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The Nature of Selenium Tetrabromide in Nonaqueous Solvents

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The results of infrared and electronic spectral determinations and electrical conductance measurements demonstrate that selenium tetrabromide is fully dissociated in a wide range of solvents to give an equilibrium mixture of selenium mono- and dibromides and elementary bromine. The electrical conductance observed when $SeBr_4$ is dissolved in nitrobenzene, acetonitrile, tetramethylene sulfone, or N,N-dimethylformamide has its source in the ionization of Se_2Br_2 and $SeBr_2$ in these solvents. The strong absorption in the infrared spectra at about 290 cm^{-1} is associated with either or both of the Se–Br stretching modes of $SeBr_2$.

Introduction

The existence of selenium tetrabromide as a discrete species has been fully established only in the solid state. Vaporization of the solid gives a gas phase having a density just half that expected for molecular $SeBr_4$; this has been interpreted[1] as indicating a complete decomposition to $SeBr_2$ and Br_2 in the vapor state. In carbon tetrachloride solution the compound is fully dissociated to yield an equilibrium mixture of $SeBr_2$, Se_2Br_2, and Br_2.[2] An infrared spectroscopic study[3] of the crystalline material gave results consistent with the formulation $SeBr_3^+Br^-$, and recently a report that $SeBr_4$ gives electrically conducting solutions with certain polar solvents has appeared.[4] With the objective of establishing the behavior of $SeBr_4$ in a range of solvents of varying polarity, we have examined a variety of $SeBr_4$ solutions and report the results in this communication.

Experimental Section

Selenium Compounds.—Selenium mono- and tetrabromides were prepared according to standard procedures[2] using 99.9% pure selenium (Fisher Scientific Corp.) and reagent grade bromine (Mallinckrodt) which had been distilled over phosphorus pentoxide under a nitrogen atmosphere. The products were stored in sealed glass ampoules. All selenium bromide handling and solution preparation were carried out under anhydrous conditions in polyethylene bags or in a Labconco Fiberglas glove box.

Solvents.—Reagent grade benzene (Fisher) was dried over sodium metal and fractionally distilled. Spectral grade acetonitrile (Eastman Organic Chemicals) was refluxed for several hours over CaH_2 (Ventron Corp.) in a 6-ft column filled with glass helices and then distilled with a high reflux ratio. A middle fraction having a specific conductance at 25° of $(3.0–4.5) \times 10^{-8}$ ohm^{-1} cm^{-1} was collected. Reagent grade tetramethylene sulfone (Aldrich Chemical Co.) was twice fractionally distilled over CaH_2 under low pressure. The product had a specific conductance at 32° of $(2.0–2.5) \times 10^{-8}$ ohm^{-1} cm^{-1}. Reagent grade nitrobenzene (Eastman Organic Chemicals) was dried over anhydrous calcium chloride and fractionally distilled under low pressure. A middle fraction was collected and redistilled over anhydrous P_2O_5 under low pressure. The middle fraction from this procedure was stored over Linde 4A Molecular Sieves; the final product had a specific conductance at 25° in the $(4–7) \times 10^{-9}$ ohm^{-1} cm^{-1} range. Spectral grade N,N-dimethylformamide (Fisher) was treated by a standard method[5] using BaO; the product had a specific conductance (25°) of 1.0×10^{-7} ohm^{-1} cm^{-1}. Spectral grade carbon tetrachloride (Fisher) was used without further purification.

Physical Measurements.—Solution resistance measurements were made in cells having smooth platinum electrodes with the aid of a General Radio 1650A impedance bridge. Infrared spectra were obtained using Beckman IR 10 and 11 and Perkin-Elmer Model 21 spectrometers and, as appropriate, polyethylene (Barnes Engineering Co.) or KBr cells. Electronic spectra were determined using a Cary Model 14 spectrophotometer and cells of 1.0-cm path length. Molecular weight measurements were made cryoscopically.

Test for Volatile Oxidants.—A solution was examined for the presence of volatile oxidants by passing, for several minutes, a stream of dried, purified nitrogen through the solution and discharging the effluent into an aqueous iodide ion–starch solution. Blank tests established that the concentration of any N_2 contaminants present was insufficient to produce any observable oxidation of iodide ion in that time period and that no detectable amount of any selenium species had been volatilized from the solution.

