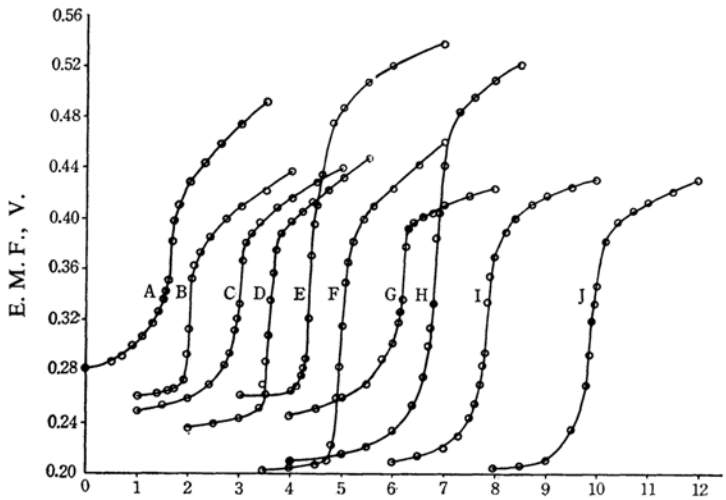


Fig. 1

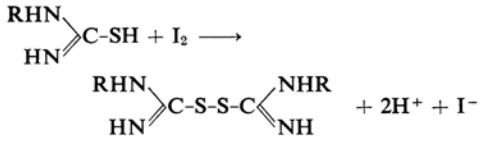
A *o*-Ethoxy phenyl thiourea
B *o*-Methoxy phenyl thiourea
C Isobutyl thiourea
D *o*-Tolyl thiourea
E Ethyl thiourea
F Thiourea
G Isopropyl thiourea
H *n*-Butyl thiourea
I *n*-Amyl thiourea
J Methyl thiourea

0.20 ml. of 1% amylose was used as an indicator, and the solution acquired a blue colour at the end-point. A series of potentiometric titrations was performed with different amounts of the compound in each case. The potentiometric titrations, one for each compound, are represented by curves A to J in Fig. 1.

From the volume of the standard (N/20) potassium bromate solution used corresponding to the end-point in each titration, the amount of each compound was calculated. Some typical results are given in Table I.

The results recorded in the table show that the listed compounds can be determined volumetrically by titrating them with standard (N/20) potassium bromate. Thiourea and its organic derivatives are oxidised by potassium bromate to their corresponding disulphides in the presence of potassium iodide in a sulphuric acid medium.

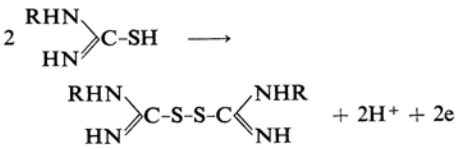
$$BrO_3^- + 6\,I^- + 6H^+ \longrightarrow Br^- + 3\,I_2 + 3\,H_2O$$



(R=hydrogen atom, alkyl or aryl group)

Summary

Potassium bromate has been used as a redox reagent in the presence of potassium iodide for the visual and potentiometric determination of thiourea and its several alkyl and aryl derivatives in a sulphuric acid medium. In visual titrations, amylose, is used as a visual indicator, turning blue at the end-point. In the potentiometric method, a bright platinum wire is used as an oxidation-reduction electrode; this is coupled with a saturated calomel electrode. The thioureas are oxidised to their corresponding disulphides with a single electron-change:



(R=hydrogen atom, alkyl or aryl group)

This direct method is simple, accurate, instantaneous and widely applicable.

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Chemistry Department
Punjabi Univesity
Patiala, India