

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

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 dissociation constant $K = [(C_6H_5)_2Se][Br_2]/[(C_6H_5)_2SeBr_2]$, was determined spectrophotometrically at 26° and found to be 5.02×10^{-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-*p*-phenoxydiphenylselenides 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 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 Photoelectric 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 cold-room 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

λ (m μ)	<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl	<i>o</i> -CH ₃	<i>m</i> -CH ₃
330	7300	4720	7360	6640	6900
340	6300	4130	6720	6030	5790
350	5200	3360	5620	5500	4680
360	4200	2650	4500	4660	3690
370	3400	2010	3420	3810	2880
380	2700	1520	2560	3020	2130
390	2200	1150	1840	2310	1470
400	1800	867	1340	1730	960
410	1500	670	940	1330	600

λ (m μ)	<i>p</i> -CH ₃	<i>p</i> -F	<i>p</i> -Br	<i>p</i> -CH ₃ O	<i>p</i> -C ₆ H ₅ O
330	7310	6260	7060	..	9760
340	6190	5490	6120	6730	8690
350	5010	4590	5200	6350	7920
360	3980	3760	4280	5570	6710
370	3060	2930	3360	4570	5390
380	2260	2130	2500	3550	4130
390	1600	1450	1800	2600	2950
400	1040	949	1300	1840	2080
410	670	583	980	1290	1440

TABLE II

MOLAR EXTINCTION COEFFICIENTS OF SYMMETRICALLY DISUBSTITUTED DIPHENYL SELENIDES

λ (m μ)	<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl	<i>o</i> -CH ₃	<i>m</i> -CH ₃
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

λ (m μ)	<i>p</i> -CH ₃	<i>p</i> -F	<i>p</i> -Br	<i>p</i> -CH ₃ O	<i>p</i> -C ₆ H ₅ O
330	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

(1) J. D. McCullough, *THIS JOURNAL*, **64**, 2672 (1942).

(2) 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.

TABLE III
DISSOCIATION CONSTANTS OF SYMMETRICALLY DISUBSTITUTED DIPHENYLSELENIUM DIBROMIDES

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

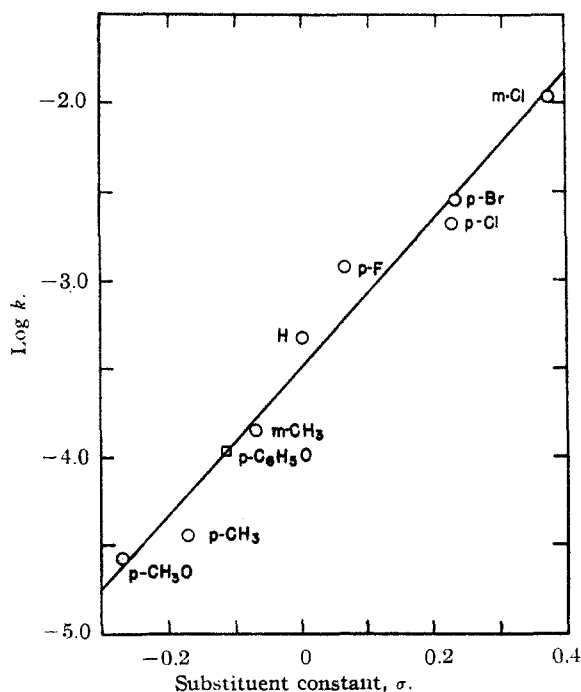


Fig. 1.—Plot of $\log k$ against Hammett's substituent constant.

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. 1. The straight line best representative of the 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*-phenoxy-diphenylselenium 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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