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Phosphine Selenides: Donor Properties Toward Iodine

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Received June 25, 1968

Concentration equilibrium quotients and extinction coefficients have been measured at 5.3, 15.0, 24.7, and 35.3° for charge transfer complexes which form, in chloroform solution, between iodine and four triarylphosphine selenides. Values of the thermodynamic constants, as calculated from these data, were as follows: $-\Delta H_{298}$, *9.10-10.45 kcal/mole;* $-\Delta F^{\circ}_{298}$, *4.91-5.40 kcal/mole and* $-\Delta S$, *13.95-16.94 eu. Among the* R_3PX *molecules, where X is a group VI element, the stabilities of the complexes have been found to increase with decreasing electronegativity of X. In addition to the increased donor tendency of X with increase in atomic number, the possible importance of mutually induced polarization as a stabilizing factor is also discussed.*

Introduction

As part of an overall study concerned with the chemistry of molecules of the type G_3MX, where G is an organic aryl or alkyl group, M a P, As or Sb atom, and X an O, S, Se or Te atom, we have been interested in studying the donor properties of these molecules toward halogens. The present study is concerned with the formation of charge-transfer complexes in chloroform solution between iodine and four triarylphosphine selenides. Systems involving the formation of charge-transfer complexes between iodine and the following related donors have been studied recently: tertiary amine N-oxides (Kubota),[1] triphenylarsine oxide (Grundnes, *et al.*),[2] trialkyl- and triphenylphosphine oxides (Gramstad and Snaprud),[3] triarylphosphine sulfides (Tefteller and Zingaro),[4] and trialkylarsine oxides (Kolar, *et al.*).[5] The availability of this data together with the results reported herein, makes possible a more meaningful comparison of the donor properties of these molecules. The acceptor, in all of these studies, has been iodine, and the donor capabilities can be compared as a function of the change in the group V atom, *e.g.*, G_3NO, G_3PO, G_3AsO; the change in the group VI atom, *e.g.*, G_3PO, G_3PS, G_3PSe; and the change in the substituents, G.

Experimental Section

Phosphine Selenides. The preparation of triphenylphosphine selenide has been described elsewhere.[6] The three other triarylphosphine selenides were prepared by refluxing the appropriate phosphine with finely powdered selenium in butanol under an atmosphere of nitrogen for periods of about 12 hours, or by direct fusion under nitrogen without any solvent. The preparation of the phosphines has been described elsewhere.[7] All of the phosphine selenides were recrystallized from butanol[*] to a constant m.p. The analytical data for the three phosphine selenides not previously reported are given in Table I.

Equilibrium Studies. Ultraviolet and visible spectra were measured on a Cary Model 14-R spectrophotometer. The charge-transfer band of the complex, located at, or very close to 325 mμ, was used to

Table I. Analytical data and melting points of triarylphosphine selenides

		Analytical Data			
Compound		%C	%H	%P or (Se)	M.p., °C
Diphenyl-4-methylnaphthylphosphine selenide	Calcd.	68.15	4.73	(19.48)	198
	Found	67.69	4.72	(19.27)	
Tris(1-naphthyl)phosphine selenide	Calcd.	73.32	4.32	6.30	272-73
	Found	73.54	4.39	6.28	
Diphenyl-1-naphthylphosphine selenide	Calcd.	67.54	4.38	7.91	200-201
	Found	67.82	4.60	7.70	

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(1) T. Kubota, *J. Am. Chem. Soc.*, *87*, 458 (1965).

(2) J. Grundnes, P. Klaeboe, and E. Plahte, «Selected Topics in Structure Chemistry», Universitetsforlaget, Oslo, p. 265 (1967).

(3) T. Gramstad and S. I. Snaprud, *Acta Chem. Scand.*, *16*, 999 (1962).

(4) W. Tefteller, Jr. and R. A. Zingaro, *Inorg. Chem.*, *5*, 2151 (1966).

(5) F. L. Kolar, R. A. Zingaro, and K. Irgolic, *J. Inorg. and Nucl. Chem.*, *28*, 2981 (1966).

(6) R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, *1*, 771 (1962).

(7) W. Tefteller, Jr., R. A. Zingaro, and A. F. Isbell, *J. Chem. Eng. Data*, *10*, 301 (1965).

