[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Some Complexes Formed from Diaryl Selenoxides and Mercury(II) Halides

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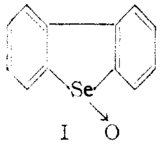
Eight complexes formed from diaryl selenoxides and mercury(II) halides have been isolated, characterized and found to have the composition $R_2SeO \cdot HgX_2$. The likelihood of a selenium–mercury linkage in these complexes is suggested.

A number of complexes formed from diaryl sulfoxides and metallic halides are described in the literature.[2] In addition, Foster and Brown[3] describe four selenoxide hydronitrates having the generalized formula, $RR'SeO \cdot HNO_3$. However, aside from these hydronitrates, there appear to be no accounts of complexes whose existence indicates a possible basic character in selenoxides.

The present study shows that three diaryl selenoxides readily form solid addition compounds with mercury(II) bromide and mercury(II) chloride, and that two of these selenoxides also form complexes with mercury(II) iodide. These complexes may be purified by recrystallization and serve as excellent derivatives for the oxides. Those selenoxides forming isolable complexes are dibenzoselenophene oxide (I), *p,p'*-dimethoxydiphenyl selenoxide and the corresponding *p,p'*-diethoxy compound.



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It should not be assumed, however, that the formation of such complexes is a reaction which is general for diaryl selenoxides and metallic halides. Attempts to prepare similar complexes from the same selenoxides, but using instead the chlorides of Cu^{II}, Cd^{II}, Fe^{III}, Ni^{II}, Cr^{III} and Zn^{II}, and using both water and 95% ethanol as solvents, resulted merely in isolation of the selenoxides used as starting materials. Selenoxides without positive substituents on the ring were not observed to form complexes with any of the halides used, including the halides of Hg^{II}; attempts to prepare complexes of unsubstituted diphenyl selenoxide and of *p,p'*-dichlorodiphenyl selenoxide were unsuccessful and resulted only in reisolation of the selenoxides. It seems curious that *p,p'*-dimethoxydiphenyl selenoxide appeared to form no isolable complex with mercury(II) iodide although it readily combines with the chloride and bromide. We at present can advance no reason for this presumably anomalous behavior of the *p,p'*-dimethoxy substituted compound.

Since no complexes of this nature seem to have been reported for aryl alkyl ethers and since similarly substituted diarylselenones apparently do not participate in complex formation, we suggest the likelihood that the bonding in the selenoxide-mercury(II) halide complexes exists between the selenium and mercury atoms. However, the possibility of pi-bonding cannot be excluded.

It is of some interest to note the increased ease of oxidation of the selenium atom of those selenides having the electron-donating alkoxy groups on the ring. The latter compounds are readily oxidized to the corresponding oxides with hydrogen peroxide in dioxane; in contrast, dibenzoselenophene and *p,p'*-dichlorodiphenyl selenide are resistant to hydrogen peroxide treatment, oxidation to the desired oxide being carried out with a 40% solution of peracetic acid. Treatment of the alkoxy selenides with the latter reagent produces compounds whose composition and properties correspond to those expected for the corresponding diaryl selenones. Table I lists the complexes prepared.

TABLE I

COMPLEXES OF DIARYL SELENOXIDES AND MERCURIC HALIDES

Complex	M.p., °C. (cor.)	Se, % Calcd.	Se, % Found	Equiv. wt. (iod.) Calcd.	Equiv. wt. (iod.) Found
$(p\text{-}MeOC_6H_4)_2SeO \cdot HgCl_2$	160	13.6	13.5	290	291
$(p\text{-}MeOC_6H_4)_2SeO \cdot HgBr_2$	115	11.8	11.8	335	335
$(p\text{-}EtOC_6H_4)_2SeO \cdot HgCl_2$	110	13.1	13.0	304	307
$(p\text{-}EtOC_6H_4)_2SeO \cdot HgBr_2$	129	11.3	11.3	349	352
$(p\text{-}EtOC_6H_4)_2SeO \cdot HgI_2$	137–138 dec.			396	395
$(C_6H_4)_2SeO \cdot HgCl_2$	182 dec.	15.3	15.2	258	260
$(C_6H_4)_2SeO \cdot HgBr_2$	191 dec.	13.0	12.9	304	302
$(C_6H_4)_2SeO \cdot HgI_2$	218 dec.			349	346

