[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Selenium Bromides. I. A Spectrophotometric Study of the Dissociation of Selenium Tetrabromide and Selenium Dibromide in Carbon Tetrachloride Solution[1,2]

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Solutions of selenium tetrabromide and systems having Br/Se ratios from 1.000 to 13.06 in dry carbon tetrachloride have been studied spectrophotometrically at 25°. All of the solutions obey Beer's law from 350 to 540 mμ over the above composition range. Selenium tetrabromide dissociates completely and all of the experimental data are consistent with the single equilibrium $2SeBr_2 = Se_2Br_2 + Br_2$ for which $K = (Se_2Br_2)(Br_2)/(SeBr_2)^2 = 0.0252$. The absorption spectrum of selenium dibromide in carbon tetrachloride solution has been determined indirectly in the equilibrium mixtures.

Introduction

There are good reasons why one might expect selenium tetrabromide to dissociate in the dissolved state. In the first place, the observation of Yost and Hatcher[3] that the density of vaporized selenium tetrabromide is just one-half the expected value indicates that some kind of dissociation takes place in the vapor phase. They interpreted their results as being due to complete dissociation according to the equation

$$SeBr_4(s) = SeBr_2(g) + Br_2(g)$$

Secondly, the dissociation of diarylselenium dihalides into the diarylselenium and free halogen has been shown by means of spectrophotometric measurements to take place in carbon tetrachloride solution. The dissociation constant, K, for a large number of equilibria of the type

$$(R_2Se)(X_2)/(R_2SeX_2) = K$$

where X_2 is bromine or iodine have been determined.[4] The observed K's range from about 0.1 to 10^{-5} at 25° when concentrations are expressed in moles per liter. There is thus strong indication that the selenium–bromine bond tends to be weak in compounds in which selenium is tetracovalent.

The present spectrophotometric study was originally undertaken to determine the extent to which the postulated dissociation takes place in

$$SeBr_4 = SeBr_2 + Br_2$$

carbon tetrachloride solution. Preliminary measurements showed that solutions formally $SeBr_4$ obey Beer's law, hence the study was extended to cover the selenium–bromine system over the range of Br/Se ratios from 1 up to 13. These limits were fixed by the observation that solutions having Br/Se ratios less than 1.00 deposit selenium spontaneously and solutions having ratios above about 13 have bromine absorbances which are too high relative to that of the selenium species present.

Experimental

Selenium.—Technical selenium was dissolved in nitric acid, filtered and evaporated to dryness. The selenious acid was dissolved in concentrated hydrochloric acid and sulfur dioxide was introduced at 15°. The precipitated selenium (tellurium remains in solution[5]) was washed with concentrated hydrochloric acid, redissolved in nitric acid and the above process repeated. The selenium was then twice converted to selenocyanate and reprecipitated.[6] Moisture was removed first by heating in an oven at 105°, then by fusion for 2 hr. *in vacuo*. The vitreous product obtained on cooling was crushed and stored in a desiccator.

Bromine.—Reagent grade bromine was mixed with reagent grade phosphorus pentoxide and gently distilled in an all-glass apparatus kept under positive pressure with dry nitrogen. The product was collected in preweighed, dry ampoules which were sealed and reweighed.

Carbon Tetrachloride.—Since reagent grade carbon tetrachloride was found to be unsatisfactory and since large quantities of pure, dry solvent were needed, technical grade carbon tetrachloride was purified. This was first distilled, the initial and final portions being discarded. Chlorine was bubbled into the center cut until a pronounced color resulted. This solution was irradiated by means of a mercury vapor lamp for 20 hr. Chlorine was removed by three extractions with aqueous sodium carbonate followed by three with water. The bulk of the remaining water was removed with anhydrous calcium chloride. Another distillation with retention of the center cut was performed. This distillate was mixed with reagent grade phosphorus pentoxide and distilled in an all-glass apparatus under positive pressure of rigorously dried nitrogen. The center cut was collected in a four-liter dispensing bottle equipped with an efficient drying tube and a greaseless, mercury-sealed stopcock. In this manner, moisture was effectively excluded over three-month periods.

Selenium Monobromide.—A weighed sample of bromine and the equivalent amount of selenium were placed in separate arms of an inverted U-shaped tube and the bromine frozen with liquid nitrogen. The tube was evacuated, sealed and warmed until all bromine had distilled onto the selenium. After heating the mixture at 100° until homogeneous, the product was cooled to room temperature and transferred to dry, preweighed ampoules which were then sealed and reweighed.