(*) Recrystallization from butanol was found to result in considerable decomposition of the selenide as was evidenced by the deposition of elemental selenium. Recrystallization from ethanol was possible without the accompanying decomposition, but large volumes of this solvent were necessary.

measure the concentration of the complex. In addition to the charge-transfer peak, less intense absorption takes place in this region due to transitions which occur in the aromatic rings. Hence, in the reference beam, a concentration of donor equal to that in the sample cell was used so that absorption of energy in this region was due entirely to charge-transfer energy. In doing this the assumption is made that the absorption by the aryl group is unaffected by complexation. It has been shown very recently[7a] that in the complex, triphenylphosphine selenide $1.5I_2$, the aromatic rings are in no way involved in the charge-transfer interaction.

Because of the large values of the formation constants, it was not practical to use the «blue-shift» band, or changes in the iodine absorption band itself for calculations. The concentrations used were so small that errors arising from taking differences between intensities in the region of iodine absorption (512 mμ) were too large to make such measurements useful.

The cells were contained in cell compartments in which temperature control was maintained well within ±1°C. The method of calculating the equilibrium constants (K) and the extinction coefficients (ε_c) are described elsewhere.[4] Spectra in the region of the charge-transfer band are shown in Figure 1 for the system triphenylphosphine selenide-iodine. In Figure 2 is shown a typical Rose-Drago plot[8] as obtained from the data in Figure 1. It should be mentioned that concentrations of all solutions were corrected for the changes in the density of chloroform with change in temperature.[9]

All of the values measured for K and their relationship to 1/T were subjected to a multiple regression analysis program. This is a standard program furnished by the Texas A&M Data Processing Center. The significance of the minimum probability is discussed elsewhere.[9a] These analyses indicated a minimum probability level of 0.995 for the equations obtained. In Figure 3, the straight line represents the best least squares fit as determined by this program.

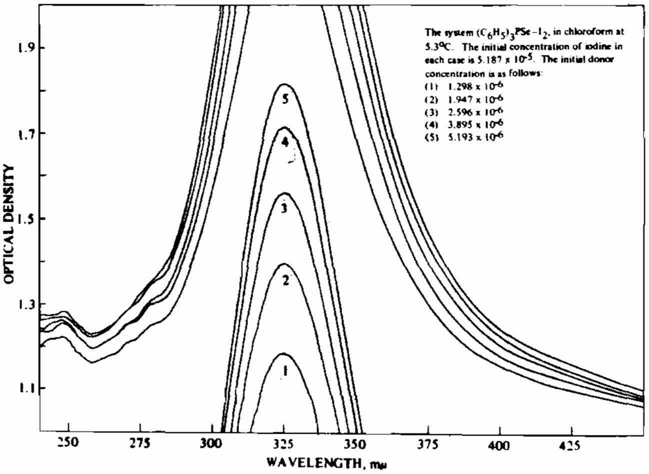

Figure 1. Charge-transfer band for the three component system iodine-triphenylphosphine selenide in chloroform. The wings are shown so as to illustrate the shape of the band. All concentrations are expressed in moles/liter.

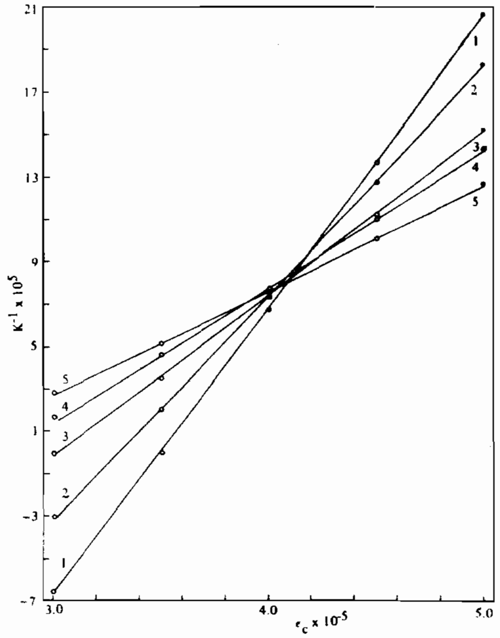

Figure 2. Rose-Drago plot for the system iodine-triphenylphosphine selenide at 5.3°C. The values plotted are based on the data of Figure 1.