Results

Infrared spectroscopic data for pure crystalline $SeBr_4$, for liquid Se_2Br_2, and for the several solutions are summarized in Table I. In Figure 1 the infrared spectra of $TMSO_2$ solutions of $SeBr_4$ are compared with those of Se_2Br_2 and Se_2Br_2–Br_2 mixtures. Although it was found that DMF solutions of Se_2Br_2 deposited elementary selenium and prevented meaningful conductance measurements, it was possible to obtain infrared spectra of such solutions before extensive reaction had occurred. Electrical conductance data are presented in Tables II–IV. The conductance data for nitrobenzene solutions are also displayed graphically in Figure 2. For purposes of this plot the formal $SeBr_4$ concentrations are halved (as though all selenium is present as Se_2Br_2), thereby enabling direct comparison with corresponding conductance data for Se_2Br_2 and Se_2Br_2–Br_2 solutions.

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[1] D. M. Yost and J. B. Hatcher, *J. Am. Chem. Soc.*, **53**, 2549 (1931).
[2] N. W. Tideswell and J. D. McCullough, *ibid.*, **78**, 3026 (1956).
[3] J. W. George, N. Katsaros, and K. J. Wynne, *Inorg. Chem.*, **6**, 903 (1967).
[4] D. A. Couch, P. S. Elmes, J. E. Fergusson, M. L. Greenfield, and C. J. Wilkins, *J. Chem. Soc.*, *A*, 1813 (1967).
[5] A. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

TABLE I

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) FOR SELENIUM BROMIDES AND THEIR SOLUTIONS

Crystalline $SeBr_4$:[a] 298 m, 265 vs, 247–227 vs, 127 s, 107 s

Liquid Se_2Br_2:[a] 286?, 260 vs, 120 s, 105 w

Benzene soln
  $SeBr_4$: 296 vs
  Se_2Br_2: 295 w, 265 vs
  Se_2Br_2–Br_2 (1:3 mole ratio): 295 vs

Carbon tetrachloride soln
  $SeBr_4$: 296 vs
  Se_2Br_2: 290 w, 265 vs

Carbon disulfide soln
  $SeBr_4$: 297 vs

Chloroform soln
  $SeBr_4$: 295 vs

Nitrobenzene soln[b]
  $SeBr_4$: 295 vs, 260?
  Se_2Br_2: 290 w, 260 vs
  Se_2Br_2–Br_2 (1:3 mole ratio): 295 vs, 260?

Acetonitrile soln
  $SeBr_4$: 290 vs
  Se_2Br_2: 290 w, 259 vs
  Se_2Br_2–Br_2 (1:3 mole ratio): 290 vs

Tetramethylene sulfone soln
  $SeBr_4$: 290 vs
  Se_2Br_2: 288 w, 263 vs
  Se_2Br_2–Br_2 (1:3 mole ratio): 290 vs

N,N–Dimethylformamide soln
  $SeBr_4$: 260 s, 188 vs
  Se_2Br_2: 258 vs
  Se_2Br_2–Br_2
    1:1 mole ratio: 258 vs, 190 m
    1:2 mole ratio: 258 s, 190 vs
    1:3 mole ratio: 258 m–s, 190 vs
    1:4 mole ratio: 258 w–m, 190 vs

[a] P. J. Hendra and P. J. D. Park, *J. Chem. Soc., A*, 908 (1968). [b] Solvent absorption at 258 cm^{-1} interferes.

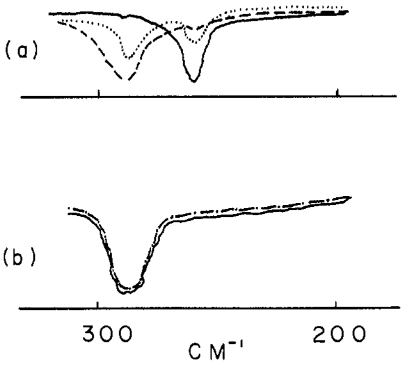

Figure 1.—Infrared spectra of selenium bromides in tetramethylene sulfone solution: (a) Se_2Br_2 (——), Se_2Br_2–Br_2 (1:1) (......), Se_2Br_2–Br_2 (1:2) (— — —); (b) Se_2Br_2–Br_2 (1:3) (—·—), $SeBr_4$ (———).

