retained.[13] The F^{19} spectrum of a CCl_4 solution at −20° shows the doublet structure which might possibly mean that P–F bond breakage occurs *via* an intermolecular collision induced exchange mechanism. Also traces of HF may be catalyzing the exchange.

Why intermolecular association apparently exists in PH_2F_3 in the liquid state and not in PHF_4 is not evident. It might be speculated that in PHF_4 (if hydrogen bonding is the cause of association) the single proton is electronically "satisfied" by intramolecular hydrogen bonding whereas in PH_2F_3 having two protons intermolecular hydrogen bonding becomes a more important energy consideration.

Supporting the presence of hydrogen bonding is the observation of a considerably negative chemical shift for the protons in PH_2F_3 and PHF_4. These values (Tables II and III) indicate that an "acidic" character is associated with the hydrogen atoms. The values are in the region observed for phenolic protons.

The F^{19} shifts of PH_2F_3 and PHF_4 are upfield compared with −31 ppm (averaged) for PCl_2F_3 and are in a direction expected[10a] on replacing chlorine atoms with less electronegative hydrogen atoms. Thus the two shifts are complementary.

The reason for the lack of observance of fluorine–proton spin coupling in the F^{19} measurements for PH_2F_3 and PHF_4 at temperatures where such coupling is present in the proton spectra is not known. Perhaps such structure would be revealed if F^{19} spectra could be obtained at slightly lower temperatures than reported here. There are additional mechanisms which contribute to spin-lattice relaxation for fluorine compared to protons, namely, anisotropy in the fluorine nuclear magnetic shielding[14] and spin-rotational interaction.[15] These mechanisms assume increasing importance in viscous media at low temperatures. However, the magnitude of these effects will only be revealed by a more detailed investigation.[16]

Acknowledgment.—The authors wish to thank E. Anderson for performing the nmr measurements and Miss D. M. Dodd for making the infrared measurements.

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[13] With loss of P–F spin coupling it would be difficult to observe whether P–H coupling was present or not in the P^{31} spectrum of PHF_4 as seen from the resultant of the envelope of the lines comprising the two quintets in the predicted low-temperature pattern (Figure 3b).

[14] H. S. Gutowsky and D. E. Woessner, *Phys. Rev.*, **104**, 843 (1956).

[15] H. S. Gutowsky, I. J. Lawrenson, and K. Shimomura, *Phys. Rev. Letters*, **6**, 349 (1961).

[16] NOTE ADDED IN PROOF.—Preparation of PHF_4 and PH_2F_3 from $(CH_3)_3SnH$ and PF_5 was reported recently by P. M. Treichel and R. A. Goodrich, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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Phosphine Sulfides: Donor Properties toward Halogens

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Equilibrium quotients and extinction coefficients have been measured at 25, 35, and 45° for charge-transfer complexes which form, in chloroform solutions, between iodine and six phosphine sulfides. Values of the thermodynamic constants have been estimated from these data. Eight crystalline complexes were isolated as the pure compounds and the fundamental P–S vibrations, $\bar{\nu}_s$(P–S), have been compared with those of the parent phosphine sulfides. It has been observed that in the R_3PX donor molecules, where X is a group VI atom, the electronegativity of X is much more important than the nature of the organic substituents in determining the stabilities of the complexes.

Introduction

As part of a continuing study involving molecular complex formation between phosphine oxides, sulfides, or selenides and halogens or interhalogens, we have studied the donor properties of six trisubstituted phosphine sulfides containing highly condensed aromatic groups toward halogens as acceptor molecules. It was thought that these phosphine sulfides might possess unique donor properties, especially in the solid state, since they might be able to coordinate either by way of the aromatic ring system or by way of the free electron pair on the sulfur atom.

The study of charge-transfer complexes involving halogens as acceptor molecules has received a great deal of attention during the past two decades, but only a limited amount of work has dealt with complexes involving phosphine oxides and chalcogenides. The first example of the formation of crystalline addition compounds between various phosphine sulfides and halogens or interhalogens were reported by Zingaro and Meyers.[2] They isolated as pure crystalline solids compounds in which triphenylphosphine sulfide, triphenylphosphine selenide, and tricyclohexylphosphine

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[1] (a) Abstracted from a dissertation submitted by J. Wilburn Tefteller, Jr., to Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1966. The complete document has been deposited with University Microfilms, Inc., Ann Arbor, Mich. (b) Author to whom correspondence concerning reprints should be addressed at the Department of Chemistry, Texas A&M University, College Station, Texas.