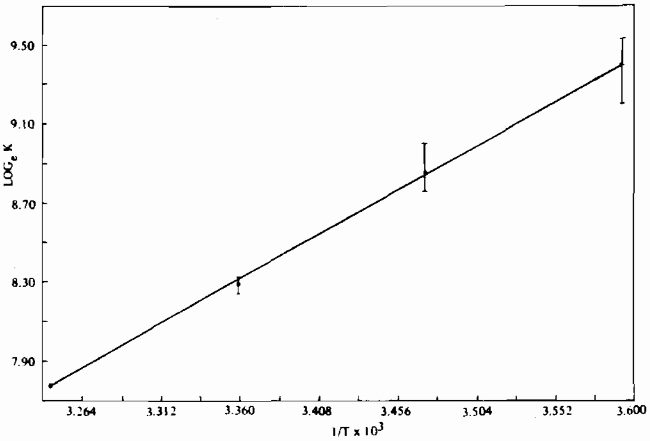

Figure 3. Plot of $\log_e$ K *vs.* 1/T for the system triphenylphosphine selenide-iodine in chloroform.

Isolation and Study of Addition Compounds. It would be highly desirable to isolate and characterize the 1:1 adducts with iodine as pure crystalline solids. Such studies are being pursued, but we have not been able to isolate materials which show any reproducible stoichiometry. Also, it has been very difficult to locate ν(P=Se) because these molecules show a great deal of strong absorption, almost certainly associated with the aromatic rings, in the region of ν(P=Se).

(7a) W. W. Schweikert and E. A. Meyers, *J. Phys. Chem.*, *72*, 1561 (1968).

(8) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, *81*, 6138 (1959).

(9) E. W. Washburn, Ed., «International Critical Tables of Numerical Data, Physics, Chemistry, and Technology», Vol. 3, p. 28, McGraw-Hill, Inc., New York, N. Y. (1928).

(9a) G. W. Snedecor, «Statistical Methods», Iowa State College Press, Ames, Iowa (1946).

The latter absorption has been reported in the range 388-559 cm^{-1}.[9b] However, 1:1 adducts which form between triphenylphosphine selenide or tricyclohexylphosphine selenide and iodine monobromide have been isolated[9b] and the expected lowering of $\nu(P{=}Se)$ on complexation has been observed.

Results and Discussion

Phosphine Selenide-Iodine Equilibria. When dilute solutions of the triarylphosphine selenides were added to dilute solutions of iodine in the same solvent, a strong charge-transfer band was observed at, or very close to 325 mμ, in the four cases studied. Because of the large value for the formation constant of iodine-phosphine selenide complex, it was not practical to use either the iodine absorption band at 512 mμ or the «blue-shift» band.[4] This was due to the experimental requirement that made it necessary to use very dilute solutions (10^{-5} *M*). Concurrently, absorptions in the region referred to were extremely weak. The molar ratios of donor to acceptor were limited to values below 10. At high donor: acceptor ratios, *e.g.*, >20, a secondary equilibrium, almost certainly involving triiodide ion, as was evidenced by absorption bands at 365 mμ and 295 mμ, was found to interfere.

The molar extinction coefficients (ε_c) and concentration equilibrium quotients (K) at 5.3, 15.0, 24.7, and 35.5°, as defined for the equilibrium

$$Ar_3PSe + I_2 \rightleftarrows Ar_3PSe \cdot I_2$$

for which the following equilibrium quotient, K, is defined

$$K = \frac{[Ar_3PSe \cdot I_2]}{[Ar_3PSe][I_2]}$$

have been measured for four triarylphosphine selenide-iodine charge-transfer complexes. The thermodynamic functions were calculated from the temperature dependence of the equilibrium quotients. The results are listed in Table II.

The value of the molar extinction coefficient of the triphenylphosphine selenide-iodine equilibrium at room temperature, 3.97×10^4 is about 10% lower while that of K, 4,000, is about 15% higher than the values previously reported ($\varepsilon_c = 4.40 \times 10^4$, K = 3370).[6] This is undoubtedly due to the correction for the absorption arising from the aromatic ring transitions in the region of the charge-transfer band which has been applied in the present study. This correction was not made in the earlier study. The new results are to be considered more reliable.

A linear relationship has been reported to exist[10] between the enthalpies and the entropies or free energies of formation of complexes which form between iodine and aromatic or oxygenated donors. In the present study, remarkably good linearity was observed in plots of ΔH *vs.* ΔF or ΔS for three of the four donors studied. Both points for tris(1-naphthyl)-phosphine selenide deviated from the lines drawn through such points in both the ΔS *vs.* ΔH and ΔF *vs.* ΔH plots.

