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Substituent Effects on the Stabilities of Cadmium Complexes of Aromatic Sulfonates

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The first stability constants for the complexes of twenty-four sulfonate anions with cadmium ion have been determined potentiometrically. In general, there are none of the expected changes in stability constants as the substituents are varied from electron-withdrawing ones to electron-releasing ones. A preliminary analysis of the factors which may be responsible for this is presented which is based upon the Branch-Calvin treatment of protonic acids. It is suggested that a general correlation of stability constants for a series of related ligands will require structural parameters other than those which are used to represent inductive effects.

While there are many reports of successful correlations between structure and stability of complex species developed on the basis of methods previously used in physical organic chemistry, there has apparently been no effort to see if strictly analogous structure-correlation procedures can be used with simple aromatic ligands. The present study had as its goal the determination of the usefulness of the Hammett equation to correlate the stability constants of the cadmium complexes of a large number of substituted benzenesulfonate anions. Since these compounds are very similar in structure to the benzoic acids, it was hoped that correlations involving the same substituent constants might be obtained. An advantage of working with the aromatic sulfonates is that the precise potentiometric method of Leden² can be used.

The purpose of this work was to determine, as accurately as possible, the stability constants of a large number of complexes of cadmium with aromatic sulfonate anions. The method used was a modification of the differential potentiometric titration developed from Leden's method by Vanderzee and Dawson.^{3,4}

Experimental

Apparatus.—The potentials were measured with a Leeds and Northrup Model K-3 potentiometer in conjunction with a galvanometer from the same company which had a sensitivity of 0.003 μ amp./mm. The cell was contained in a vessel which had a jacket on its sides and bottom, through which water from a constant temperature bath (at 25.00 \pm 0.01°) was circulated. The cells used were similar to those of Vanderzee except that a concentric arrangement was utilized with the fixed half-cell in the center, a salt bridge next, and then, in the largest compartment, the cell into which the ligand solution was titrated. Connection between the parts of the cell was through ground glass joints rather than the fritted glass disks used by Vanderzee and Dawson. The cells were allowed to stand for from thirty minutes to 4 hr. to come to thermal equilibrium before the titration was begun. These cells were found to reattain a steady equilibrium potential after the addition of ligand solution in from one to three minutes. The solution was stirred with a magnetic stirrer.

Chemicals.—Where possible commercially available sodium salts were used after recrystallization twice from methanol. When only the sulfonic acids were available, these were converted to the sodium salts by titrating an aqueous solution to pH 7 with sodium hydroxide solution. The recrystallized salts were dried *in vacuo* using an Abderhalden drying pistol which contained boiling methanol. The dried salts were then sealed in bottles and stored in a desiccator until use. Sodium analyses were run by converting these salts to anhydrous sodium sulfate through

repeated heating with concentrated sulfuric acid and then ignition. The abbreviations in Table I are: E for Eastman Kodak Co., A for Aldrich Chemical Co., and B for British Drug Houses Ltd.

TABLE I

Anion	Source	K ₁	σ
1. 4-Aminobenzenesulfonate	E	0.1983	-0.660
2. 4-Methylbenzenesulfonate	E	.3604	- .170
3. Benzenesulfonate	E	.4185	
4. 2-Chloroaniline-4-sulfonate	A	.5451	
5. Benzene 1,3-disulfonate	B	.6960	
6. 4-Chlorobenzenesulfonate	E	.8540	+ .227
7. 4-Bromobenzenesulfonate	E	.9215	+ .232
8. 2,4,6-Trimethylbenzenesulfonate	A	1.505	
9. 2,5-Dimethylbenzenesulfonate	E	1.586	
10. 4-Amino-3-methylbenzenesulfonate	E	1.743	
11. 3-Aminobenzenesulfonate	B	1.759	- .161
12. 2-Aminophenyl-4-sulfonate	B	2.247	
13. 2,5-Dichloro-4-aminobenzenesulfonate	E	2.411	
14. 4-Chloro-3-methylbenzenesulfonate	E	2.460	
15. 2,4-Dimethylbenzenesulfonate	E	2.700	
16. 2-Hydroxy-4-methoxy-benzophenone-5-sulfonate	A	2.748	
17. 4-Hydroxybenzenesulfonate	E	2.822	- .357
18. 4-Toluidine-2-sulfonate	B	2.839	
19. 1-Methylbenzenesulfonate	B	3.153	
20. 2-Chloroaniline-5-sulfonate	A	3.213	
21. 1-Benzaldehydesulfonate	E	3.496	
22. 3-Toluidine-4-sulfonate	B	12.76	
23. 2,5-Dichlorobenzenesulfonate	B	13.92	
24. Aniline-N-methylsulfonate	A	29.52	

Procedure.—The innermost and outermost cell compartments each contained a cadmium amalgam electrode (about 1%) and a solution 0.001 *M* in Cd(ClO₄)₂, 0.01 *M* in HClO₄ and 2.98 *M* in NaClO₄. The intermediate compartment of the cell contained the same solution and functioned as a salt bridge. This means that the first stability constant can be obtained via extrapolation to a region where the liquid junction potential is essentially zero. The titration was carried out by introducing into the outermost compartment of the cell various amounts of a solution which contained the ligand species as the sodium salt and a sufficient amount of sodium perchlorate to make the total ionic strength of the solution equal to three. After each addition, the solution in the outermost compartment was allowed to come to equilibrium and the potential of the cell was determined. The cell usually attained an equilibrium value of the potential within three minutes, but fifteen minutes was allowed to insure a steady reading after each addition. The calculations were carried out on an IBM 650 computer by the use of a program which gave a least

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(2) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

(3) C. E. Vanderzee, *J. Am. Chem. Soc.*, **74**, 4806 (1952).