Selenium Tetrabromide.—This substance, unlike the monobromide, exhibits an appreciable bromine vapor pressure at room temperature and must be handled in dry air containing considerable bromine vapor. The compound was prepared in a manner similar to that described for the monobromide except that an excess of bromine over the 4:1 theoretical ratio was used. The crystalline tetrabromide was slowly sublimed (in the sealed tube) at 115°. The tube was then cooled to room temperature, opened and a stream of dry air nearly saturated with bromine vapor was passed over the solid to remove excess bromine. The reddish-brown crystals were transferred to dry, preweighed ampoules, sealed and reweighed. Determinations of the oxidation equivalent weight[7] gave values 99.8% of theoretical for $SeBr_4$.

A yellow crystalline form of selenium tetrabromide was observed when saturated solutions of the above material in carbon tetrachloride were rapidly cooled. These crystals show the same oxidation equivalent weight and spectrum in solution as the reddish-brown form. However, the X-ray powder diffraction patterns are distinctly different. The

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[1] Abstracted from the thesis submitted by Norman W. Tideswell to the Graduate Division of the University of California at Los Angeles in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1955.

[2] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.

[3] D. M. Yost and J. B. Hatcher, THIS JOURNAL, **53**, 2549 (1931).

[4] For reference to this work see J. D. McCullough and B. A. Eckerson, *ibid.*, **73**, 2954 (1951).

[5] E. Keller, *ibid.*, **19**, 771 (1897).

[6] T. W. Campbell and J. D. McCullough, *ibid.*, **67**, 1965 (1945).

[7] J. D. McCullough, T. W. Campbell and N. N. J. Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

relationships between the two forms are being investigated further.

Stock Solutions.—Solutions with relatively high formal concentrations and with Br/Se ratios of 1.000, 1.431, 2.016, 4.000 and 13.06 were prepared by crushing ampoules of the monobromide or tetrabromide, either alone or with ampoules of bromine, under the surface of dry carbon tetrachloride in a reagent bottle. The resulting solutions were transferred to volumetric flasks, diluted to volume, then sealed in convenient-sized ampoules until needed. A stock solution of bromine was also prepared and stored as above.

Spectrophotometric Measurements.—Absorbance measurements were made on a Cary Recording Spectrophotometer, Model 11 PMS. Matched cells with lengths of 1.000 mm., 1.000 cm. and 10.000 cm. were used as needed to bring the measurements within the range of maximum accuracy (0.200 to 0.700). Samples were prepared by dilution of the stock solutions as needed. Each dilution was independently prepared and its spectrum measured from four to nine times on separate days. Several different dilutions were studied for each stock solution. Before each analysis the sample cell was rinsed with solvent and flushed with dried air. Care was taken to check the instrument for possible shift in the zero adjustment at frequent intervals during the measurements. The temperature of the solutions during measurement in the thermostated room was always within 1° of 25°.

Results and Discussion

Except for some of the most dilute solutions, where hydrolysis caused by unavoidable traces of moisture would have its greatest effect, the absorbance measurements at all Br/Se ratios were found to obey Beer's law within the limits of error of the instrument. There are a number of circumstances and combinations of circumstances which could account for this behavior. Among these are the following.

1. No equilibria exist between the various possible selenium bromides.
2. All of the species with Br/Se ratios greater than unity dissociate completely at all concentrations to give the monobromide and bromine, which separately obey Beer's law.
3. Only equilibria whose reactions have the same number of molecules on each side of the equation are involved. Since dilution would cause no shifts in the points of equilibrium in these cases, the solutions would obey Beer's law.

This third possibility with the single equilibrium

$$2SeBr_2 = Se_2Br_2 + Br_2$$

appeared most attractive. There are two facts which support this view. First, the non-existence of $SeBr_4$ in the vapor state casts some doubt on its existence in solution. Second, it is quite evident that bromine reacts with selenium monobromide in carbon tetrachloride solution since there is a moderately rapid and very definite color change which takes place *after* solutions of bromine and of selenium monobromide in the solvent are thoroughly mixed. A test of this hypothesis showed that it was possible to account quantitatively for the spectra of all of the mixtures in terms of the independently measured spectra of bromine and of selenium monobromide, a calculated spectrum for selenium dibromide, and the equilibrium constant given in the expression

$$(Se_2Br_2)(Br_2)/(SeBr_2)^2 = K$$

Values for the molar absorptivity of selenium dibromide were treated as unknowns (one value for each wave length at which calculations were made) while the equilibrium constant, K, was treated as an unknown independent of wave length. For a given solution at a fixed wave length, it is possible to write the four simultaneous equations

$$D_nE_n/F_n^2 = K \qquad (1)$$

$$B_n = D_n + E_n + F_n \qquad (2)$$

$$S_n = 2D_n + F_n \qquad (3)$$

$$A_n = b_n(D_nd + E_ne + F_nf) \qquad (4)$$

The expression of these equations has been simplified by use of the following symbols

D_n, E_n and F_n represent the molar concn. of the species Se_2Br_2, Br_2 and $SeBr_2$, resp., in the nth soln.

d, e and f represent the molar absorptivities of the above species at some fixed wave length

B_n and S_n represent the *total moles* of bromine and the *total gram-atoms* of selenium per l., resp., in the nth soln.