Experimental

Preparation of the Selenides.—*p,p'*-Dimethoxydiphenylselenium dichloride was prepared from selenium oxychloride and anisole as described by Alquist and Nelson.[4] The corresponding diethoxy compound was prepared from phenetole in the same way. The dichlorides were reduced to the corresponding selenides by pulverizing the solids, suspending them in chloroform, and shaking the mixture in a separatory funnel with a concentrated solution of potassium iodide which was also 1.0 *N* in sulfuric acid. Small portions of a concentrated solution of sodium thiosulfate were added and the shaking continued until the iodine color disappeared permanently from both layers. The organic layer was withdrawn, dried over anhydrous magnesium sulfate, filtered and the chloroform stripped off. The crude diaryl selenide remaining as residue was crystallized twice from boiling methanol. The final yields of selenides (based on the aryl alkyl ethers used) were 45% in both cases.

Diphenyl selenide and *p,p'*-dichlorodiphenyl selenide were prepared by the method of Leicester and Bergstrom.[5] Dibenzoselenophene was prepared by the method of Campbell, McCullough and Gould.[6]

Diphenyl selenoxide was prepared by the method of Foster and Brown.[3]

Dibenzoselenophene oxide was prepared as described in a previous communication.[6]

***p,p'*-Dichlorodiphenyl Selenoxide.**—This oxide was also prepared by oxidation of the corresponding diaryl selenide with peracetic acid.[6] The product, after 3 recrystallizations from methanol, melted at 212° (dec.).

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(2) (a) K. A. Hofmann and K. Ott, *Ber.*, **40**, 4930 (1907); (b) R. W. Pickard and J. Kenyon, *J. Chem. Soc.*, **91**, 896 (1907).

(3) D. G. Foster and S. F. Brown, THIS JOURNAL, **50**, 1182 (1928).

(4) F. N. Alquist and R. E. Nelson, *ibid.*, **53**, 4033 (1931).

(5) H. M. Leicester and F. W. Bergstrom, *ibid.*, **51**, 3587 (1929).

(6) T. W. Campbell, J. D. McCullough and E. S. Gould, *ibid.*, **72**, 5753 (1950).

Anal. Calcd. for $C_{12}H_{10}Cl_2SeO$: equiv. wt. (iodometric),[7] 159.1. Found: equiv. wt., 159.8.

***p,p'*-Dimethoxydiphenyl Selenoxide.**—Ten grams of *p,p'*-dimethoxydiphenyl selenide was dissolved in 30 ml. of warm dioxane. The temperature of the solution was brought to 80°, and small portions of a 30% solution of hydrogen peroxide were carefully added to the hot solution. The foaming and oxygen evolution following each addition was allowed to cease before adding a subsequent portion. After a total of 40 ml. of peroxide solution had been added, the mixture was evaporated to cloudiness on a hot-plate. The crystals formed upon letting the solution cool overnight were filtered off, dried for a few hours in air, and dissolved in boiling benzene. The hot benzene solution was treated with anhydrous magnesium sulfate and Norite, then filtered. The white prisms which separated on cooling were twice recrystallized from benzene; yield 6.5 g. (63%); m.p. 144° (dec.).

Anal. Calcd. for $C_{14}H_{14}O_3Se$: Se, 25.5; equiv. wt. (iod.), 154.5. Found: Se, 25.5; equiv. wt., 154.1.

***p,p'*-Diethoxydiphenyl selenoxide** was prepared as described for the methoxy compound; yield 58%; m.p. 150° (dec.).

Anal. Calcd. for $C_{16}H_{18}O_3Se$: Se, 23.4; equiv. wt. (iod.), 168.5. Found: Se, 23.4; equiv. wt., 169.0.

Oxidation of *p,p'*-Dimethoxydiphenyl Selenide with Peracetic Acid.—Ten grams of the diaryl selenide was added in small portions to 25 ml. of a 40% solution of peracetic acid in glacial acetic acid. The reaction was quite vigorous. The mixture was carefully heated to boiling, then quickly cooled. The solution was carefully made basic by addition of concentrated ammonium hydroxide, whereupon a considerable quantity of oil separated. The oil solidified after standing one hour; the dark-colored solid was filtered off, dissolved in boiling benzene, and the benzene solution treated with anhydrous magnesium sulfate and Norite, then filtered. Cooling yielded a white solid which was recrystallized from benzene. The product weighed 4.5 g. and melted at 148.5–149.5. A solution of the solid in alcohol did not oxidize acidified potassium iodide solution, indicating that the product was not a selenoxide.

