

Interaction of Bromamine-T with Metal Ions

B N USHA, H S YATHIRAJAN & RANGASWAMY*

Department of Post-graduate Studies & Research in Chemistry,
University of Mysore, Manasagangothri, Mysore 570 006

Received 7 April 1983; revised 7 May 1983; accepted 30 May 1983

Bromamine-T (BAT) produces precipitates with Ag(I), Hg(II), Th(IV) and Zr(IV) in aqueous solutions. Ag(I) and Hg(II) form simple salts with BAT, while Th(IV) and Zr(IV) react with BAT to form only dibromamine-T (DBT).

In continuation of our earlier work on organic haloamines¹, we report in this note the results of our studies on the reactions of bromamine-T (BAT) with some metal ions, viz. Ag(I), Hg(II), Th(IV) and Zr(IV).

Silver nitrate, mercuric chloride, thorium chloride, thorium nitrate, zirconium oxychloride and zirconium nitrate were of AR grade and their solutions were prepared in distilled water. Bromamine-T was prepared by the method described elsewhere² and its solutions were also in distilled water. All other chemicals used were of reagent grade.

Conductance measurements were made at room temperature (27°) using a Phillips PR 9500 conductivity bridge with a diptype conductivity cell (cell constant = 0.66 cm⁻¹).

Silver and mercuric salts were prepared by mixing silver nitrate and mercuric chloride separately with BAT in 1:1 and 1:2 molar ratios respectively. The precipitates obtained were washed several times with water and air-dried. The compounds were yellowish white solids. The compound of Ag(I) analysed for (CH₃C₆H₄SO₂NBr)Ag (Found: N, 3.84; S, 8.9; Br, 22.3; Ag, 30.01. Required: N, 3.92; S, 8.97; Br, 22.4; Ag, 30.24%). The compound of Hg(II) analysed for (CH₃C₆H₄SO₂NBr)₂Hg (Found: N, 3.94; S, 9.12; Br, 22.76; Hg, 28.52. Required: N, 4.01; S, 9.16; Br, 22.83; Hg, 28.72). Silver compound decomposes at 172-76° and Hg(II) compound at 163-66°. Further silver salt is light sensitive and gradually turns violet upon exposure to light. Aqueous solutions of both the compounds liberate iodine from acidified potassium iodide solution.

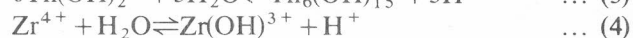
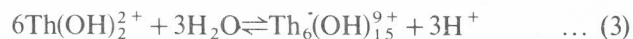
Conductivity titration curves of AgNO₃ and HgCl₂ with BAT show breaks at 1:1 and 1:2 molar ratios, in accordance with composition in solid state. The stoichiometric equations can be represented as in (1) and (2).



where R is H₃CC₆H₄SO₂. The UV and IR spectra of BAT, (RNBr)Ag and (RNBr)₂Hg are superimposable indicating that they are simple salts.

The yellow solid obtained by the addition of a solution of Th⁴⁺ or Zr⁴⁺ to a solution of BAT was filtered, washed with water and estimated iodometrically in glacial acetic acid medium. The unreacted BAT in the filtrate was also determined iodometrically. The amount of H⁺ reacted was calculated by titration against NaOH. It is found that BAT and H⁺ have reacted approximately in 1:1 molar ratio and the amount of product formed is nearly half the amount of BAT reacted. The solid obtained in the reaction of thorium nitrate melted at 93° with decomposition and analysed for dibromamine-T (DBT or RNBr₂) (Found: N, 4.23; S, 9.65; Br, 48.5. Required: N, 4.26; S, 9.73; Br, 48.6%). Similar conductivity titrations of thorium and zirconium solutions against BAT show breaks at 1:3 and 1:1 molar ratios respectively.

When carefully neutralised solutions of Th⁴⁺ and Zr⁴⁺ with NaOH were mixed with BAT, no precipitation was observed. These results indicate that H⁺ produced during the hydrolysis of these ions in aqueous solution is actually involved in the formation of DBT. The hydrolysis equilibria³ of Th⁴⁺ and Zr⁴⁺ in aqueous solution can be represented by Eqs (3) and (4).



The precipitate obtained could be dibromamine-T (DBT) which is only sparingly soluble in water. The breaks obtained at 1:3 and 1:1 molar ratios in conductometric titrations of Th⁴⁺ and Zr⁴⁺ with BAT probably indicate the formation of RNHBr. The disproportionation reactions of RNHBr have already been reported⁴ and are shown in Eqs (5-7).



The UV and IR spectra of the precipitates and DBT prepared by literature method⁵ were identical confirming the formation of DBT.

One of us (BNU) thanks the UGC, New Delhi, for the award of a senior research fellowship.

References

- 1 Rangaswamy, Usha B N & Yathirajan H S. *Analyst* (in press).
- 2 Nair C G R, Lalithakumari R & Senan P I. *Talanta*, **25** (1978) 525.
- 3 Mahadevappa D S & Rangaswamy, *Indian J Chem.* **14A** (1976) 463.
- 4 Hardy F E & Johnston J P. *J chem Soc, Perkin II* (1973) 742.
- 5 Nair C G R & Indrasenan P. *Talanta*, **23** (1976) 239.