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

selenide functioned as donor molecules. The effect of halogen complexing on the P–O, P–S, and P–Se vibrations in some phosphine oxides, sulfides, and selenides has also been investigated recently.[3,4] It was found that complexing with halogen or interhalogen brings about a shift in the P–X vibration (where X = O, S, or Se) to lower frequencies. A spectrophotometric study of the equilibria between iodine, iodine monochloride, and iodine monobromide and various phosphine oxides, sulfides, and selenides has also been reported.[5] A marked decrease was noted in the magnitude of the formation constants which followed the order of Se > S > O in those cases where 1:1 complexes were the principal ones formed. The present study was undertaken primarily to determine whether complexing could occur by way of π interaction with aryl substituents and also to obtain some thermodynamic data so that a more quantitative comparison with other donor molecules could be made.

Experimental Section

Phosphine Sulfides.—The phosphine sulfides were prepared by refluxing the phosphines with elemental sulfur in 1-butanol or 1-hexanol and purified by recrystallization from an appropriate solvent, as described elsewhere.[6]

Crystalline Addition Compounds.—These compounds were prepared by the direct combination of a solution of the halogen, or interhalogen, in carbon tetrachloride with a chloroform solution of the phosphine sulfide. Cooling of the reaction mixture in a Dry Ice–acetone bath and the addition of petroleum ether generally brought about rapid precipitation of the product. The growth of large single crystals was achieved in only one case, by allowing a dilute solution of the components in a chloroform–carbon tetrachloride mixture containing a small amount of petroleum ether to stand on a vibration-free surface for several weeks. The following description of the preparation of bis(4-methylnaphthyl)phenylphosphine sulfide–iodine will serve to furnish details.

Preparation of Bis(4-methylnaphthyl)phenylphosphine Sulfide·I_2.—To 0.50 g (0.0012 mole) of bis(4-methylnaphthyl)phenylphosphine sulfide dissolved in a minimum of chloroform was added 100 ml of a saturated solution of iodine in carbon tetrachloride (0.0012 mole of I_2). The solution was cooled in a Dry Ice–acetone bath, and petroleum ether was added until the solution became turbid. Upon continued cooling a heavy oily layer formed. The solvent was decanted off and about 3 ml of diethyl ether was added to the oily residue to facilitate crystallization. The reaction flask was then returned to the cooling bath and the mixture was stirred with a glass rod until crystallization occurred. The product was filtered off, washed several times with petroleum ether, and dried in air.

Preparation of Tris(4-methylnaphthyl)phosphine Sulfide·I_2 Using Molten Naphthalene as a Solvent.—A mixture consisting of 1.0 g (0.0021 mole) of tris(4-methylnaphthyl)phosphine sulfide, 0.52 g (0.21 mole) of iodine, and 20 g of naphthalene was heated and held in the molten state for 20 min and then allowed to solidify. To the cooled mass was added about 175 ml of chloroform, which dissolved the naphthalene. The slightly soluble residue was then filtered off and washed several times with chloroform. The filtrate and washings were combined, covered with filter paper, and allowed to stand for several days until all of the solvent had evaporated. A small amount of chloroform was added to dissolve any remaining naphthalene. The crystalline complex was filtered off and washed again with chloroform and finally with petroleum ether.

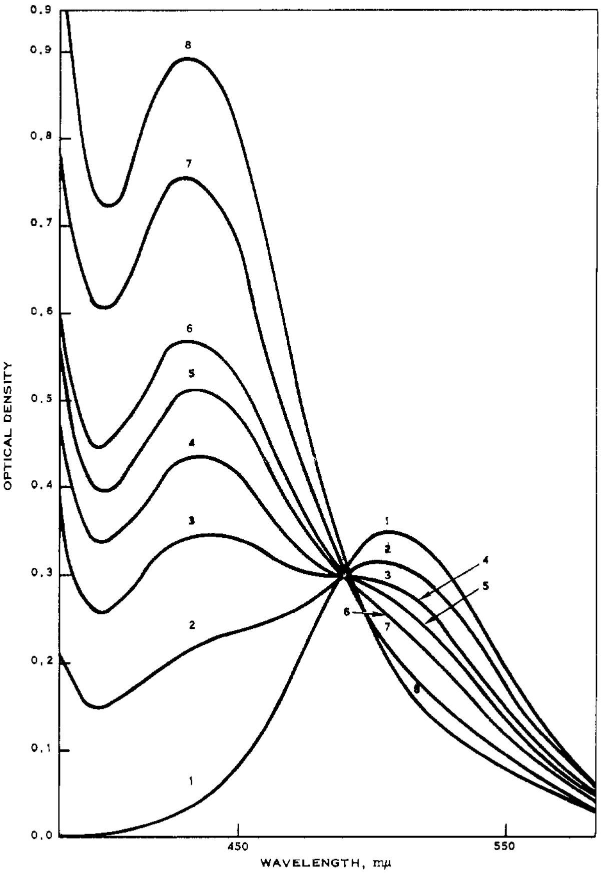

Figure 1.—Absorption spectra for the system diphenyl-4-methylnaphthylphosphine sulfide–iodine in chloroform. The initial concentration of iodine is 3.55×10^{-4} *M* in each case. Initial concentrations of the donor are: (1) 0; (2) 1.77×10^{-3} *M;* (3) 3.55×10^{-3} *M;* (4) 5.23×10^{-3} *M;* (5) 7.10×10^{-3} *M;* (6) 8.87×10^{-3} *M;* (7) 17.74×10^{-3} *M;* (8) 35.48×10^{-3} *M*. This donor, as were all others studied, was completely transparent in this region.

