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

The Spectrophotometric Determination of the Dissociation Constants of Diphenylselenium Dibromide and Diphenylselenium Diiodide

BY JAMES D. McCULLOUGH

Several properties of the diphenylselenium dihalides indicate a rather loose bonding of the halogen atoms to selenium. Krafft and Lyons[1] found that when heated just above its melting point in a sealed tube, diphenylselenium dibromide undergoes a self bromination in the ring, yielding *p,p'*-dibromodiphenylselenium, diphenylselenium and hydrogen bromide. The analogous reaction with the dichloride was also found to occur. Leicester[2] found that upon dissolving diphenylselenium dibromide in acetone, the solvent was brominated with formation of diphenylselenium. The dichloride did not undergo a similar reaction. X-Ray investigations of the crystal structure of diphenylselenium dibromide[3] and of diphenylselenium dichloride[4] show selenium–halogen bond distances which are somewhat large; the observed distances being 2.52 Å. for Se–Br and 2.30 Å. for Se–Cl. The distances calculated using covalent radii are 2.31 and 2.16 Å., respectively. The melting points,[5] 148° for the dibromide and 183° for the dichloride are somewhat out of line in view of the similarity in molecular and crystal structures for the two dihalides, indicating possible dissociation, at least in the case of the dibromide.

The object of the present work has been to establish the fact that diphenylselenium dibromide does dissociate into diphenylselenium and bromine, to show that diphenylselenium and iodine combine to a limited extent, even though the solid diiodide does not separate at room temperature, and to determine the dissociation constants for the dibromide and the diiodide.

Experimental

Preparation of Materials.—Diphenylselenium dibromide was prepared by adding pure bromine to Eastman Kodak Company diphenylselenium in carbon tetrachloride solution. The resulting solid was recrystallized from carbon tetrachloride three times. The purity of the material was checked by the analysis described later. A solution of pure diphenylselenium in carbon tetrachloride was prepared by adding excess powdered C. P. zinc and a weighed sample of pure diphenylselenium dibromide to the solvent. The mixture was shaken until all of the dibromide was dissolved and the solution became colorless. The solution was then filtered, the solid was washed several times with carbon tetrachloride and the washings were added to the filtrate. The filtrate was then made up to the desired volume. The concentration of diphenylselenium in the solution was based on the weight of the dibromide taken and the final volume of the solution. Bromine, iodine and carbon tetrachloride were purified by the usual methods.

Apparatus and Procedure.—All spectrophotometric measurements were made by means of a Beckman Quartz Photoelectric Spectrophotometer. Carbon tetrachloride was used as the solvent in all cases, and loss of volatile materials from the absorption cells was reduced so as to be inappreciable by capping the cells with cover glass slips held down firmly with cellulose tape. No provision was made for maintenance of constant temperature but in all cases a thermometer was kept near the absorption cells and read from time to time. At the end of each series of measurements, the temperature of the solutions was checked. All temperatures were within one degree of 26°. The transmission of light by a given solution is measured relative to the transmission of the pure solvent which is arbitrarily set at 1.000. The cells used had a depth of 1.30 cm. Corrections were applied for the slight differences in depth from cell to cell, the maximum correction being well under 1%.

Extinction coefficients for diphenylselenium, bromine and iodine were each determined at three different concentrations, and Beer's law was found to hold over the range of concentrations used in the equilibrium measurements. These extinction coefficients, as well as those of the dibromide and diiodide are shown in Table I and in Fig. 1.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF DIPHENYLSELENIUM DIBROMIDE, DIPHENYLSELENIUM DIIODIDE AND THEIR DISSOCIATION PRODUCTS

λ, mμ	Diphenylselenium dibromide	Diphenylselenium diiodide	Diphenylselenium	Bromine	Iodine
320	8850		35.1		
330	7910		7.8	3.1	28
340	6910	11200	3.5	5.4	22
350	5600	13200	2.1	12.3	16
360	4670	13200	1.3	26	12
370	3530	11600	0.8	53	9
380	2620	9100	.6	87	7
390	1760	6700	.4	129	6
400	1130	4620	.4	166	6
410	745	3240	.4	192	10
420	410		.3	188	23

In order to determine the extinction coefficients for the undissociated diphenylselenium dibromide molecule, meas-

---

[1] F. Krafft and R. E. Lyons, *Ber.*, **27**, 1761 (1894).

