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

The Dissociation Constants of Some Unsymmetrically Substituted Diphenylselenium Dibromides[1]

BY JAMES D. MCCULLOUGH AND MAX K. BARSH

In earlier communications measurements of the dissociation constants of diphenylselenium dibromide[2a] and some symmetrically disubstituted diphenylselenium dibromides[2b] have been reported. The equilibria involved are of the type

$$R_2SeBr_2 = R_2Se + Br_2$$

Spectrophotometric measurements on carbon tetrachloride solutions of the dibromides at measured temperatures near 25° enabled determination of the concentrations of the species involved. The dissociation constants, $K = (R_2Se)(Br_2)/(R_2SeBr_2)$ were then readily computed and ranged in value from 2.7×10^{-5} for the di-*p*-methoxydiphenylselenium dibromide to 1.1×10^{-2} for the di-*m*-chloro compound. When the values of log K for the symmetrically disubstituted dibromides were plotted against Hammett's[3] substituent constants, σ, a reasonably close approximation to a straight line resulted.

The study of unsymmetrically substituted diphenylselenium dibromides reported in the present communication was undertaken primarily to test a postulate of additivity of the σ value for a substituent on one ring to the σ value for a substituent on the other ring. Additivity of these values is to be expected if pronounced resonance effects are not produced by the combination of substituents. It is conceivable that in the symmetrically disubstituted compounds, the very symmetry of the molecules might either enhance or suppress the effect of the substituents. The additivity postulate was tested by making a single plot of the log K values for all types of dibromides against the sums of the σ values involved.

A second objective of the investigation was a more accurate treatment of the effects of temperature on the equilibria through better control of the temperatures of the solutions at the time of measurement. This has permitted a better evaluation of ΔH and ΔS for the dissociations.

Experimental

Materials.—The selenides used in this investigation were synthesized by the methods of Campbell and McCullough.[4] The identity of these compounds is supported by the methods of synthesis (taken into consideration with the starting materials) and by the equivalent weights of the dihalides as determined by the method of McCullough, Campbell and Krilanovich.[5] Physical constants for the compounds prepared are given in Table I.

TABLE I

PHYSICAL CONSTANTS OF UNSYMMETRICALLY SUBSTITUTED DIPHENYLSELENIDES AND THEIR DIHALIDES

	Melting points, °C. (uncor.)			Equivalent weights, g.			
				Dichloride		Dibromide	
Substituents	Selenide	Dichloride	Dibromide	Expt.	Theor.	Expt.	Theor.
m-Cl	[a]	103–104	[a]	168.9	169.2		
p-Cl[b]	[a]		117–118.5			211	213.8
p-CH_3, *p'*-Cl	72–73		120			221.9	220.8
m-CH_3[b]	[a]	110–111.5	[a]	158.5	159.0		
p-CH_3	[a]		137–138			203.6	203.5
p-OCH_3	46.3	162–164	[a]	167.7	167.1		

[a] Crystalline solid could not be obtained. [b] New compounds.

Carbon tetrachloride and bromine were of reagent grade and were carefully dried and distilled before use.

Procedure.—The dissociation constants were determined spectrophotometrically using a Beckman Model DU Quartz Spectrophotometer. For those selenides which form stable crystalline dibromides, the method was essentially that described earlier.[1a] Where crystalline dibromides were not obtainable, the selenides (which in these cases were liquid) were purified through several recrystallizations of the dichlorides from carbon tetrachloride. The dichlorides were then reduced by refluxing their carbon tetrachloride solutions for several hours with C. P. zinc dust in excess. The solid phases were then removed by filtration through sintered glass and the carbon tetrachloride distilled off, finally using a pressure of 100 mm. at 40° for two days in order to remove the solvent as completely as possible with minimum decomposition of the selenides. The selenides thus purified are colorless oils. By ordinary reduced pressure distillation they are at best light orange in color, due to decomposition. Solutions of the selenides having known concentrations were made up by weighing the pure liquids. Dibromide solutions were prepared by addition of the required amount of a carbon tetrachloride solution of bromine from a microburet. From this point the procedure was the same as that used when the solid dibromide is obtainable.

Temperature Control.—The temperature of the solutions was held constant within 0.2° by means of a specially built chamber inserted between the main part of the spectrophotometer and the photo-tube compartment. The central segment of the chamber consisted of the absorption-cell compartment furnished with the instrument and was flanked on both sides by brass plates $^7/_{16}''$ thick.

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(1) Based primarily on research performed under Contract N6 onr-275 between the University of California at Los Angeles and the Office of Naval Research.

(2) (a) J. D. McCullough, THIS JOURNAL, **64**, 2672 (1942); (b) J. D. McCullough and B. A. Eckerson, *ibid.*, **67**, 707 (1945).

(3) L. P. Hammett, "Physical Organic Chemistry," Chapter VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(4) T. W. Campbell and J. D. McCullough, THIS JOURNAL, **67**, 1965 (1945).

