The Dissociation Constants of Some Symmetrically Disubstituted Diphenylselenium Dibromides

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In an earlier investigation,¹ diphenylselenium dibromide was found to dissociate in carbon tetrachloride solution with formation of diphenylselenium and bromine. The value of the disso-ciation constant $K = [(C_6H_6)_2Se][Br_2]/[(C_6H_6)_2-SeBr_2]$, was determined spectrophotometrically at 26° and found to be 5.02 $\times 10^{-4}$. The object of the present investigation has been to study the effect of ring substituents on the dissociation of the selenium-bromine bonds. This has been accomplished by measuring the dissociation constants of a number of symmetrically disubstituted diphenylselenium dibromides. It has also been of interest to correlate these equilibrium constants with the generalizations of Hammett² drawn from the ionization constants of substituted benzoic acids and from other systems.

Experimental

Preparation of Materials .--- The di-p-methoxy- and di-pphenoxydiphenylselenides were prepared by the method of Alquist and Nelson³ which involves reaction of selenium oxychloride with the appropriate phenyl ether. The resulting dichlorides were reduced with powdered zinc to give the selenides. The other selenides were prepared by the method of Leicester and Bergstrom⁴ which makes use of the reaction of potassium selenide with the diazonium salt of the appropriate aniline derivative. The authors are indebted to Mr. Tod Campbell for the synthesis of most of the selenides used in this investigation.

The solid selenides were purified through several recrystallizations from methanol or a methanol-benzene mixture. The di-p-fluoro- and di-m-chlorodiphenyl selenides as well as the di-m-tolyl selenide are liquids at the usual as well as the ut-m-tory second are notice at the unified laboratory temperatures and were accordingly purified through recrystallization of their dibromides. Weighed samples of these purified dibromides were then reduced with powdered zinc in carbon tetrachloride to give colorless solutions of the selenides. Dibromides of all of the selenides except those substituted in the ortho position were prepared by addition of a carbon tetrachloride solution of pure bromine to solutions of the selenides in that solvent. In each case the product was recrystallized a number of times from purified carbon tetrachloride containing a small amount of bromine. The ortho substituted selenides form unstable dibromides which exist only in solution.

Bromine and carbon tetrachloride were purified by customary methods.

Procedure .- The dissociation constants were determined spectrophotometrically using a Beckman Photo-electric Quartz Spectrophotometer. The procedure and methods of calculation have been described in a previous publication.¹ Since there was no means of thermostating the solutions, their actual temperatures were observed during and at the end of each series of measurements. Variation of laboratory temperature from day to day and the heating effect of the light source caused the solution temperatures to vary from 26 to 32°, although there was little variation during any given set of equilibrium measurements. By making some determinations in a coldroom it was possible to calculate temperature coefficients for three of the dissociation constants and to use these coefficients in correcting all equilibrium constants to 25° for comparison purposes.

Results and Discussion

Molar extinction coefficients for the various dibromides are given in Table I while those for the selenides appear in Table II. The calculated dissociation constants are given in Table III for the actual temperatures at which measurements

