or adsorbed oxygen and water vapor. The reproducibility is in no way related to the composition of the sulfide sample. The coefficient of friction was calculated as the ratio of the force in grams to the load (508 grams). The coefficient of friction of graphite was measured as a check on the apparatus. Found: 0.12±0.01. Literature value: 0.1 (*2*).

DISCUSSION

Figure 1 shows the correlation between the coefficients of friction and the cell volumes of the system. The composition cell volume plot is according to Kuznetsov and Ch'ih-fa (*6*). The areas labeled α, β, and γ are the solid solution areas discussed previously.

The α and $\alpha + \beta$ areas have coefficients of friction which appear to be controlled by the α, or orthorhombic tin(II) sulfide, phase. In the β, or teallite, region, the structure of the crystal is still orthorhombic, but the coefficients of friction are decreasing owing to the increasing amounts of lead sulfide in the solid solution. That the minimum in the coefficients of friction coincides with the maximum solid solution of lead sulfide in teallite and the maximum cell volume of teallite is to be expected because, as the cell volume increases, the bonds between atoms are lengthened and weakened, making sliding or breaking of bonds between crystal planes easier. In the $\beta + \gamma$ region, the cubic γ phase has only a small effect on the coefficients of friction, as evidenced by the slight increase in the values in this region. An abrupt change in the measured values occurs between 85 and 90 mole % lead sulfide. It is thought that the change should coincide closely with the disappearance of the β phase in this area of the phase diagram.

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Preparation and Properties of Tropyl Selenide

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The preparation, infrared spectrum, and other physical properties of tropyl selenide are compared to those of tropyl sulfide and of tropylium salts.

THE SELENIDE, the third member of the tropyl chalcogen (*7, 8*) series and the most likely of these to be ionic, is covalent in character, like the oxide and sulfide. The infrared spectrum [3030(s), 1450(w), 1410(w), 1228(w), 1204(w), 1165(w), 1088(w), 965(w), 948(w), 923(w), 884–895(m), 844(w), 787(w), 760(m), 709(s) cm.$^{-1}$] is similar to that of the sulfide [3030(s), 1773(vw), 1695(vw), 1445(w), 1410(w), 1392(w), 1227(w), 1203(w), 1166(w), 1082(vw), 993(w), 966(vw), 951(vw), 938(w), 928(w), 895(w), 860(w), 794(w), 739(m), 717(w), 695(m − s) cm.$^{-1}$]. These spectra are very similar to that of cycloheptatriene and are not closely related to the ionic cycloheptatrienylium (tropylium) bromide (*8*) whose spectrum is akin to that of the internally ionic tropone (*5, 6*) and to that of known ionic (*1, 3, 10–12*) and π-bound (*4*) tropylium metal "sandwich" complexes. The spectra of the sulfide and selenide have fewer and less pronounced (muted) absorption bands than cycloheptatriene. The physical properties of tropyl sulfide and tropyl selenide resemble in pattern those of other analogous Group VI pairs, such as the diphenyl derivatives.

The relative instability of the covalent compounds is probably a measure of the relative bond strength of the C—X— bonds (X = O, S, or Se), as the order of decreasing stability is: C—O— > C—S— > C—Se—. Unlike the others, decomposition of the selenide is not only heat-induced but is rapidly catalyzed by sunlight, which is suggestive of a radical mechanism, possibly induced by a charge transfer excitation. The tropyl radical which would be formed evidently exists as a reactive intermediate in reductive-one-electron transfer reactions of the tropylium ion (*8, 13*).

EXPERIMENTAL

Infrared and Ultraviolet Spectra. Infrared absorption spectra were determined on a Beckman Model I.R.-4 double-beam recording spectrophotometer, in carbon tetrachloride and carbon disulfide solutions. The ultraviolet spectra were determined on a Beckman DU spectrophotometer.

Hydrogen Selenide. The hydrogen selenide was prepared by hydrolysis of aluminum selenide. Both this procedure and preparation of the aluminum selenide were carried out according to Brauer (*2*).