Except for the DMF solutions of selenium bromides, conductance values were stable with time, remaining constant for 30 hr or more. DMF solutions, however, displayed decreasing resistances over a period of several hours. Such behavior for DMF solutions of organotin and organogermanium chlorides has been reported[5] to result from trace amounts of moisture. It is also possible that solvent impurities, dimethylamine in particular, may have reacted with $SeBr_4$ and/or that a slow complexation reaction of the solvent with the selenium halides present resulted in an increase in the concentration of change carriers; either effect could result in time-dependent resistance values. The addition of minute amounts of water to solutions for which constant resistance values had been reached resulted in further and very rapid decreases in these resistances. The conductance values reported in Table IV represent measurements made as soon following solution preparation as was consistent with the requirement of temperature equilibration.

TABLE II

CONDUCTANCE DATA FOR SELENIUM BROMIDES AND BROMINE IN ACETONITRILE (25 °)[a]

$SeBr_4$			Se_2Br_2–Br_2 (1:1 mole ratio)	
10^3C	10^6k	μ	$10^3C_{Se_2Br_2}$	10^6k
0.5	2.8	5.6	0.48	3.1
0.9	3.1	3.6	1.2	3.6
1.0	3.5	3.5	1.9	4.5
1.3	4.2	3.2	8.9	11.0
2.7	7.4	2.8	15.0	13.0
9.0	25.0	2.7		

Se_2Br_2			Se_2Br_2–Br_2 (1:3 mole ratio)	
10^3C	10^6k	μ	$10^3C_{Se_2Br_2}$	10^6k
1.7	1.0	0.58	0.47	3.4
2.8	1.1	0.37	1.6	7.9
5.5	1.5	0.27	3.2	18.0
			5.6	25.0

Br_2		
10^3C	10^7k	μ
0.13	0.50	0.39
4.1	8.4	0.20
5.6	10.0	0.18
22.0	22.0	0.10

[a] In Tables II–IV C represents the molar concentration, k is the specific conductance ($\text{ohm}^{-1}\ \text{cm}^{-1}$), and μ is the molar conductance ($\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$).

The electronic spectra of Se_2Br_2 in these solvents showed a strong absorption beginning around 450 mμ with absorption increasing to the 380-mμ limit of these measurements. The spectra of $SeBr_4$ solution were dominated by a strong absorption whose λ_{max} was located at about 415, 426, 386, $<$380, and $<$380 mμ for C_6H_6, $C_6H_5NO_2$, CH_3CN, $TMSO_2$, and DMF solutions, respectively; these wavelengths correspond to those shown by Br_2 solutions. A second maximum, in the form of a shoulder on the Br_2 peak, was observed for each $SeBr_4$ solution at approximately 495, 492, 470,

TABLE III

CONDUCTANCE DATA FOR SELENIUM BROMIDES AND BROMINE IN TETRAMETHYLENE SULFONE

$SeBr_4$ (32°)			Se_2Br_2–Br_2 (1:1 mole ratio, 32°)	
10^3C	10^6k	μ	$10^3C_{Se_2Br_2}$	10^6K
1.4	5.2	3.7	1.8	5.6
2.4	6.5	2.7	3.3	9.2
3.9	8.5	2.1	3.9	11.0
5.5	10.0	1.8	6.7	14.0
8.2	14.0	1.7		
12.0	20.0	1.5		

Se_2Br_2 (30°)			Se_2Br_2–Br_2 (1:3 mole ratio, 32°)	
10^3C	10^6k	μ	$10^3C_{Se_2Br_2}$	10^6k
2.5	1.1	0.43	1.7	7.8
4.9	1.4	0.29	3.2	12.0
10.0	2.8	0.27	3.8	12.0
12.0	3.2	0.27	6.3	18.0
18.0	4.2	0.23		

Br_2 (30°)		
10^3C	10^6k	μ
4.8	1.7	0.36
9.0	1.8	0.20
14.0	1.9	0.13
21.0	2.3	0.11

TABLE IV

CONDUCTANCE DATA FOR SELENIUM BROMIDES AND BROMINE IN N,N-DIMETHYLFORMAMIDE (25°)

$SeBr_4$ (25°)			Se_2Br_2–Br_2 (1:3 mole ratio, 26°)	
10^3C	10^4k	μ	$10^3C_{Se_2Br_2}$	10^4k
5.2	3.5	69	1.9	2.9
9.5	4.2	44	3.1	3.1
11.0	4.5	41	6.1	3.6
14.0	5.1	36		

Br_2 (26°)		
10^4C	10^7k	μ
5.0	6.5	1.3
10.0	9.0	0.9

480, and 475 mμ for the same sequence of solutions. For each solvent the spectrum of $SeBr_4$ was found to be very similar to that of a 1 : 3 mole ratio solution of Se_2Br_2 and Br_2.