Anal. Calcd. for $C_{14}H_{14}O_4Se$: Se, 24.3. Found: Se, 23.9.

Oxidation of *p,p'*-diethoxydiphenyl selenide in the same way yielded a similar product, melting at 176–177°.

Anal. Calcd. for $C_{16}H_{18}O_4Se$: Se, 22.5. Found: Se, 22.4.

When either of the above two products was mixed with an equimolar quantity of any of the three mercury(II) halides and the mixture of solids dissolved in a minimum quantity of boiling ethanol, cooling the solution yielded no complex. Instead one of the starting materials crystallized. In the case of the mixtures with mercury(II) bromide or chloride, the product first separating was the selenium-containing compound. In the case of the mixtures with mercury(II) iodide, the first product separating was the yellow form of HgI_2 which changed upon standing to the familiar red form.

Preparation of the Complexes.—A mixture of one millimole of the halide and 1.10 millimoles of the selenoxide was dissolved in a minimum quantity of boiling 95% ethanol. Cooling the solution yielded the desired complex; in those cases where no solid complex was formed, one or both of the starting components separated instead. The complex could usually be distinguished from either of its components or a mixture of both of them by differences in crystalline form. In doubtful cases, a constant composition corresponding to that of $Ar_2SeO{\cdot}HgX_2$ retained by the solid after successive recrystallizations was taken as a criterion of complex formation. The complexes formed from mercury(II) bromide and mercury(II) chloride are colorless, those of mercury(II) iodide a bright yellow color.

Analytical Methods.—Iodometric equivalent weights of the complexes were obtained by dissolving a weighed sample in warm methanol, adding an excess of acidified potassium iodide solution in water, and titrating the triiodide ion released with standard sodium thiosulfate solution, using the starch end-point. It was found that addition of a few ml. of chloroform to the solution being titrated when the triiodide color became indistinct sharpened the end-point and increased the reliability of the titration.

The analyses for the selenium content were carried out as follows: the sample was thoroughly digested in a mixture of nitric and sulfuric acids, and the resulting solution was diluted with water. Excess nitrous acid was destroyed by addition of urea, and excess potassium iodide was added. The triiodide formed from the reaction of the selenious acid and the iodide was titrated by a method previously described.[7] This method could not be applied to complexes containing iodine since treatment with the sulfuric–nitric acid mixture oxidized a portion of the iodine in the complex to iodate, thus invalidating the titration. A more detailed description of this method, together with an evaluation of its applicability toward other types of organoselenium compounds, will appear in a subsequent communication.

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[7] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

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Zirconium Chloranilate Complexes

BY B. J. THAMER[1] AND A. F. VOIGT

Spectrophotometric measurements at 25° in 1 to 2 *M* perchloric acid solutions of ionic strength of 2 have shown the equilibria: $Zr(IV) + H_2Ch \rightleftarrows Zr(IV)Ch^{++} + 2H^+$, $K_1 = (5.69 \pm 0.08) \times 10^{+5}$, $Zr(IV)Ch^{++} + H_2Ch \rightleftarrows Zr(IV)Ch_2 + 2H^+$, $K_2 \simeq 6000$, where Zr(IV) represents the zirconium monomer, H_2Ch undissociated chloranilic acid and the constants are in terms of concentrations. A precipitate that forms in these solutions with concentrations of the reactants of roughly 5×10^{-4} molar is shown to have a Zr:Ch ratio of 1 to 1.24. A spectrophotometric method is developed for determining zirconium at formalities of 2×10^{-6} to 5×10^{-5} using chloranilic acid and measurement at 3400 Å. The color reaction proceeds rapidly and yields a true solution that is stable indefinitely. The characteristics of chloranilic acid as a colorimetric reagent for zirconium are compared briefly with those of other such reagents.

During a study of various organic complexing agents for zirconium it was found that chloranilic acid gave a bright magenta solution with low concentrations of zirconium even in concentrated acid. Since this reaction had potential practical value as an analytical reaction for zirconium and considerable theoretical interest, the formulas of the products and the formation constants were determined spectrophotometrically.

Non-complexing solutions with constant ionic strength were prepared using perchloric acid plus lithium perchlorate to give a constant total perchlorate concentration of two molar and perchloric acid concentrations from 1 to 2 molar. Measurements were made at 25 ± 1°. Under these conditions and at the zirconium concentrations em-

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[1] Taken from part of the Ph.D. thesis of B. J. Thamer, Iowa State College, 1950.