[2] H. M. Leicester, THIS JOURNAL, **57**, 1901 (1935).

[3] McCullough and Hamburger, *ibid.*, **63**, 803 (1941).

[4] McCullough and Hamburger, *ibid.*, **64**, 508 (1942).

[5] Lyons and Bush, *ibid.*, **30**, 835 (1908).

urements were made on solutions in which the dissociation was suppressed by the presence of a large excess of diphenylselenium. The values so obtained were verified over a part of the wave length range by a series of measurements in which the dissociation was suppressed by the presence of a large excess of bromine. The contribution of the excess reagent to the absorption of light was in each case determined by making measurements on solutions containing the excess reagent at the same concentration in the absence of diphenylselenium dibromide. Transmission data and the resulting extinction coefficients are shown in Tables II and III. In making these calculations, allowance was made for the fact that the dissociation was not completely suppressed, the degree of dissociation being calculated by use of the dissociation constant given later.

TABLE II

EXTINCTION COEFFICIENTS FOR DIPHENYLSELENIUM DIBROMIDE (DIPHENYLSELENIUM IN EXCESS)

Solution 1, 2.0 × 10^{-2} M in diphenylselenium; Solution 2, 2.0 × 10^{-2} M in diphenylselenium and 7.1 × 10^{-5} M in diphenylselenium dibromide.

λ, mμ	Transmission (1)	Transmission (2)	ε
330	0.625	0.120	7920
340	.810	.192	6920
350	.860	.271	5550
360	.895	.341	4620
370	.936	.447	3530
380	.961	.555	2620
390	.975	.676	1760
400	.978	.770	1130
410	.978	.835	745
420	.980	.896	410

TABLE III

EXTINCTION COEFFICIENTS FOR DIPHENYLSELENIUM DIBROMIDE (BROMINE IN EXCESS)

Solution 1, 1.12 × 10^{-2} M in bromine; Solution 2, 1.12 × 10^{-2} M in bromine and 5.1 × 10^{-5} M in diphenylselenium dibromide.

λ, mμ	Transmission (1)	Transmission (2)	ε
320	0.887	0.232	8850
330	.895	.268	7900
340	.834	.292	6900
350	.667	.281	5650
360	.413	.201	4720

The dissociation constant for diphenylselenium dibromide is given by the expression

$$K_1 = \frac{[(C_6H_5)_2Se][Br_2]}{[(C_6H_5)_2SeBr_2]} = \frac{\alpha^2}{1-\alpha}M \qquad (1)$$

where α is the degree of dissociation and M the molarity. If we represent the extinction coefficients of diphenylselenium dibromide; diphenylselenium and bromine by ϵ_1, ϵ_2 and ϵ_3, respectively, then the optical density, d, of a solution of diphenylselenium dibromide is given by the equation

$$d = lM[\epsilon_1(1-\alpha) + \alpha(\epsilon_2 + \epsilon_3)] = \log_{10}(I_0/I) \qquad (2)$$

where l is the distance the light travels through the solution, I_0 the intensity of the incident light and I the intensity of the emergent light. From the measured values of the transmission, I/I_0, and the extinction coefficients, we may calculate α and hence K_1. Absorption data on solutions of diphenylselenium dibromide of various concentrations and values of K_1 derived therefrom are shown in Table IV.