The present study provides unequivocal confirmation of the observation that in the G_3PX compounds, where G is an alkyl or aryl group and X a group VIA atom, there is a progressive increase in the equilibrium quotient as X changes from O to S to Se.[4] This trend is further emphasized by a comparison of the enthalpy changes. Gramstad and Fuglevik[11] reported a value of ΔH = −3.2 kcal/mole for the system triethyl phosphate-iodine in CCl_4 while Tsubomura and Kliegman[12] report ΔH = −2.94 kcal/mole for the system tributyl phosphate-iodine, in heptane solution. However, in these two systems the donor, the P=O group, is attached to the organic moieties *via* an oxygen atom, *i.e.*, P–O–C bonding is present. The only thermodynamic data for a phosphine oxide-iodine system is that of Gramstad and Snaprud.[3]

Table II. Equilibrium quotients and extinction coefficients for 1:1 phosphine selenide-iodine complexes in chloroform

Phosphine selenide deriv.	T, °C	λ_{max} C-T band mμ	$\Delta\bar{\nu}_{1/2}$ cm^{-1}	$\varepsilon_c \times 10^{-4}$	Range of ε_c	K l/mole $\times 10^{-3}$	Range of K	−ΔH kcal/mole	$-\Delta F^\circ_{289}$ kcal/mole	−ΔS eu
Triphenyl-	5.3	325	521	4.09	3.82-4.29	12.0	10.0 -13.9			
	15.0	[a]	[b]	3.61	3.28-3.84	7.40	6.40- 8.20			
	24.7	[a]	[b]	3.97	3.83-4.13	4.00	3.82- 4.13	9.33	4.91	14.83
	35.3	[a]	[b]	4.36	—	2.40	—			
Tris(1-naphthyl)-	5.3	325	663	3.66	3.57-3.74	33.1	29.7 -36.8			
	15.0	[a]	[b]	3.72	3.61-3.81	16.7	15.3 -18.0			
	24.7	[a]	[b]	3.55	3.10-3.84	9.09	7.14-12.4	10.45	5.40	16.94
	35.3	[a]	[b]	3.74	3.53-3.97	5.26	—			
Diphenyl-1-naphthyl-	5.3	326	612	3.97	3.92-4.04	19.7	18.7 -20.8			
	15.0	[a]	[b]	3.57	3.32-3.73	10.4	9.30-12.2			
	24.7	[a]	[b]	4.07	—	5.15	—	9.99	5.06	16.54
	35.3	[a]	[b]	3.38	3.14-3.60	3.38	2.99- 3.73			
Diphenyl-4-methyl-naphthyl-	5.3	325	606	3.91	3.63-4.10	13.5	11.6 -15.4			
	15.0	[a]	[b]	3.65	—	7.63	—			
	24.7	[a]	[b]	3.67	3.15-3.91	4.70	3.80- 5.81	9.10	4.94	13.95
	35.3	[a]	[b]	4.07	3.86-4.25	2.68	2.57- 2.94			

[a] The location of the charge-transfer band did not shift sufficiently, over the range of temperature studied, to be measured.
[b] The half-band widths did not change to a measurable degree over the range of temperature studied.

(9b) R. A. Zingaro, *Inorg. Chem.*, 2, 192 (1963).

(10) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 79, 4839 (1957).

For the system $(C_2H_5)_3P{=}O$-iodine in carbon tetrachloride the reported K=83.17 at 20° and $\Delta H = -4.9$ kcal/mole. Although a more meaningful discussion could be presented if thermodynamic data on a triarylphosphine oxide were available, a useful comparison can be made. Thus, ΔH, which averages –5.9 kcal/mole for complexes which form between six phosphine sulfides and iodine[4] is about 20% greater than the value reported when a trialkylphosphine oxide is the donor. This difference would probably be greater if a comparison could be made with a triarylphosphine oxide because of the electron withdrawing tendencies of the aromatic rings. The present study reveals that the enthalpies of formation of the iodine complexes, with phosphine selenides as the donor molecules, average –9.8 kcal/mole, or about 65% greater than the values observed for the phosphine sulfide analogues.

The trends in the values of the association equilibrium quotients further clarify this trend. Thus, K_{ass} for the triarylphosphine sulfide-iodine equilibrium averages 130 while the average value of K_{ass} for the donors which are the subject of this report is 5730. The increase in K_{ass} in going from P=S to P=Se is considerably greater than the change in going from P=O to P=S. This trend in the values of K is, of course, directly reflected in the corresponding free energy losses which accompany the formation of the complexes in the respective systems.