A_n represents the measured absorbance of the nth soln. at the wave length selected

b_n is the optical path length or cell length, for the nth soln.

Since the four equations above contain five unknowns when applied to a single solution, it is necessary to consider four additional equations for a second solution in which the ratio B_n/S_n is different from that in the first solution. In this way, only three additional unknowns are brought in so that we now have eight equations (two sets of four with differing values of n) in the eight unknowns: D_1, E_1, F_1, D_2, E_2, F_2, f and K.

By successive elimination of unknowns, one obtains equation 5 which contains the single unknown, K.

$$\frac{-B_1 + \sqrt{(B_1 - S_1)^2 + 4KS_1(2B_1 - S_1)}}{-B_2 + \sqrt{(B_2 - S_2)^2 + 4KS_1(2B_2 - S_2)}} = \frac{b_2[2A_1 - b_1e(2B_1 - S_1) - b_1dS_1]}{b_1[2A_2 - b_2e(2B_2 - S_2) - b_2dS_2]} \qquad (5)$$

Direct determination of K at each wave length is tedious, so the following simplification was made. The left-hand side of equation 5 contains only the quantities K, B_1, B_2, S_1 and S_2 and its value must be constant, independent of wave length. The right-hand side of equation 5 contains the molar absorptivities which change with wave length. However, the value of the right-hand side must be independent of wave length if the species and equilibrium selected are correct. The wave length independence of the right-hand side of equation 5 is shown in Table I, in which the absorbance ratios for two pairs of solutions are compared over a range of wave lengths. The agreement is seen to be very good. In general, the agreement is good over this range of wave length for all solutions except the most dilute ones in which hydrolysis has its greatest effect. That the trouble in the most dilute solutions is due to hydrolysis was demonstrated by using carbon tetrachloride in some cases which was deliberately contaminated with moisture. The absorbances in these cases were shifted still further in the direction of error in the most dilute solutions to which no moisture was purposely added.

The observed absorbance measurements listed in Table II which were obtained by use of 0.1000 cm. cells are typical of the data obtained. In order to illustrate the degree to which Beer's law ($\log_{10} P_0/P = \epsilon bc = A$, the absorbance) holds for the various solutions, a complete set of absorbance

TABLE I

COMPARISON OF ABSORBANCE RATIOS (EQUATION 5) OF SOLUTIONS IN 1.000 MM. CELLS HAVING Br/Se RATIOS OF 1.431, 2.016 AND 4.000

Wave length, mμ	Absorbance ratios 1.431/2.016	Absorbance ratios 2.016/4.000
350	0.356	0.827
360	.359	.840
370	.363	.849
380	.359	.841
390	.356	.843
400	.352	.844
410	.349	.843
420	.350	.835
430	.348	.840
440	.350	.846
Av.	0.354	0.841
Mean dev. from av., %	1.2	.5
K from av.	0.0254	.0251

measurements on solutions of selenium tetrabromide in carbon tetrachloride is given in Table III. Since calculation of absorbance ratios of the type given in Table I requires the molar absorptivities of bromine and selenium monobromide, these were carefully measured and the values obtained are listed in Table IV.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED ABSORBANCES OF SELENIUM-BROMINE MIXTURES IN CARBON TETRACHLORIDE SOLUTION AT 25°

Cell thickness 0.1000 cm; concentrations ten times those given in Table V.

λ, mμ	Absorbance Br/Se = 1.431 Obsd.	Br/Se = 1.431 Calcd.	Br/Se = 2.016 Obsd.	Br/Se = 2.016 Calcd.
350	1.774	1.772	1.179	1.159
360	0.943	0.953	0.625	0.627
370	.602	.613	.404	.411
380	.523	.529	.358	.359
390	.504	.505	.360	.362
400	.478	.477	.360	.364
410	.430	.437	.344	.351
420	.363	.360	.313	.317
430	.293	.290	.270	.275
440	.230	.228	.232	.237

Values for the equilibrium constant could presumably be computed by setting the left side of equation 5 equal to the appropriate absorbance ratios. However, graphical solution of the resulting equation is much simpler. The graphs are prepared by selecting suitable arbitrary values of K and computing the resulting values for the left side of the equation. These values are plotted as a function of K and the answer is then read from the graph.