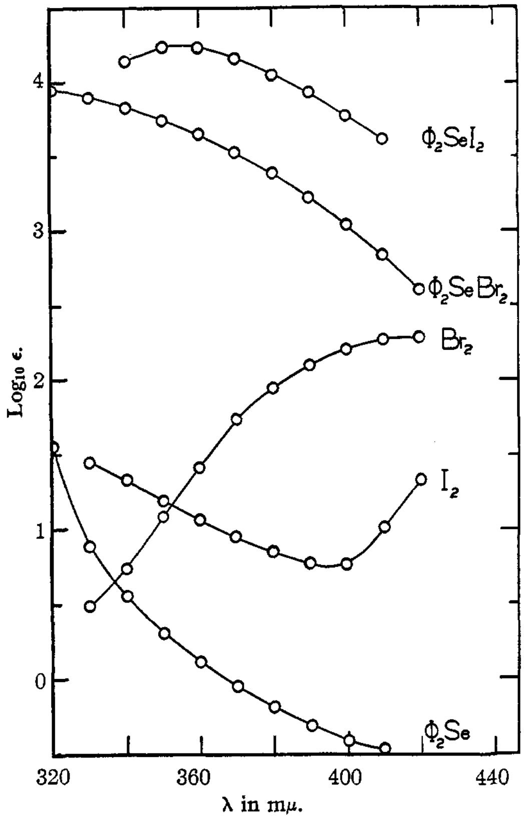

Fig. 1.—Molar extinction coefficients for several substances in carbon tetrachloride solution.

Because of the much larger dissociation constant of diphenylselenium diiodide, it is not practical to attempt complete suppression of the dissociation. The extinction coefficients and dissociation constant for the diiodide are accordingly simultaneously determined by a method different from that just employed for the dibromide.

When using light of such wave length that the undissociated molecule is the only important absorber, the measured optical densities, d_1 and d_2 at the molarities M_1 and M_2 are directly proportional to the concentrations of the undissociated compound. Using C_1 and C_2 to represent the concentrations of diphenylselenium (or of iodine) in the two solutions, we have

$$K_2 = C_1^2/(M_1 - C_1) = C_2^2/(M_2 - C_2) \qquad (3)$$

and

$$d_2/d_1 = (M_2 - C_2)/(M_1 - C_1) \qquad (4)$$

TABLE IV

THE TRANSMISSION, T, AND THE DISSOCIATION CONSTANT, K_1, FOR DIPHENYLSELENIUM DIBROMIDE AT SEVERAL CONCENTRATIONS

The upper figures are the transmissions and the lower figures (in parentheses) are the calculated values of $K_1 \times 10^4$.

λ, mμ	Concentration × 10⁴ 1.62	2.00	2.67	4.00
330	0.448 (4.9)	0.327 (5.0)	0.168 (4.9)	
340	0.500 (4.9)	0.386 (5.1)	0.218 (5.0)	
350	0.572 (4.9)	0.465 (5.1)	0.292 (5.0)	
360	0.632 (5.0)	0.537 (5.3)	0.372 (5.4)	0.140 (4.9)
370	0.680 (4.7)	0.594 (5.0)	0.442 (5.0)	0.212 (4.7)
380	0.742 (4.8)	0.680 (5.5)	0.549 (5.4)	0.313 (4.8)
390	0	0.743 (5.4)	0.640 (5.4)	0.435 (4.9)
400		0.793 (5.1)	0.713 (5.3)	0.548 (4.9)

Av. K_1 5.02 × 10^{-4}

For a given pair of solutions, the ratio d_2/d_1, should be constant with varying wave length. After correction is made for absorption due to diphenylselenium and iodine based on the assumption of complete dissociation, this ratio is actually fairly constant as shown in Table V.

TABLE V

TRANSMISSIONS AND OPTICAL DENSITIES OF SOLUTIONS OF DIPHENYLSELENIUM DIIODIDE

Solution 1, 6.0 × 10^{-4} M in iodine and 6.0 × 10^{-4} M in diphenylselenium; Solution 2, 12.0 × 10^{-4} M in iodine and 12.0 × 10^{-4} M in diphenylselenium.