The results of molecular weight measurements gave average values of 212 and 267 in $C_6H_5NO_2$ and $TMSO_2$, respectively; in neither case was concentration dependence of the experimental values observed.

In C_6H_6, $C_6H_5NO_2$, CH_3CN, DMF, and $TMSO_2$ solutions of $SeBr_4$ the presence of a volatile oxidant was demonstrated by the moderately rapid appearance of the blue starch–iodine complex under the test conditions described.

Discussion

The data reported here suggest that in these solvents selenium tetrabromide undergoes dissociation followed by the establishment of an equilibrium involving selenium(I) and selenium(II) species

$$SeBr_4(c) \rightarrow SeBr_2(soln) + Br_2(soln)$$

$$2SeBr_2(soln) \rightleftharpoons Se_2Br_2(soln) + Br_2(soln)$$

The infrared spectra of solutions of $SeBr_4$ in solvents of zero or low dielectric constant (C_6H_6, CCl_4, CS_2, $CHCl_3$) are uniform in showing a very strong absorption in the ~295-cm^{-1} region; these $SeBr_4$ solution spectra differ from that of crystalline $SeBr_4$ and from those of $SeBr_2$ and its solutions. Since progressive addition of Br_2 to Se_2Br_2 in C_6H_6 produces a steady decrease in the intensity of the 265-cm^{-1} band and a parallel intensity increase in the 295-cm^{-1} absorption, it is reasonable to assume that the equilibrium above is operative. The electronic spectra of benzene solutions of $SeBr_4$ are in accord with this proposal; the addition of Se_2Br_2 to an $SeBr_4$ solution resulted in increased absorption at 495 mμ relative to the bromine absorption at 415 mμ. A previous spectrophotometric investigation of CCl_4 solutions of $SeBr_4$ has established that λ_{max} for $SeBr_2$ lies at 507 mμ and that the above equilibrium fully describes the system.[2] In view of the similarity of the infrared spectra of $SeBr_4$ and $SeBr_2$ in C_6H_6 and CCl_4 and of the spectral results for benzene solutions described here, it is suggested that the 295-cm^{-1} infrared absorption is associated with one or both of the infrared-active Se–Br stretching modes of $SeBr_2$ and that the equilibrium also satisfactorily summarizes the nature of $SeBr_4$ in benzene. This strong infrared absorption at 295 cm^{-1} is also the dominant feature of the spectra of $SeBr_4$ in both CS_2 and $CHCl_3$ and suggests a similar state of affairs in these solvents.

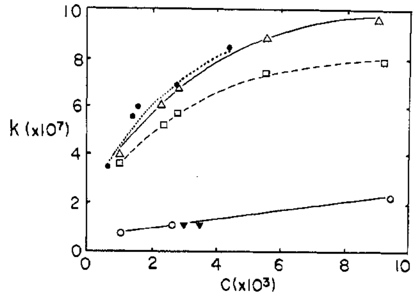

Figure 2.—Specific conductances, 10^7k, in ohm^{-1} cm^{-1} *vs.* molar concentrations, 10^3C, of nitrobenzene solutions of selenium bromides and bromine. Concentrations of all selenium-containing solutions are expressed in terms of Se_2Br_2: $SeBr_4$ (.... ● ...), Se_2Br_2–Br_2 (1:3) (——△——); Se_2Br_2–Br_2 (1:1) (— — □ — —), Se_2Br_2 (—○—), Br_2 (▼).