TABLE III

OBSERVED AND CALCULATED ABSORBANCES OF SOLUTIONS OF SELENIUM TETRABROMIDE IN CARBON TETRACHLORIDE AT 25°

λ, mμ	Absorbance, Obsd. values, Cell length, b, in cm., Formal concn., F: 0.1000 cm. 2.00×10^{-2}, F^a	1.000 cm. 2.00×10^{-3}, F	10.00 cm. 2.00×10^{-4}, F	Calcd. values
350	0.340	0.346	0.356	0.364
360	.248	.232	.240	.246
370	.250	.236	.234	.241
380	.304	.301	.302	.300
390	.400	.396	.398	.395
400	.482	.478	.480	.478
410	.528	.524	.524	.528
420	.526	.526	.522	.532
430	.504	.502	.498	.506
440	.468	.464	.462	.467

[a] Solubility of $SeBr_4$ in carbon tetrachloride is less than this at 25°. These values computed by means of Beer's law from data on 1.378×10^{-2} F $SeBr_4$.

TABLE IV

MOLAR ABSORPTIVITIES OF BROMINE AND SELENIUM BROMIDES IN CARBON TETRACHLORIDE

λ, mμ	Molar absorptivities Br_2 obsd.	Se_2Br_2 obsd.	$SeBr_2$ calcd.
350	14	4100	80
360	34	2210	41
370	65	1420	23
380	107	1230	14
390	151	1170	18
400	186	1090	26
410	206	961	34
420	207	794	39
430	196	624	41
440	178	478	43
450	162	364	48
460	148	292	62
470	136	242	82
480	125	203	102
490	110	171	120
500	95	145	132
510	79	120	134
520	63	97	128
530	50	77	113
540	37	61	95

As a check on the results thus obtained, absorbances for all solutions were computed by use of equation 4. The compositions of the samples used for the absorbance measurements in 1.000 cm. cells are given in Table V. The formal concentrations indicate the manner in which the solutions were prepared while the molar concentrations show the actual composition of the resulting equilibrium mixtures. The compositions of solutions used in 1.000 mm. and 10.00 cm. cells are, respectively, ten times and one-tenth the figures given in the table. The solutions having the formal composition $SeBr_4$ were made up in three different ways: from Se_2Br_2 and Br_2 as indicated, and from each of the two crystalline modifications of solid $SeBr_4$. The absorbances calculated by use of equation 4 are given in Tables II and III beside the corresponding observed values. In all cases these agree with the observed values within the errors of the determination. Where absorbances change rapidly with wave length, as they do at the short wave length end of the range, the errors are naturally larger than in the other regions.

Taking into consideration all of the reliable data in the wave length range from 350 to 440 mμ, the average value of K is 0.0252 at 25°. The standard deviation of this value is probably less than 0.0005 or 2.0% of K. With the value of K thus deter-

TABLE V

COMPOSITION OF EQUILIBRIUM MIXTURES USED IN ABSORBANCE MEASUREMENTS IN 1.000 CM. CELLS AT 25°

Ratio Br/Se	Concentration				
	Br_2		Se_2Br_2		$SeBr_2$
	Formal	Molar	Formal	Molar	Molar
1.431	3.036×10^{-4}	1.94×10^{-5}	7.048×10^{-4}	4.21×10^{-4}	5.68×10^{-4}
2.016	1.068×10^{-3}	2.7×10^{-4}	1.051×10^{-3}	2.5×10^{-4}	1.61×10^{-3}
4.000	3.000×10^{-3}	2.04×10^{-3}	1.000×10^{-3}	4.5×10^{-5}	1.91×10^{-3}
13.06	3.473×10^{-3}	3.19×10^{-3}	2.882×10^{-4}	2×10^{-6}	5.72×10^{-4}

mined, it is possible to compute values of the molar absorptivity for selenium dibromide. These are given in Table IV.

It is interesting to compare the results of the present study with those on related systems and molecules in the literature. The equilibrium

$$2SCl_2 = S_2Cl_2 + Cl_2$$

was studied in the liquid phase, without solvent, by Spong.[8] In this case

$$(S_2Cl_2)(Cl_2)/(SCl_2)^2 = K = 0.013$$

a value which is comparable to that found in the present study.

