[CONTRIBUTION NO. 823 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Dielectric Polarization Studies of Metallic Chelates

BY ROBERT G. CHARLES AND HENRY FREISER

The dielectric polarizations of dioxane solutions of lead 8-hydroxyquinolinate and disalicylidenemethylamine copper have been measured at 30°. These compounds, as do the acetylacetonates, are found to have abnormally high atomic polarizations. It is possible that most metallic chelates exhibit this phenomenon. The solubilities of some metallic 8-hydroxyquinolinates in benzene and dioxane at 25° have also been measured.

This study was undertaken as part of an over-all program designed to relate the structure of chelating reagents with their analytical behavior. It was decided to apply the dipole moment technique in order to correlate the charge distribution within the molecules of metallic chelates with their structures and stabilities. To be suitable for the present work, a metallic compound must have the following characteristics: (1) Definite composition. (2) It must be anhydrous and have no solvent of crystallization, with the possible exception of the solvent used in the measurement of polarization. (3) Sufficient solubility in such solvents as dioxane or benzene to permit accurate dielectric constant measurements.

Because of its analytical importance and the number of metals with which it combines, 8-hydroxyquinoline was first investigated. The limited solubilities of metallic 8-hydroxyquinolinates in benzene and dioxane prevented the full use of these chelates and the metal salts of Schiff bases, which give similarly constructed chelates, were also investigated.

Experimental

Preparation and Purification of Materials.—Jones and Laughlin reagent-grade benzene was used after careful fractionation as described previously.[1] Carbide and Carbon Co. dioxane was purified by the procedure outlined in Weissberger and Proskauer[2] and distilled from sodium before use. Lemke Co. 8-hydroxyquinoline was recrystallized from alcohol and water and melted at 72.4°. The metallic hydroxyquinolinates were prepared by precipitation with oxine from an aqueous solution of the metal ion in the manner described by Welcher[3] and were dried at the recommended temperature in a constant temperature oven. Salicylidenemethylamine copper was prepared from salicylaldehyde and methylamine as described by Pfeiffer[4] and purified by recrystallization from alcohol and from dilute dioxane. The corrected melting point of the salt was found to be 158.4–159.2°. The purity of this compound was also established by the electrolytic determination of copper. The salt was decomposed by evaporation with a mixture of hydrochloric, nitric and sulfuric acids to fumes of sulfur trioxide and then diluted to a volume of 200 ml. and electrolyzed in the usual manner. *Anal.* Calcd. for $C_{16}H_{16}O_2N_2Cu$: Cu, 19.15. Found: Cu, 19.15, 19.16, 19.08.

Solubility of Metallic 8-Hydroxyquinolinates.—The solubilities of a number of metallic 8-hydroxyquinolinates in benzene and dioxane were determined by weighing the residue obtained from the evaporation of a weighted portion of the saturated solution. The solution was prepared by extracting the solid compound in a Soxhlet extractor, and allowing the solution to cool to room temperature. The results are summarized in Table I, where the solubilities are given in terms of mole fractions.

Dipole Moment Measurements and Calculations.—The dielectric polarizations of lead 8-hydroxyquinolinate and of disalicylidenemethylamine copper was measured in the manner previously described. The results are summarized in Table II where the dielectric constants, ϵ, and the densities, d, of dioxane solutions containing mole fraction, f_2, of the chelate are given along with the molar polarization and molar fraction. Because the solutions were colored no direct measurement of molar refraction was made. Calculation of molar refractions were made from appropriate group refractions.

TABLE I

SOLUBILITIES OF SOME 8-HYDROXYQUINOLINATES AT 25°

	Solvent	
Metal	Benzene	Dioxane
Lead	0.00013	0.0016
Cadmium	Negligible	Negligible
Uranium	.....	0.00051
Iron(III)	0.00028	.....
Copper(II)	0.000032	.....
Bismuth	.....	0.000428

The concentrations are given in terms of mole fractions.

TABLE II

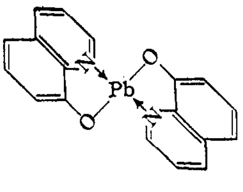
DIELECTRIC POLARIZATION DATA AT 30°

f_2	ϵ	d	P_2	MR_D	$\mu_{app.}$
		Lead 8-hydroxyquinolinate			
0.0000	2.2310[a]	1.0204			
.0016[b]	2.2363	1.0204	187	105	2.0
		Disalicylidenemethylamine copper			
0.00000	2.2310	1.02039	...		
.003453	2.2523	1.02406	158		
.006913	2.2700	1.02773	150		
.008798	2.2839	1.02973	155		
.01044	2.2905	1.03145	151	104	1.22

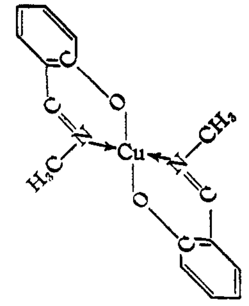
[a] Determined by comparison with benzene. [b] Only one measurement was made due to the limited solubility of this compound.

Discussion

The two chelates whose polarizations were determined have the structures



Lead 8-hydroxyquinolinate



Disalicylidenemethylamine copper

There is a striking resemblance between the five-membered 8-hydroxyquinoline chelate ring and the six-membered chelate ring of the salicylidenemethylamine compound. Both structures possess

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[1] R. K. Keswani and H. Freiser, THIS JOURNAL, **71**, 218 (1949).

[2] Weissberger and Proskauer, "Organic Solvents," The Clarendon Press, 1935.