λ	Solution 1 T	$d_{\text{cor.}}$	Solution 2 T	d_{cor}	Ratio d_2/d_1
340	0.698	0.139	0.260	0.544	3.91
350	.667	.162	.217	.635	3.92
360	.670	.165	.222	.632	3.83
370	.706	.142	.271	.550	3.87
					Av. 3.88

The average value of this ratio, 3.88, when used in equations 3 and 4 leads to a value 0.035 for K_2. Extinction coefficients for diphenylselenium diiodide are now readily calculated from the absorption data in Table V and are given in Table I. In the wave length range λ 380 to λ 410, the extinction coefficients are based on the 0.00120 M solution since the more dilute solution absorbs too little in this region for accurate measurements.

In order to check the value of K_2 obtained by the above method, measurements were made on several solutions containing diphenylselenium in excess of iodine. The concentrations of the various species present at equilibrium were calculated from the transmissions and extinction coefficients by means of the equation

$$d = l[\epsilon_1 C_1 + \epsilon_2(C_2 - C_1) + \epsilon_3(C_3 - C_1)] \qquad (5)$$

where the subscripts 1, 2 and 3 refer to diphenylselenium diiodide, diphenylselenium and iodine, respectively. The concentrations of diphenylselenium and iodine, as represented by C_2 and C_3 are those that would be present if no combination took place. The transmission data and values of K_2 calculated in this way are shown in Table VI. The agreement is excellent considering that the concentration ratio of diphenylselenium to iodine was over 300 in some runs while the data in Table V were obtained from solutions in which the two reactants were present in equimolar quantities.

TABLE VI

TRANSMISSIONS OF SOLUTIONS CONTAINING DIPHENYLSELENIUM AND IODINE, THE DISSOCIATION CONSTANT FOR DIPHENYLSELENIUM DIIODIDE

λ, mμ	Concn. diphenylselenium, × 10^3	Concn. iodine, × 10^5	T	Concn. diphenylselenium diiodide, × 10^5	K_2
390	28.8	17.0	0.209	7.7	0.035
400			.350	7.4	.037
410			.467	7.6	.036
340	6.1	17.0	.397	2.5	.036
350			.356	2.5	.036
360			.367	2.4	.037
370			.420	2.4	.037
380			.503	2.5	.036
390			.612	2.4	.037
400			.718	2.3	.039
410			.780	2.5	.036
400	6.1	102	.118	15	.035
410			.231	15	.035
350	22.3	6.9	.290	2.7	.035
360			.313	2.6	.037
370			.378	2.6	.037
380			.467	2.7	.035
390			.583	2.6	.037
400			.676	2.7	.035
410			.750	2.8	.033
				Av.	0.0360

Direct measurement of the dissociation constant for diphenylselenium dichloride was found to be impractical because of the low degree of dissociation even at low concentrations. An attempt was made to determine the value of this constant by observing the extent of the reaction

$$(C_6H_5)_2SeCl_2 + Br_2 = (C_6H_5)_2SeBr_2 + Cl_2 \quad (6)$$

On adding bromine to diphenylselenium dichloride solution, the transmission is reduced much more than would be expected if no reaction took place, but the problem is complicated by two additional equilibria

$$Br_2 + Cl_2 = 2BrCl \quad (7)$$

$$(C_6H_5)_2SeBr_2 + (C_6H_5)_2SeCl_2 = 2(C_6H_5)_2SeBrCl \quad (8)$$

Reaction (7) is well known and (8) was demonstrated to occur by making absorption measurements on the three solutions (1) 0.0027 M in diphenylselenium dichloride, (2) 0.00022 M in diphenylselenium dibromide, (3) 0.0027 M in diphenylselenium dichloride + 0.00022 M in diphenylselenium dibromide.

The transmission of the third solution should be equal to the product of the transmissions of the first two if no reaction takes place. The individual transmissions and the product of the transmissions of solutions 1 and 2 are compared in Table VII.