(5) J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Anal. Chemistry*, **18**, 638 (1946).

TABLE II

EQUILIBRIUM DATA AND THERMODYNAMIC QUANTITIES (25°) FOR DISSOCIATION OF UNSYMMETRICAL DIPHENYLSELENIUM DIBROMIDES

Substituent	Temp., °C.	log K	log K (25°)	σ	ΔF, kcal./mole	ΔH, kcal./mole	ΔS, cal./mole/deg.
p-OCH$_3$	32.2	−3.91	−4.19	−0.268	5.74	14.4	29
	9.2	−4.76					
p-CH$_3$	29.5	−3.54	−3.68	− .170	5.15		
m-CH$_3$	31.5	−3.41	−3.64	− .069	4.98	11.3	21
	23.8	−3.68					
None	30.6	−3.29	−3.42	0	4.69	9.7	17
	9.0	−3.82					
p-CH$_3$, p'-Cl	30.8	−3.08	−3.26	.057	4.46		
p-Cl	30.8	−2.78	−2.96	.227	4.15	13.1	30
	9.8	−3.48					
m-Cl	32.0	−2.42	−2.64	.373	3.62		

These plates were drilled to fit the instrument and to provide paths for the light beam and for circulation of the thermostating fluid. The thermoregulator was carried in a well in one plate and a thermometer in the other. The thermostating fluid (water in the present case) was circulated from a thermostated bath placed nearby.

Results and Discussion

The temperatures at which the spectrophotometer measurements were made for each dibromide and the corresponding values for log K are given in columns two and three of Table II. For purposes of comparing the dissociation constants of the various compounds it was necessary to compute values for the constants at some fixed temperature, in this case 25°. In the work of McCullough and Eckerson[1b] this correction was made by use of an average value (8.6 kcal./mole) for ΔH for three different dibromides. An average value was used because the observed values showed no correlation with Hammett's sigma values. Actually there should be a linear relationship between ΔH and σ. This follows from the reasonable assumption that ΔS is constant for a given reaction series. With ΔS constant at some fixed temperature, the equation

$$\Delta H = \Delta F + T\Delta S \qquad (1)$$

becomes

$$\Delta H = \Delta F + b \qquad (2)$$

where b is a constant. Substituting for ΔF, we have

$$\Delta H = -RT \log K + b \qquad (3)$$

But log K is a linear function of σ, thus

$$\log_{10}K = \rho\sigma + \log_{10}K^\circ \qquad (4)$$

where $\log_{10}K^\circ$ is a constant.

Substituting in equation (3), changing to ordinary logarithms and combining constants leads to the equation

$$\Delta H = -2.30\, RT\rho\sigma + A \qquad (5)$$

where A and ρ are constant for a given reaction series.

Attempts to correlate equation (5) with the experimentally determined ΔH values were disappointing. Although the seven experimental values (four from the present work and three from the work of McCullough and Eckerson) show a trend in the right direction, the points are so badly scattered that a significant line cannot be drawn through them. This scattering is considerably greater than can be attributed to experimental errors alone and indicates that ΔS is not constant for the reaction series.

Log K values for 25° were obtained from the values at higher and lower temperatures in those cases where determinations were made at two temperatures. In the three remaining cases, log K (25°) was obtained through use of an average ΔH value of 10.6 kcal. per mole obtained from the seven experimental ΔH values. Errors in log K

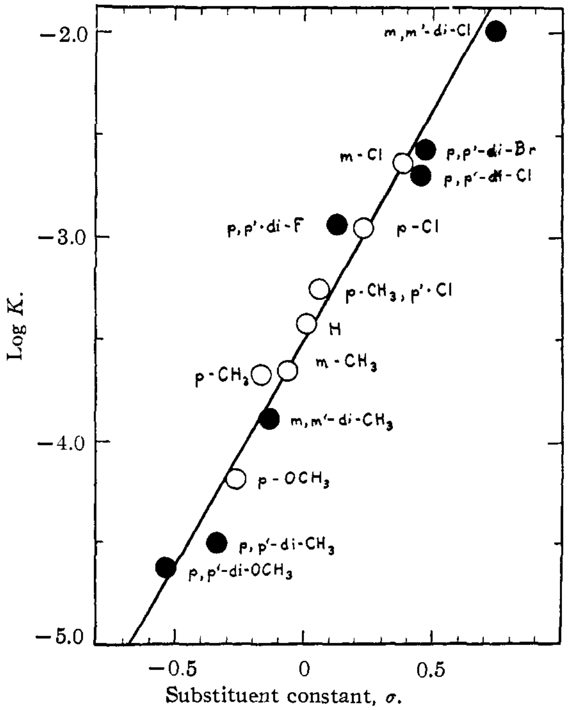

Fig. 1.—Graph of log K vs. Hammett's substituent constant for substituted diphenylselenium dibromides: ○, present work; ●, McCullough and Eckerson.

caused by this approximate treatment are not large because of the shortness of the temperature intervals involved.