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF SYMMETRICALLY DISUBSTITUTED DIPHENYLSELENIUM DIBROMIDES

| 21001 | | | | | |
|--|--|--|--|---|--|
| λ(mµ) | o-C1 | <i>m</i> -Cl | p-C1 | o-CH | m-CH ₁ |
| 330 | 7300 | 4720 | 7360 | 6640 | 6900 |
| 340 | 63 00 | 4130 | 6720 | 6030 | 5790. |
| 350 | 52 00 | 3360 | 5620 | 5500 | 4680 |
| 360 | 4200 | 2650 | 450 0 | 4660 | 3690 |
| 370 | 3400 | 2 010 | 3420 | 3810 | 288 0 |
| 380 | 2700 | 1520 | 2560 | 3020 | 2130 |
| 390 | 2200 | 1150 | 1840 | 2310 | 1470 |
| 400 | 1800 | 867 | 1340 | 1730 | 960 |
| 410 | 15 00 | 670 | 940 | 1330 | 600 |
| | | | | | |
| λ(mμ) | <i>p</i> -CH₃ | p-F | p-Br | <i>p-</i> CH₂O | p-CeHiO |
| λ(mµ) 330 | ∌-Сн ₁ 7310 | р-F 6260 | ⊅-Br 7060 | <i>p-</i> CH₂O | р-СаНаО 9760 |
| λ(mμ) 330 340 | р-Сн а 7310 6190 | ₽-F 6260 5490 | p-Br 7060 6120 | р-Сн.О 6730 | р-СаНаО 9760 8690 |
| λ(mμ) 330 340 350 | р-Сн. 7310 6190 5010 | <i>p</i> -F 6260 5490 4590 | <i>p</i> -Вr 7060 6120 5200 | p-CH₂O 6730 6350 | p-CaH3O 9760 8690 7920 |
| λ(mμ) 330 340 350 360 | ⊅-Сн. 7310 6190 5010 3980 | <i>p</i>-F 6260 5490 4590 3760 | <i>p</i> -Вr 7060 6120 5200 4280 | <i>p</i>-CH₁O 6730 6350 5570 | p -C₀H₅O 9760 8690 7920 6710 |
| λ(mμ) 330 340 350 360 370 | р-Сн. 7310 6190 5010 3980 3060 | <i>p</i>-F 6260 5490 4590 3760 2930 | <i>p</i>-Вг 7060 6120 5200 4280 3360 | p-CH ₄ O 6730 6350 5570 4570 | <i>p</i>-C₆H₆O 9760 8690 7920 6710 5390 |
| λ(mμ) 330 340 350 360 370 380 | <i>p</i> -CH ₁ 7310 6190 5010 3980 3060 2260 | <i>p</i>-F 6260 5490 4590 3760 2930 2130 | <i>p</i>-Br 7060 6120 5200 4280 3360 2500 | p-CH ₁ O 6730 6350 5570 4570 3550 | p -C₀H₀O 9760 8690 7920 6710 5390 4130 |
| λ(mμ) 330 340 350 360 370 380 390 | <i>p</i> -CH ₄ 7310 6190 5010 3980 3060 2260 1600 | р-F 6260 5490 4590 3760 2930 2130 1450 | <i>p</i>-Br 7060 6120 5200 4280 3360 2500 1800 | <i>p</i> -CH₄O 6730 6350 5570 4570 3550 2600 | p -C ₄ H ₄ O 9760 8690 7920 6710 5390 4130 2950 |
| λ(mμ) 330 340 350 360 370 380 390 400 | <i>p</i> -CH ₁ 7310 6190 5010 3980 3060 2260 1600 1040 | <i>p</i>-F 6260 5490 4590 3760 2930 2130 1450 949 | <i>p</i>-Br 7060 6120 5200 4280 3360 2500 1800 1300 | ¢-CH4O 6730 6350 5570 4570 3550 2600 1840 | p-CaHaO 9760 8690 7920 6710 5390 4130 2950 2080 |
| λ(mμ) 330 340 350 360 370 380 390 400 410 | <i>p</i> -CH ₁ 7310 6190 5010 3980 3060 2260 1600 1040 670 | <i>p</i>-F 6260 5490 4590 3760 2930 2130 1450 949 583 | <i>p</i>-Br 7060 6120 5200 4280 3360 2500 1800 1300 980 | <i>p</i> -CH ₄ O 6730 6350 5570 4570 3550 2600 1840 1290 | p -C ₆ H ₄ O 9760 8690 7920 6710 5390 4130 2950 2080 1440 |

TABLE II

MOLAR EXTINCTION COEFFICIENTS OF SYMMETRICALLY DISUBSTITUTED DIDUENVI SPLENIDES

| | D1200211 | 10100 | DIFIIGNIN | OFFERI | 153 |
|-----------------|-------------|--------------|-----------|----------------|-----------------|
| $\lambda(m\mu)$ | o-Ci | <i>m</i> -C1 | p-C1 | o-CH: | m-CHe |
| 330 | 20.0 | 7.3 | 29.2 | 6.9 | 18. 2 |
| 340 | 5.3 | 1.4 | 3.7 | 2.6 | 3.9 |
| 350 | 2.0 | 1.1 | 2.1 | 2.1 | 2.4 |
| 360 | 1.4 | 0.8 | 1.7 | 1.7 | 1.6 |
| 370 | 0. 9 | 0.5 | 1.2 | 1.2 | 1.0 |
| 380 | | | 0.7 | 0.7 | 0.7 |
| 390 | | | 0.3 | | |
| $\lambda(m\mu)$ | ¢-CH₁ | <i>p</i> -F | p-Br | <i>p</i> -CH₂O | ⊅-C ₀H₀O |
| 33 0 | 23.7 | 5.2 | 31.4 | | 51.5 |
| 340 | 6.8 | 2.5 | 5.5 | 24.3 | 13.2 |
| 350 | 4.2 | 1.8 | 2.6 | 6.0 | 4.0 |
| 360 | 2.6 | 1.2 | 2.0 | 2.4 | 2.7 |
| 370 | 1.6 | 0.7 | 1.5 | 1.2 | 1.9 |
| 380 | 0.8 | 0.4 | 1.0 | 0.7 | 1.4 |
| 390 | | 0.2 | 0.5 | 0.4 | 0.9 |

J. D. McCullough, THIS JOURNAL, 64, 2672 (1942).
 Louis P. Hammett, "Physical Inorganic Chemistry," Chapter VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

⁽³⁾ Alquist and Nelson, THIS JOURNAL, 53, 4033 (1931).