TABLE VII

EVIDENCE FOR INTERACTION BETWEEN DIPHENYLSELENIUM DIBROMIDE AND DIPHENYLSELENIUM DICHLORIDE

	Transmission				
λ, mμ	(1) Diphenylselenium dichloride	(2) Diphenylselenium dibromide	(3) Mixed solution	(4) Product (1) × (2)	Ratio (3)/(4)
350	0.355	0.415	0.099	0.147	0.67
360	.575	.499	.244	.287	0.85
370	.739	.582	.430	.429	1.09
380	.834	.662	.590	.552	1.07
390	.900	.728	.722	.655	1.09
400	.934	.795	.814	.742	1.10

The dissociation of the diarylselenium dihalides makes possible a rapid and accurate volumetric procedure for their determination. When the dibromides or dichlorides are shaken either in the solid state or the dissolved state with excess aqueous potassium iodide, an equivalent quantity of iodine is liberated. This iodine may then be titrated as usual with sodium thiosulfate solution. The solid material (0.1 to 0.5 g.) is weighed and added to a glass-stoppered flask containing about 25 ml. of approximately 0.3 N potassium iodide solution which has been acidified with 1–2 ml. of 6 N sulfuric acid. The addition of about 5 ml. of carbon bisulfide just before adding the dihalide speeds up the reaction by dissolving the solid. This mixture is shaken for a few seconds and then titrated at once with standard sodium thiosulfate. Starch solution is added near the end-point. The concentration of a solution of a diarylselenium dihalide may be determined in the same manner. Data in support of the quantitative nature of this procedure are shown in Table VIII.

TABLE VIII

VOLUMETRIC ANALYSIS OF DIARYLSELENIUM DIHALIDES

Compound	Sample, g.	Volume $Na_2S_2O_3$ (0.05132 N), ml.	Equiv. wt. Anal.	Equiv. wt. Calcd.
Diphenylselenium dibromide	0.2594	25.76	196.4	196.5
	.2444	24.24	196.8	
Diphenylselenium dichloride	.1545	19.84	151.9	152.1
Di-p-tolylselenium dibromide	.3425	31.70	210.5	210.5
	.3567	33.08	210.1	

The dissociation of the diphenylselenium dihalides is, from a structural standpoint, analogous to the dissociation of phosphorus pentachloride and related molecules into the trihalides and free halogen. The similarity of molecular structure between diphenylselenium dihalides and phosphorus pentachloride was predicted by Pauling[6] and verified by crystal structure determinations.[3,4] The molecular structure of phosphorus pentachloride is that of a trigonal bipyramid, the phosphorus atom being at the center of the common base, three chlorine atoms being in the equatorial positions at a distance[6] of 2.04 Å. from the phosphorus atom and the other two chlorine atoms at the apices of the bipyramid at a distance of 2.11 Å. from the phosphorus atom. The last two chlorine atoms are less firmly bonded than the other three as indicated by the dissociation $PCl_5(g) = PCl_3(g) + Cl_2(g)$ which takes place in phosphorus pentachloride vapor and by the lower bond energy[6] (39.4 kcal./mole) for an apical P–Cl bond, as compared to the value 62.8 kcal./mole for a normal P–Cl bond. In the diphenylselenium dihalides, the halogen atoms occupy the apical positions and it is not surprising that the selenium–halogen bond distances are longer than for normal bonds and that the molecules dissociate into diphenylselenium and free halogen.

In a structural investigation of the trimethylantimony dihalides, Wells[7] found similar structures with the halogen atoms in the apical positions at distances somewhat greater than for normal Sb–X bonds. Considering all these facts, one might expect that in molecules of the general types R_3

---

[6] Pauling, "The Nature of the Chemical Bond," second edition. Cornell University Press, Ithaca, N. Y., pp. 57, 109, 111.