[3] Welcher, "Organic Analytical Reagents," Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 265 ff.

[4] Pfeiffer, *J. prakt. Chem.*, **153**, 270 (1939).

a high degree of symmetry which makes it unlikely that either of these compounds has a significant dipole moment. According to X-ray diffraction data on both lead[5] and copper[6] compounds similar to these, both salts have planar configurations.

It would be possible for a planar salt to have a moment if the molecule were of *cis* configuration (both nitrogen atoms on the same side) and indeed, disalicylidenemethylamine copper is known to exist in two crystalline forms. Of these two forms, the green modification (the one used) is the more stable and therefore is probably the *trans*.

It would appear from this discussion that the results might be reasonably interpreted in terms of the presence of abnormally high atomic polarization as has been observed by Finn, Hampson and Sutton[7] for metallic acetylacetonates. The measurements reported here and those of Sutton and co-workers lead to the doubt of the existence of any metallic chelates which do *not* have any abnormally large atomic polarization. This unfortunately obscures the useful application of the technique of dipole moments to the evaluation of charge distribution in these interesting molecules. There does exist a possibility of evaluation of the dipole moment from the atomic polarization if the latter is viewed as arising from molecular oscillation as described by Coop and Sutton.[8] Coop and Sutton propose an equation relating the atomic polarization to the dipole moment of half of the molecule and to the force constant associated with the corresponding bending of the molecule. If the force constant could be evaluated from infrared absorption data, then it should be possible to apply the Coop and Sutton[8] equation to solve the dipole moment of half the chelate molecule. Without a knowledge of the force constants, atomic polarization data could not give more than the qualitative order of the ring to metal moments of a series of salts of a given chelating agent or of a series of chelates of a given metal and this, only if it could be assumed that the force constants were of approximately the same magnitude.

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[5] E. G. Cox, A. J. Shorter and W. Wardlaw, *Nature*, **139**, 72 (1937).

[6] E. G. Cox, W. Wardlaw and Webster, *J. Chem. Soc.*, 775 (1936).

[7] Finn, Hampson and Sutton, *ibid.*, 1254 (1938).

[8] Coop and Sutton, *ibid.*, 1269 (1938).

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The Partial Additive Chlorination of the Benzene Ring. I. Alpha Benzene Tetrachloride

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Photochlorination of benzene in the presence of iodine results, in part, in the formation of benzene tetrachloride, a new compound. A steric isomer, designated as alpha benzene tetrachloride, has been isolated and a number of its physical and chemical properties have been determined. The chlorination of benzene tetrachloride to benzene hexachloride has been shown to occur *via* a free radical mechanism. From the photochlorination of alpha benzene tetrachloride, the alpha and gamma isomers of benzene hexachloride were obtained. Bromination and oxidation of alpha benzene tetrachloride yielded two new compounds, 1,2-dibromo-3,4,5,6-tetrachlorocyclohexane and 2,3,4,5-tetrachlorohexanedioic acid, respectively. The partial additive chlorination of chlorobenzene to pentachlorocyclohexene indicates that this type of chlorination reaction may be applicable to a variety of aromatic compounds.

Introduction

The di- and tetrachlorides of benzene, $C_6H_6Cl_2$ and $C_6H_6Cl_4$, have been suggested[3,4,5] as possible intermediates in the additive chlorination of benzene to 1,2,3,4,5,6-hexachlorocyclohexane (benzene hexachloride, BHC). However, no reference to the isolation or confirmation of even the transitory existence of either intermediate has been found in the literature.

The photochlorination of benzene has been shown to occur by means of a free radical mechanism[6] and some estimates of chain lengths and quantum efficiencies have been made.[5,7] On the basis of such a mechanism it may be assumed that the following reactions occur in the formation of dichlorocyclohexadiene

$$Cl_2 \xrightarrow{\text{light}} 2Cl\cdot \qquad (1)$$

$$Cl\cdot + C_6H_6 \longrightarrow ClC_6H_6\cdot \qquad (2)$$

$$ClC_6H_6\cdot + Cl_2 \longrightarrow C_6H_6Cl_2 + Cl\cdot \qquad (3)$$

Because of its expected reactivity, it is possible that dichlorocyclohexadiene might chlorinate to tetrachlorocyclohexene *via* a free radical or an ionic mechanism, or both. It is to be expected that tetrachlorocyclohexene would be a less reactive intermediate than dichlorocyclohexadiene, and that there would be more likelihood of its isolation by modifying the addition chlorination of benzene by means of appropriate reagents.

We have isolated a steric isomer of 3,4,5,6-tetrachlorocyclohexene from the product of the photochlorination of benzene in the presence of iodine. Chlorination of this new compound in the dark at room temperature resulted in no detectable reaction, whereas the rate of photochlorination was rapid under comparable conditions, indicating

[1] Hobart College, Geneva, New York.

[2] Wayne University, Detroit, Michigan.

[3] H. Müller, *J. Chem. Soc.*, **15**, 41 (1862).

[4] A. Slator, *ibid.*, **83**, 729 (1903).

[5] H. P. Smith, W. A. Noyes, Jr., and E. J. Hart, THIS JOURNAL, **55**, 4444 (1933).

[6] R. Luther and E. Goldberg, *Z. physik. Chem.*, **56**, 43 (1906).

[7] H. N. Alyea, THIS JOURNAL, **52**, 2743 (1930); K. Ueda, *Botyu-Kagaku*, **15**, 149 (1950).