The spectrum of selenium dibromide in the vapor state has been studied by Wehrli.[9] The strongest band in the vapor was found at 513.8 mμ while the absorption maximum in solution was found in the present study at 507 mμ. The general region of strongest absorption also agrees in the two cases. The spectra found for tellurium dichloride and tellurium dibromide[10] vapor are also similar to that of selenium dibromide in carbon tetrachloride solution.

It is also of interest to note that although $SeBr_4$ exists as a crystalline solid, it does not exist in either the gaseous or the dissolved state. On the other hand, while $SeBr_2$ exists in the gaseous state and in solution, it has not been isolated as a pure phase.

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[8] A. H. Spong, *J. Chem. Soc.*, 1547 (1933).

[9] M. Wehrli, *Helv. Phys. Acta*, **9**, 329 (1936).

[10] M. Wehrli, *ibid.*, **9**, 208 (1936).

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Silver Perfluorobutyrate[1]

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The soft waxy crystals of silver perfluorobutyrate are monoclinic with $a = 6.46 \pm 0.01$, $b = 9.01 \pm 0.02$, $c = 13.11 \pm 0.04$ Å., $\beta = 100.2 \pm 0.3°$, space group C2 and two *dimeric* molecules within the unit cell. Spectrometric (MoKα) $h0l$ and $0kl$ intensity data from the best available specimens show that the excessive softness of the crystals arises from extraordinarily large thermal motions, *e.g.*, the anisotropic thermal parameter of the heavy silver atom varies between 3.4 and 7.6 Å.^{2} Dimeric molecules, involving formation of an eight-membered central ring of two silver atoms and two carboxyl groups, exist in the crystal; the central ring approximates to 2/m but the dimer as a whole has only a twofold axis in consequence of twisting within the fluorocarbon groups. Molecular models, the real Fourier synthesis $\rho(x,z)$, and finally the complex synthesis $\rho(y,z)$, give approximate positions of fluorine atoms and provide further support for this interpretation.

Introduction

Examination of the photographic X-ray data afforded by several fluorinated succinates, butyrates and acetates suggested that a determination of structure for silver perfluorobutyrate should be relatively simple. This compound is quite soluble in benzene and in ether, whereas the perfluorobutyrates of sodium, lithium, calcium and lead are but sparingly soluble.[2] Silver perfluorobutyrate is also a good deal less soluble in water and in methanol than are the others but is nearly insoluble in petroleum ether.[2]

Experimental

Silver perfluorobutyrate was prepared by mixing equivalent amounts of freshly precipitated silver oxide and an aqueous solution of perfluorobutyric acid. The material first used was furnished by Dr. Elliot Bergman of this Laboratory. In order to get usable crystals it was necessary to recrystallize from a mixed solvent, roughly one part of benzene to ten parts of petroleum ether. The crystals are typically thin diamond-shaped plates, so soft and fragile as to make them very difficult to handle without injury. They are stable in air except for superficial decomposition apparently produced by the action of ordinary light.

Oscillation and Weissenberg photographs show the X-ray symmetry 2/m, with the longer diagonal of the diamond-shaped plate as the direction of the unique monoclinic axis and the shorter diagonal conveniently chosen as the direction of the secondary axis, a. Lattice constants, as determined with CuKα radiation ($\lambda = 1.5418$ Å.), are $a = 6.46 \pm 0.01$, $b = 9.01 \pm 0.02$, $c = 13.11 \pm 0.04$ Å., $\beta = 100.2 \pm 0.3°$. The systematic vanishings, hkl with $h + k$ odd, are those required by the space groups C2/m, C2 and Cm. The assumption of four (monomeric) molecules within the cell, subsequently confirmed by the analysis of the diffraction data, leads to a calculated density of 2.84 g./cc.

Intensity measurements were carried out on two bar-shaped specimens cut from plates along the principal diagonals, *i.e.*, cut parallel to a and b, respectively. Average dimensions normal to a and b were 0.085 by 0.22 mm. and 0.065 by 0.17 mm. It seemed out of the question to cut specimens down to square cross-section without introducing intolerable distortion. The excessive softness of the crystals doubtless arises from extraordinarily large thermal motions in the crystal, for despite the presence of silver atoms, the range of recordable reflections is limited to $\sin \theta/\lambda \leq 0.72$. A General Electric XRD-3 Geiger Counter Spectrometer, adapted for single crystal work with convergent beam technique by Dr. R. E. Hughes, was used to measure the integrated intensities of all $0kl$ and $h0l$ reflections recordable with MoKα radiation. The most important ad-

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[1] Supported by the Atomic Energy Commission under Contract No. AT(30-1)-878 with Cornell University.

[2] Brochure entitled, "Heptafluorobutyric Acid," Minnesota Mining and Manufacturing Co., St. Paul, Minn.