Cycloheptatrienylium Bromide. Essentially the method of Doering (*8*) was used. A purer tropylium bromide and better yields in purification were desired. The crude tropylium bromide was taken up in boiling ethanol (dried over magnesium sulfate) and cooled in chloroform–dry ice mixture (−64° C.) for 2 hours. The resulting yellow crystals

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were filtered through a suction filter (previously cooled with liquid nitrogen) and dried under vacuum (1 mm. of Hg pressure) for 4 days at room temperature. On exposure to the atmosphere, a greenish tinge developed in a few days, and these greenish crystals produced a slight turbidity on dissolution in water, which was removed by filtration before using the solution in reactions. Pure tropylium bromide was obtained when the ethanol was kept dry and the product kept cold in chloroform-dry ice slush (1 mm. of Hg pressure during the first 2 hours of drying) until the adsorbed ethanol and/or that of crystallization (*8*) was removed. The presence of ethanol in the tropylium bromide at higher temperatures produces some tropyl ethyl ether. The infrared and ultraviolet spectra of the fresh dry ethanol-free crystals, their solutions, and the filtered solution of greenish tropylium bromide all were in accord with Doering's spectra.

The ethanol of crystallization, etc., could also be removed by dropping the crystals in boiling tetrahydrofuran immediately after the first filtration and cold ethanol rinse, and then rapidly refiltering and drying the crystals under vacuum (1 mm. of Hg) for 4 hours.

A cold-finger sublimation of the crude tropylium bromide (involving heating the sample in a bath whose temperature was kept at 210° C., while maintaining 1 mm. of Hg pressure) caused a rapid transfer, but the material had a low melting point (165° C.).

Tropyl Selenide. Tropyl selenide was prepared in a fashion analogous to that for tropyl sulfide (*5,6*). Modifications of the procedure were made only where they were needed because of the instability of the selenide.

An integrated apparatus setup was used which contained the hydrogen selenide generator and the reactor flask, and which had ground glass fittings throughout. This was desirable to decrease the possibility of decomposition of hydrogen selenide, and to allow for the toxicity of the selenium compounds and the instability of the tropyl selenide. The exiting gas, after passing through a sodium hydroxide trap solution, was vented directly to the hood port. Rubber gloves and a gas mask were used.

Hydrogen selenide in a stream of nitrogen carrier gas was bubbled for 5 minutes into a solution of 6.0 grams of tropylium bromide in 100 ml. of distilled water. A white, curdy precipitate formed immediately. After 5 minutes more the flow of nitrogen was stopped and the precipitate filtered. The mother liquor was returned to the reaction flask and hydrogen selenide bubbled through the solution for another 5 minutes. The combined precipitates on the filter funnel were rinsed with 50 ml. of distilled water.

The tropyl selenide was dissolved in 100 ml. of ethyl ether and this solution was dried over 10 grams of anhydrous magnesium sulfate, with occasional manual agitation, for 10 to 15 minutes. The solution was filtered and the ether removed. The yield of 4.3 grams of crude dry tropyl selenide was 95% of the theoretical. The tropyl selenide was recrystallized either from ether, or alternately from pentane and ether, by dissolving the selenide at room temperature and crystallizing it at −64° C. (chloroform-dry ice). The pure selenide melted at 64.7–65.2° C. Tropyl selenide was stable for at least a week when kept at dry ice temperature. The use of excess hydrogen selenide (or simply passing the gas for as long as ½ hour) produced an undesired side product or mixture of side products which were not easily separated from the tropyl selenide. Analyses of products obtained in this way showed a high selenide content (between that of the selenide and diselenide). Ether extraction of the original reaction mixture always resulted in a high selenide content. On observation of the recrystallization of these mixtures, two types of crystals were visually observed: the second type had an orange tinge. Contact between the hydrogen selenide and the tropyl selenide was minimized by removing it as a solid, not as an ether solution, and by washing the precipitate immediately with water. Working in a darkened room seemed to reduce the rate of visible decomposition (which may be due to any of the selenium containing materials present—soluble or not). Hydrogen selenide is known to decompose to red selenium and a reddish precipitate was observed from time to time..

Analysis. The tropyl selenide was analyzed for selenium according to Gould (*9*). To provide a smoother digestion of the compound, approximately 0.5 ml. of concentrated nitric acid was added to the sample before digestion (at the time of the addition of sulfuric acid). Six analyses were made: Calculated for $C_{14}H_{14}Se$: Se; 30.23. Found: Se; 30.6, 30.1, 29.9, 29.9, 29.9, 30.3. Average: Se; 30.1.

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