(4) C. E. Vanderzee and H. J. Dawson, Jr., *ibid.*, **75**, 5659 (1953).

squares fit of the data. A correction was made for the changes in volume because of the low values of the equilibrium constants and the relatively large volumes of titrant added during a run. Under such conditions it is necessary to note that Leden uses the term "x" for two different quantities. The first is the initial concentration of free cadmium present which is used with the Nernst equation. This concentration does not change and the "x" is constant. The second is the total maximum possible value of the free cadmium ion concentration in the solutions to which titrant has been added and this decreases continually throughout the titration. It is for this second usage that the corrections for volume change have been introduced.

Results and Discussion

The results of the titrations are listed in Table I. Aside from the attempted use of nitro-substituted sulfonates, the only difficulty encountered was with the limited solubility of some of the sodium salts in the highly concentrated sodium perchlorate solutions. The nitro compounds behaved very erratically and gave every evidence that they were undergoing a chemical reduction by the cadmium in the amalgam. This resulted in very erratic potential readings and it was not found possible to derive satisfactory stability constants from the data. The constants for the first complex were found to fall in the range 0.2 to 30. (The first constant for the sulfate complex² is 8.) The first stability constant may be defined as

$$K_1 = \frac{[\text{CdA}^+]}{[\text{Cd}^{++}][\text{A}^-]}$$

The most obvious possibility for correlation of these data is a Hammett-type equation by using the original substituent constants and variants thereof⁵ or a more generalized treatment such as that of Branch and Calvin.⁶

A cursory examination shows that a correlation which involves a simple Hammett-type relation will not be very satisfactory. The order of stability constants for these ligands is simply not consistent with any simple scheme which merely considers an inductive effect of the type used in correlations of the strengths of aromatic carboxylic acids. Thus the order for some typical ligands is 2,5-dichloro-4-aminobenzenesulfonate \sim 4-chloro-3-methylbenzenesulfonate $>$ 4-chlorobenzenesulfonate $>$ benzenesulfonate $>$ 4-methylbenzenesulfonate. That such a simple correlation is not found is surprising, since there are numerous cases where a good correlation is found between the stability constants and structural features which regulate the base strength of the ligand.⁷⁻¹⁵

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 184-228; H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(6) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, Ch. VI.

(7) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

(8) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950); A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 158-160.

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When these correlations are examined in greater detail we see that the validity of the correlation varies over rather wide limits. In some cases^{7,13} it is necessary to draw *several* straight lines across a plot of pK vs. the log of the stability constant. In such cases it is apparent that no simple general linear correlation can be valid. The conditions which must be met before such a simple correlation can obtain may be seen by applying arguments used by Branch and Calvin in a treatment of structural changes and acid strengths of organic acids. Thus, by this analogy, the differences in the log of the stability constants of complexes of the cadmium ion with two related but slightly different organic ions can be expressed as

$$\Delta \text{Log } K = I + R + H + P + S$$

where K is the stability constant, I represents the contribution from the polar or inductive effect, R the contribution from different resonance possibilities, H the purely steric contribution, P the contribution from changes in the polarizabilities of the bonds and S the contribution from differences in interactions which involve the solvent molecule. Such an absolute division is as artificial for complexes as it is for acids, but it has the real advantage of showing how demanding a purely structural correlation must be. As a general condition, the inductive and resonance terms will have to predominate if a correlation of the type represented by the Hammett equation is to be obtained. It is also easy to see that if H , S or $H + S$ are comparable in magnitude to I , R or $I + R$,¹⁶ a simple correlation of general validity which involves only one structural parameter per substituent will be most highly improbable. That a simple correlation which involves the regular σ constants does not suffice may be seen from Table I. The σ constants used here are from the tabulation of H. H. Jaffe.¹⁷

When the multiply substituted sulfonate complexes are considered, it is obvious that factors other than simple inductive effects are operative. In general, multiple substitution leads to complexes which are more stable than the benzenesulfonate complex. Furthermore, there appears to be no consistent obvious evidence of steric hindrance which arises from ortho substitution. There is the possibility that some correlation of the average K for the first few complexes might be found as has been reported in many other cases.¹⁸ This has not been attempted in the present case for the simple reason that the K_1 's (for the first complex) have been determined much more accurately than the stability constants for any successive complexes so any such correlation would be suspect here as well as difficult to reconcile with the lack of correlation of the K_1 's. This is by no means the first

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(14) V. Armeanu and C. Luca, *Z. physik. Chem.*, **214**, 81 (1960).