It is quite reasonable to expect that the stability of the phosphine chalcogenide complexes with iodine should follow the observed order, *viz.*, P=Se> P=S>P=O. Pursuing an argument previously presented,[4] in somewhat greater detail, it should be recalled that the electron pair occupying the σ_{sp} orbital on the chalcogen atom is more favorably situated with respect to σ-bonding to the vacant $\sigma_u(5p_z)$ level on the acceptor iodine molecule. The σ_{sp} electron pair referred to occupies a tetrahedral sp^3 orbital in the valence bond sense. The tetrahedral orientation of the electron pair on the sulfur atom of triphenylphosphine sulfide in the complex $2\Phi_3PS{\cdot}3I_2$ has been demonstrated in a convincing manner.[7a] The P–S–I bond angle in this molecule was found to be 107°.

The concurrent formation of a $\pi_{m.o}$ involving the mixing of a pπ iodine (filled) and dπ chalcogen (empty) level may play an important role in determining the stability of the complex. The absence of any dπ orbital in oxygen has already been used to explain the observation that phosphine oxides appear to be the weakest donors toward iodine among this group of molecules. Pursuing the argument of $p\pi_I \rightarrow d\pi_X$ interaction, it is quite reasonable to expect the 5p level on iodine to mix with a 4d level (on Se), because of the greater proximity of their energies, much more effectively than with a 3d level (on S) which is much lower in energy.

Another simple and more classical argument can be related to the sizes of the atoms involved in the donor-acceptor interaction. The donor-acceptor interaction occurs, in the case of the present study, between two large, polarizable atoms, Se and I. Contributing structures of the type $Ar_3P{=}\overset{\delta+}{S}\ldots I\text{--}\overset{\delta-}{I}$ or $Ar_3P{=}S\overset{+}{I}\ldots\overset{-}{I}$ would induce polarization in the neighboring atom. In the general case, $Ar_3P{=}X \rightarrow I_2$, the degree of stability resulting from mutually induced polarization would necessarily follow the order of polarizability of X, the group VIA atom, *viz.*, Se>S>O. The trend in stabilities is consistent with this idea. This argument could be expressed in terms of «soft-soft» interactions, but we tend to concur with Williams and Hale[13] that in effect, this amounts to an indulgence in the use of neologisms. This argument also finds support in the observation of Gramstad and Fuglevik[11] who compared the relative donor strengths of $(EtO)_3P{=}O$ and $(EtO)_3P{=}S$ in hydrogen bonding with complex formation with iodine. Thus, K_{ass}, for hydrogen bond formation between phenol or pentachlorophenol and $(EtO)_3P{=}O$ was, at 20°, 350.5 and the enthalpy of formation was –6.7 kcal/mole. The corresponding values, when $(EtO)_3P{=}S$ was the donor, were 4.5 and –3.2 kcal/mole. On the other hand, when iodine was the acceptor, K_{ass} was found to be 6.2 with a ΔH value of –3.2 kcal/mole when $(EtO)_3P{=}O$ was the donor. With $(EtO)_3PS$ as the donor the corresponding values with iodine were 10.0 and –5.9 kcal/mole. Although basic m.o. ideas have been used to interpret these data[11,14] the explanation based on the respective polarizabilities, *i.e.*, two nonpolarizable atoms are involved in the $(RO)_3P{=}O\ldots HX$ interaction while two polarizable atoms are involved in the $(RO)_3P{=}S\ldots I_2$ interaction, is also consistent with the facts.

It would be predicted, according to this line of reasoning, that phosphine sulfides and selenides should coordinate preferentially with polarizable cations. Nicpon and Meek[15] have, in fact, been able to prepare complexes of phosphine sulfides, phosphine selenides and arsine sulfides with the polarizable metal ions Hg^{II}, Pd^{II}, Pt^{II}, Cd^{II}, and Ag^{I} but *not* with the considerably less polarizable cations Co^{II}, Ni^{II} or Cu^{II}. On the other hand, Bannister and Cotton[16] were able to prepare triphenylphosphine oxide complexes with Mn^{II}, Fe^{III}, Co^{II}, Cu^{II}, and Zn^{II}. These observations are consistent with the predicted behavior of this group of donors.

Acknowledgment. This work is part of a program which is receiving support from The Robert A. Welch Foundation of Houston, Texas and the United States Atomic Energy Commission under contract AT-(40-1)-2733. (One of the authors (B.R.C.) was a Summer Research Participant at Texas A&M University and was supported by a grant from the National Science Foundation.)

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