Since it has been reported that the infrared spectrum of crystalline $SeBr_4$ is consistent with the $SeBr_3^+Br^-$ formulation, it might be expected that solvents having moderate dielectric constants and/or coordinating capability could stabilize such ions derived from solid $SeBr_4$. The various data for such solutions, however, demonstrate that these $SeBr_4$ solutions are readily identified as equilibrium systems of $SeBr_2$, Se_2Br_2, and Br_2. Thus, as previously reported for nitrobenzene solutions,[6] volatilization tests gave evidence for the presence of a strong oxidant, presumably Br_2, in acetonitrile, tetramethylene sulfone, and N,N-dimethylformamide solutions of $SeBr_4$. The electronic

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(6) N. Katsaros and J. W. George, *Chem. Commun.*, 662 (1968).

spectra confirmed this for $C_6H_5NO_2$ and CH_3CN solutions; the λ_{max} for Br_2 in $TMSO_2$ and DMF are too low for conclusive identification.

If solutions prepared from $SeBr_4$ are indeed the equilibrium systems suggested above, 1:3 mole ratio mixtures of Se_2Br_2 and Br_2 should be identical with $SeBr_4$ solutions of equal total Se concentration. Examination of the infrared data in Table I and the electrical conductance results in Tables II–IV offers significant support for this proposal. Thus, inspection of the infrared spectra of $TMSO_2$ solutions of selenium bromides pictured in Figure 1 shows a pattern very similar to that described above for C_6H_6 solutions when Br_2 is added to dissolved Se_2Br_2. As another example, the electrical conductance results for nitrobenzene (Figure 2) show the specific conductances of $SeBr_4$ and 1:3 mole ratio Se_2Br_2–Br_2 mixtures to be very similar. Further, it is noted that the specific conductances of 1:1 mole ratio Se_2Br_2–Br_2 solutions are greater than the simple sum of the specific conductances of the solutions of the individual components. This is consistent with the occurrence of a chemical reaction between Se_2Br_2 and Br_2. It seems clear that the substance displaying enhanced electrolyte capacity, in view of the infrared data, must be $SeBr_2$.

Similar results were found, and parallel interpretation may be given, the selenium bromide systems involving the other solvents used in this study. The DMF solutions are particularly interesting owing to the relatively high conductances found for $SeBr_4$ solutions and their very different infrared spectra as compared to those of $SeBr_4$ in the other solvents. In the Results section certain difficulties with the DMF solutions, particularly with the conductance measurements thereof, are noted. It will be observed in Table IV that specific conductance values for $SeBr_4$ solutions do not compare well those of Se_2Br_2–Br_2; the source of these discrepancies may lie in the difficulties attending the solvent purification. Although impurities in DMF or the solvent itself reduced Se_2Br_2 to Se when the monobromide was dissolved alone, the presence of bromine in the solvent prevented any observable reduction; thus the preparation of experimentally useful 1:3 mole ratio $SeBr_2$–Br_2 solutions was possible.

The infrared absorption data for DMF solutions listed in Table I show a strong correspondence between $SeBr_4$ and Se_2Br_2–Br_2 in 1:3 mole ratio. The frequency of the stronger of the two absorptions is lower than that of the weaker—a different pattern than that observed for the other solvents considered here. It is possible that $SeBr_2$ is extensively coordinated by DMF in these systems and that the Se–Br stretching frequency is substantially reduced from that found in the other solutions.

Although the molecular weight findings for nitrobenzene solutions of $SeBr_4$ are in full accord with the dissociation and subsequent equilibrium suggested for these solutions, the results for $TMSO_2$ solutions are significantly higher than that expected for a two particle per formula unit dissociation. Since the other data for $TMSO_2$ solutions unambiguously support the $SeBr_2$, Se_2Br_2, and Br_2 equilibrium system, and assuming the absence of systematic errors, association effects involving these species are indicated. Cryoscopic measurements on both Br_2 and Se_2Br_2 solutions showed clearly the monomeric character of these substances in $TMSO_2$.

In the previous report[4] of the behavior of $SeBr_4$ in polar solvents, the electrolyte character, but neither the nature nor the source of the charge carriers, was noted. The results in the present study suggest that any selenium-containing ions in these solutions arise, not from selenium(IV) species, but rather from the ionization of selenium mono- and dibromides. The electrolyte nature of selenium mono- and dichlorides in CH_3CN has been described.[7] The dissociative behavior of $SeBr^4$ in polar solvents is decidedly different from that of other chalcogen tetrahalides; a further report of these matters is in preparation.[8]

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(7) H. G. Heal and J. Kane, *J. Inorg. Nucl. Chem.*, **29,** 1539 (1967).

(8) N. Katsaros and J. W. George, *Inorg. Chim. Acta,* in press.