[7] A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

(P, As, Sb, Bi)X_2, R_2 (S, Se, Te)X_2, and RIX_2, the halogen atoms would occupy apical positions in a trigonal bipyramidal structure at distances from the central atom which are greater than for normal M–X bonds. It is also reasonable to expect that all of these molecules show more or less tendency to dissociate in solution, giving the free halogen, X_2, as one product. A number of these dissociation constants are now being determined in this Laboratory.

Summary

1. Spectrophotometric studies of diphenylselenium dibromide and diphenylselenium diiodide indicate that these substances dissociate in carbon tetrachloride solution into diphenylselenium and the free halogen.

2. Dissociation constants for both compounds have been determined at 26° ± 1° at which $K_1 = [(C_6H_5)_2Se][Br_2]/[(C_6H_5)_2SeBr_2] = 5.02 \times 10^{-4}$; and $K_2 = [(C_6H_5)_2Se][I_2]/[(C_6H_5)_2SeI_2] = 3.60 \times 10^{-2}$.

3. Molar extinction coefficients for diphenylselenium, diphenylselenium dibromide and diphenylselenium diiodide are shown in Table I and in Fig. 1.

4. An accurate volumetric procedure for the determination of diarylselenium dihalides is described.

LOS ANGELES, CAL. RECEIVED JUNE 19, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXV. The Photochemical Decomposition of *n*-Butyl Methyl Ketone

BY WALLACE DAVIS, JR.,[1] AND W. ALBERT NOYES, JR.

The photochemical decompositions of *n*-butyl methyl ketone and of other ketones containing multi-carbon alkyl groups attached to the carbonyl have been investigated by Norrish and his co-workers.[2] On the basis of their results these authors have suggested that such ketones undergo two types of decomposition, which they designate as I and II

Type I: $R_1CH_2CH_2CH_2COR_2 = CO + (R_1CH_2CH_2CH_2R_2 + R_2R_2 + (R_1CH_2CH_2CH_2)_2)$

Type II: $R_1CH_2CH_2CH_2COR_2 = R_1CH{=}CH_2 + CH_3COR_2$.

Thus for *n*-butyl methyl ketone the reactions would be

Type I: $CH_3CH_2CH_2CH_2COCH_3 = CO +$ hydrocarbons (ethane, pentane, and octane)

Type II: $CH_3CH_2CH_2CH_2COCH_3 = CH_3CH{=}CH_2 + CH_3COCH_3$.

The theoretical discussion of this photochemical reaction will be reserved for a later article in which further data will be presented. It may be pointed out in passing that Norrish and his co-workers have come to the conclusion that the Type I reaction probably proceeds by a free radical mechanism whereas Type II proceeds in a single step leading to the final products. Others have discussed methods by which such a one-step process could occur,[3] and still others are inclined to the belief that Type II can also be explained by a free radical mechanism.[4]

Since acetone, if formed, would decompose photochemically to give carbon monoxide, any photochemical experiment leading to a large percentage decomposition of *n*-butyl methyl ketone would yield carbon monoxide as a secondary product. Furthermore, Norrish found that the yield of carbon monoxide was low. Since the stability of RCO radicals may vary markedly with the temperature, the quantum yields of all the products should be determined over a wide range of conditions.

The objects of the present investigation were as follows: (1) to apply and if necessary devise methods for the micro-analysis of the products formed during the photochemical decomposition of *n*-butyl methyl ketone so that the initial stages of the reaction could be investigated; (2) to determine the quantum yields of the various prod-

---

[1] Eastman Kodak Company Fellow in Photochemistry at the University of Rochester, 1941–1942. Mr. Davis resigned from this Fellowship in February, 1942, to accept a research position connected with National Defense, and being unable to continue the problem, the preliminary results he obtained are being published at the present time.

[2] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1531 (1938).

[3] F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

[4] G. B. Kistiakowsky; for mention see V. R. Ells and W. Albert Noyes, Jr., THIS JOURNAL, **61**, 2495 (1939); see W. Albert Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York, N. Y., 1941, p. 365.