⁽⁴⁾ Leicester and Bergstrom, ibid., 51, 3587 (1929); cf. "Organic Syntheses," Coll. Vol. II.

DISSOCIATION CONSTANTS OF SYMMETRICALLY DISUBSTI-TOTED DIPHENYLSELENIUM DIBROMIDES

| | Temp., | | |
|-----------------------------------|--------|----------------------|----------------------|
| Substituent | °C. | K | K(25.0°C.) |
| None | 26.0 | 5.0×10^{-4} | $4.8 	imes 10^{-4}$ |
| 0-C1 | 30.0 | 1.1×10^{-1} | $8.5	imes10^{-2}$ |
| m-Cl | 31.0 | $1.4 	imes 10^{-2}$ | $1.1	imes10^{-2}$ |
| p-Cl | 31.5 | $2.9	imes10^{-3}$ | $2.1	imes10^{-3}$ |
| | 12.2 | $1.2	imes10^{-3}$ | |
| 0-CH3 | 30.0 | 8.9×10^{-3} | 7.0×10^{-3} |
| m-CH _a | 29.0 | $1.7	imes10^{-4}$ | $1.4 	imes 10^{-4}$ |
| p-CH ₃ | 32.0 | $5.0	imes10^{-6}$ | $3.6	imes10^{-5}$ |
| | 2.0 | 1.4×10^{-5} | |
| <i>p</i> -F | 29.2 | 1.5×10^{-3} | $1.2 	imes 10^{-3}$ |
| p-Br | 31.4 | $3.8	imes10^{-3}$ | $2.8	imes10^{-3}$ |
| | 14.8 | 1.5×10^{-3} | |
| p -CH₃O | 30.5 | $3.5	imes10^{-6}$ | 2.7×10^{-5} |
| p-C ₆ H ₅ O | 27.3 | $1.2	imes10^{-4}$ | 1.1×10^{-4} |

were made as well as for the comparison temperature, 25° . Dissociation constants for the *p*chloro, *p*-bromo and *p*-methyl compounds are



Fig. 1.—Plot of log k against Hammett's substituent constant.

each given for two different temperatures and calculation of their heats of dissociation in solution are thus permitted. The calculated values of this heat effect are 7.8, 9.7 and 8.4 kcal./mole, respectively. The average of these values, 8.6 kcal./mole, was used in making temperature corrections to 25° for all of the dibromides.

Following the method of Hammett, the logarithms of the dissociation constants have been plotted against the substituent constants in Fig. The straight line best representative of the 1. points was located by use of the method of least squares. The slope of this line, designated as ρ , has the value 4.2 and is a measure of the susceptibility of the dissociation to changes in electron density on the selenium atom. The positive value indicates that the selenium-bromine bond is weakened by a lowering of the electron density on the selenium atom. The value found for ρ is quite high, in fact higher than any tabulated by Hammett. It should be borne in mind, however, that the compounds are symmetrically disubstituted and the value for ρ should be taken as half of 4.2 or 2.1. This value still indicates a rather high sensitivity to changes in electron density. The investigation of a series of monosubstituted diphenylselenium dibromides is now in progress.

No substituent constant for the *p*-phenoxy group could be located in the literature. The point on the line in Fig. 1 corresponding to the observed dissociation constant for di-*p*-phenoxydiphenylselenium dibromide is indicated by a square. This point corresponds to a substituent constant of -0.114.

Summary

1. Dissociation constants for a number of symmetrically disubstituted diphenylselenium dibromides have been determined and are listed in Table III.

2. The heats of dissociation have been calculated for three of the dibromides.

3. The dissociation constant has been found to be quite sensitive to changes in electron density about the selenium atom.

4. The substituent constants (σ values) of Hammett have been found to apply quite satisfactorily to this equilibrium.

5. Molar extinction coefficients for several dibromides and the corresponding selenides are shown in Tables I and II.

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