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(16) It is often found that I and R can be considered conveniently together as a single term which varies in a well-defined manner with some suitable structural parameter when the ionization of organic acids is treated.

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instance reported where there is a lack of correlation between factors which are expected to govern the acid strength and the stability constants.^{19,20}

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Compounds with the Hexagonal Barium Titanate Structure^{1,2}

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A number of compounds of the type $Ba(M,Ti)O_3$ where $M = Ti^{3+}, V, Cr, Mn, Fe, Co, Ru, Rh, Ir, Pt$ have been prepared and are shown to have the hexagonal barium titanate structure. The phases probably have a composition close to $Ba(M_{1/3}Ti_{2/3})O_3$ and are in some cases oxygen-deficient. Evidence from X-ray and magnetic studies indicates that the M cation is concentrated mainly in the 4-fold position in the hexagonal cell and is bonded directly to a titanium ion in the neighboring position. The adoption of the structure appears to be dependent upon the formation of a metal-metal bond through overlapping d-orbitals.

Introduction

A high temperature form of barium titanate was first observed by Megaw³ who suggested that it was rhombohedral. Single crystals were grown from alkali carbonate fluxes⁴ and Matthias,⁵ using a modification of this procedure, obtained amber colored flat hexagonal plates of the compound which were used by Burbank and Evans⁶ to determine the structure. The amber color of the crystals, which was attributed to dissolved platinum acquired from the reaction vessel, could be removed by heating in air at 200° for a few hours.⁵

The transition from cubic to hexagonal $BaTiO_3$ occurs with the formation of an intermediate phase at 1450°, according to Statton,⁷ but Race and Roy⁸ have reported a reversible transition at 1460°. The same authors have found that the transition temperature is raised by the addition of Ca^{2+} , TiO_2 , SiO_2 and $BaCl_2$ but is lowered by K^+ .^{9,10} Wood has noted that the hexagonal form may be obtained at 1200° by using barium chloride, potassium and sodium carbonates as fluxes with appropriate quantities of barium carbonate and titanium dioxide.¹¹

In a previous communication from this Laboratory, it was suggested that the platinum was instrumental in bringing about the formation of the hexagonal phase, and it was shown that the presence of many ions other than platinum led to this structure.¹² This paper describes the characterization of some of these phases.

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(2) Abstracted from the Doctoral Thesis of John Guy Dickinson submitted to the University of Connecticut 1960.

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Experimental

An intimate mixture of the reactants in stoichiometric proportions was prepared by grinding in an agate mortar. Ordinarily the powders were pelleted to minimize reaction with the containers. Those samples which had to be protected from oxidation were sealed in evacuated silica capsules, the others were heated in open zirconium silicate boats in a muffle furnace. With the vacuum preparations, the samples were given a preliminary heating of about 0.5 hr. and were again mixed by grinding and heated under controlled conditions usually for 24 hr. periods. Examination of the products for homogeneity was made microscopically and by X-rays. Most of the products were microcrystalline powders. The presence of the hexagonal barium titanate phase could be detected readily by examining the forward reflections obtained with a General Electric XRD-5 diffractometer. If the tracing revealed the presence of other phases, the grinding and heating cycle was repeated until no change was observed.

From the nature of the ions which appeared to favor the incidence of the hexagonal phase, it was assumed that they were being substituted for part of the titanium in the $BaTiO_3$ crystal.¹² Several systems were examined on this basis.

1. $Ba(Pt_xTi_{1-x})O_3$.—Crystals prepared by the procedure of Matthias⁵ were a deep amber color. No change was observed in the color upon heating the crystals for extended periods of time from 500 to 1300° in zirconium silicate boats in air. At 1500° melting or reaction with the boat occurred with the separation of metallic platinum. The residue contained tetragonal barium titanate. The amber crystals when ground to a fine powder gave a diffraction pattern which could be completely indexed using the lattice parameters given by Burbank and Evans.⁶

Mixtures of barium carbonate, titanium dioxide and platinum dioxide hydrate corresponding to the formula where x ranged from 0.005 to 0.5 were heated in air and also *in vacuo* at temperatures from 400 to 1250°. The purest phase appeared to be formed at $x = 0.1$. Above this value, platinum lines and below this value tetragonal barium titanate lines were found in the diffraction pattern. Attempts to extend the proportion of platinum in the crystal were made by heating the samples in oxygen, *in vacuo* and by incorporating various amounts of potassium carbonate in the mixtures. None of these attempts was successful.

2. $Ba(M_xTi_{1-x})O_3$ where $M = Ru, Rh, Pd, Os, Ir$.—The hexagonal barium titanate structure was not obtained by use of either palladium or osmium. All of the others, however, gave the hexagonal phase upon heating in air appropriate mixtures composed of the platinum metal, barium carbonate and titanium dioxide. The metals (99.9+%) were in powder form (325 mesh).

At first it seemed that a wide homogeneity range existed in the case of the iridium system,¹² and it was decided on this basis to give it a more exhaustive examination.

Comparison of the diffractometer tracings of three carefully prepared samples of the preparations $Ba(Ir_xTi_{1-x})O_3$