Polar Solution Behaviour of Selenium Tetrabromide

By N. KATSAROS and J. W. GEORGE*

(*Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, U.S.A.*)

IT has been reported[1] that selenium tetrabromide behaves as a partially ionized solute in various polar solvents, but that in dimethylformamide the electron-donor properties of the solvent result in a conductance much higher than expected for a 1 : 1 electrolyte. Our own observations of these solutions has given somewhat different results. We report our findings for nitrobenzene solutions of $SeBr_4$ and suggest the identity of the species therein.

Cryoscopic molecular weight determinations in nitrobenzene gave a concentration-independent average value of 212 (formula weight of $SeBr_4$ is 399). I.r. spectroscopic results were: $SeBr_4$; 295s, 260m; Se_2Br_2; 290w, 260vs; Se_2Br_2 and Br_2 (1 : 3 mole ratio); 295s, 260m. The measured molar conductance at 25° of a $1{\cdot}4 \times 10^{-3}$ M solution of $SeBr_4$ was 0·24 $ohm^{-1}cm.^2mole^{-1}$, considerably less than that previously reported.[1] Passage of a stream of dry, purified nitrogen through a $PhNO_2$ solution of $SeBr_4$, and discharge of the stream into an aqueous iodide ion–starch solution, gave a pronounced blue colour; blank tests excluded N_2 contaminants and selenium species as oxidants.

The molecular weight results suggest a dissociation of each $SeBr_4$ formula unit into two particles in solution. Since the molar-conductance value is appreciably below the customary range (20—30) found for 1 : 1 electrolytes in $PhNO_2$ it is unlikely that the solution process yields $SeBr_3^+$ and Br^- ions in any significant concentration. The far i.r. solution spectra of $SeBr_4$ and Se_2Br_2 plus Br_2 in 1 : 3 mole ratio were identical, but differed in several ways from the spectrum of crystalline $SeBr_4$ (298m, 265vs, 247—227vs, 127s, 107s) for which the ionic formulation $SeBr^+{}_3Br^-$ has been proposed.[2] Further, the significant difference in the intensity ratios of the 295 and 260 $cm.^{-1}$ absorptions for $SeBr_4$ and Se_2Br_2 solutions suggest the presence of another substance, probably $SeBr_2$. These considerations, together with the implied presence of elementary bromine in the $SeBr_4$ solution, point to the conclusion that the tetrabromide is dissociated principally to an equilibrium system of $SeBr_4$, Se_2Br_2, and Br_2. Such behaviour has been postulated for carbon tetrachloride solutions of $SeBr_4$ from absorption spectrophotometric measurements.[3]

We thank the National Science Foundation for financial support.

(*Received, April 1st*, 1968; *Com.* 403.)

[1] D. A. Couch, P. S. Elmes, J. E. Fergusson, M. L. Greenfield, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1967, 1813.
[2] J. W. George, K. J. Wynne, and N. Katsaros, *Inorg. Chem.*, 1967, **6**, 903.
[3] N. W. Tideswell and J. D. McCullough, *J. Amer. Chem. Soc.*, 1956, **78**, 3026.