Log K, ΔF, ΔH and ΔS values for the dissociations are given in Table II. In Fig. 1, the log $K(25°)$ values are plotted against the substituent constant, σ. The data from the present work are indicated by open circles while the data of McCullough and Eckerson are indicated by full circles. The sigma values employed for the disubstituted diphenylselenium dibromides are the sums of the two individual sigma values concerned (twice Hammett's sigma values in the cases of the symmetrically disubstituted compounds). The straight line shown is the result of a least squares treatment of all of the data and has a slope, ρ, of 2.2. This indicates a rather high susceptibility of the selenium–bromine bond to changes in electron density on the selenium atom.

The fact that all of the log K values lie reasonably close to a single straight line is convincing evidence of the additivity of the effects of a substituent on the first ring to those of a substituent on the second ring in this type of system.

Summary

1. Dissociation constants for a number of unsymmetrically substituted diphenylselenium dibromides in carbon tetrachloride solution have been determined and the values (as log K) are given in Table II.

2. The values of log K (25°) from the present study have been plotted together with those from an earlier study of symmetrically disubstituted dibromides against Hammett's substituent constant, σ. The fact that all log K values lie reasonably close to a single straight line with slope, ρ, of 2.2 shows that the σ value for a substituent on one ring is additive to that for a second substituent on the other phenyl group.

3. The quantities ΔF, ΔH and ΔS at 25° have been evaluated for the dissociations and are listed in Table II.

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Spectrophotometric Studies of Dilute Aqueous Periodate Solutions[1]

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The solubility behavior of various sparingly soluble periodates was found to be anomalous as interpreted through the equilibrium constants for the dilute aqueous periodate system as reported in the literature. Thus it was necessary to investigate these equilibria as a possible reason for the anomaly. Reinterpretation of this solubility behavior in light of the results of this investigation will be reported at a later date.

The ionization of periodic acid in aqueous solutions has been studied previously by various authors.[2,3] Giolitti[2a] and Partington and Bahl[3] found evidence of the dibasicity of periodic acid. Dubrisay[2b] found somewhat doubtful evidence of a third replaceable hydrogen. Rothmund and Drucker[4] reported the dissociation constant $K_1 = 2.3 \times 10^{-2}$ for paraperiodic acid, H_5IO_6. Rae[5] ran a conductometric titration of paraperiodic acid with sodium hydroxide and obtained two breaks. The first is in accord with the K_1 value reported by Rothmund and Drucker and from the second break he estimated that K_2 may be of the order of 10^{-6}. The literature generally concurs with the fact that paraperiodic acid, H_5IO_6, is the only solid periodic acid which is capable of existence in equilibrium with aqueous solutions of the acid. Hill[6] estimated a K_3 value of 4.6×10^{-11} using the previously reported values of K_1 and K_2 as a basis for his estimate.

In this study we have confirmed the previously reported value of $K_1 = 2.3 \times 10^{-2}$ and have assigned new values of $K_2 = 4.35 \times 10^{-9}$ and $K_3 = 1.05 \times 10^{-15}$. K_1 was confirmed from spectrophotometric studies, K_2 was estimated from spectrophotometric and potentiometric studies and K_3 was estimated using the method of Hill[6] and was confirmed by spectrophotometric data.

Aqueous solutions of periodate in the absence of interfering ions show an absorption maximum at 222.5 mμ in the ultraviolet region of the spectrum over a limited pH range. Since the start of this investigation MacDonald, Thompsett and Mead[7] reported an absorption maximum at 222 mμ and indicated that Beer's law was obeyed but neglected to mention the critical nature of pH. The full importance of pH is adequately described below.

Experimental

In the spectrophotometric studies a Beckman Quartz Spectrophotometer (Model DU) and a Cary Recording Spectrophotometer (Model 12) were employed. A Beckman Glass Electrode pH Meter (Model H-2) was used in carrying out the potentiometric titrations. Sources of periodate were paraperiodic acid manufactured by the

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[1] This document is based on work performed in the Ames Laboratory, Atomic Energy Commission.

[2] (a) Giolitti, *Atti reale Accad. Lincei*, **14**, 217 (1905); (b) Dubrisay, *Compt. rend.*, **157**, 1150 (1913).

[3] Partington and Bahl, *J. Chem. Soc.*, 1088 (1934).

[4] Rothmund and Drucker, *Z. physik. Chem.*, **46**, 850 (1903).

[5] Rae, *J. Chem. Soc.*, 876 (1931).

[6] Hill, THIS JOURNAL, **65**, 1564 (1943).

[7] MacDonald, Thompsett and Mead, *Anal. Chem.*, **21**, 315 (1949).