Infrared Spectra.—Spectra in the region of $\bar{\nu}_s$(P–S) were recorded either on a Perkin-Elmer Model 21 spectrometer with CsBr optics or on a Perkin-Elmer Model 521 using KBr pellet sampling techniques.

Equilibrium Studies.—Solution equilibria were measured in chloroform using a Beckman DK-1 spectrophotometer. The "blue-shift," the shift in the free iodine absorption from 512 mμ to a higher frequency upon complex formation, is shown in Figure 1. Using data of the type shown in Figure 1, the graphical method of Rose and Drago[7] was used to calculate the extinction coefficient (ϵ_c) and the equilibrium quotient (*K*) for the 1:1 complex. The method involves the use of the linear equation

$$K^{-1} = \frac{A}{\epsilon_c} - C_I - C_D + \frac{C_D C_I}{A}(\epsilon_c)$$

in which *A* is the absorbance of the blue-shift band and C_I and C_D are the initial concentrations of acceptor and donor, respectively. Suitable values of ϵ_c are selected and corresponding values of K^{-1} are calculated. Plots of K^{-1} *vs.* ϵ_c then give a series of straight lines which have a common intercept which correspond to the correct values of ϵ_c and K^{-1}. A typical example of such a plot is shown in Figure 2.

Resistivity Measurements.—Because it has been demonstrated that the molecular complexes of iodine with pyrene and

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

(4) R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961).

(5) R. A. Zingaro, R. E. McGlothlin, and E. A. Meyers, *ibid.*, **66**, 2579 (1962).

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

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

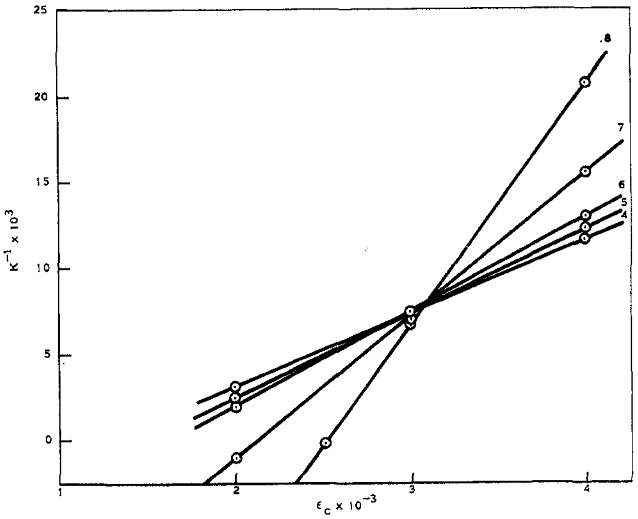

Figure 2.—Rose–Drago plot for the system diphenyl-4-methylnaphthylphosphine sulfide–iodine.

perylene possess electrical conductivities in the semiconductor range,[8] the electrical resistivities of the crystalline addition compounds were measured. The polycrystalline powders were packed in a hollow Teflon cylinder of 0.20 cm diameter and pressed between cylindrical graphite electrodes. The sample was connected in series with a 4.5-v battery and a Keithly high-impedance dc electrometer–voltmeter. Careful shielding of the sample and the circuit was essential. This was accomplished by complete enclosure in a grounded cage made of aluminum foil or fine copper wire mesh. The resistivities measured between 10^7 and 10^{18} ohm-cm. These compounds are obviously insulators at room temperature.

Results and Discussion

Phosphine Sulfide–Halogen Addition Compounds.—Eight phosphine sulfide–halogen complexes were isolated as pure crystalline compounds. The analytical data and pertinent physical properties are listed in Table I. The infrared spectra of the crystalline complexes in the region of $\tilde{\nu}_s$(P–S) (600–635 cm^{-1}) show that the fundamental P–S stretching frequencies are shifted to lower values upon halogen complexing. This observation tends to corroborate the suggestion that coordination with the halogen acceptor occurs by way of the thiophosphoryl sulfur, since the direction of this shift reflects a decrease in the P–S bond order. Without making any assumptions concerning the geometry of the phosphine sulfide–halogen complexes, and since they are 1:1 complexes, it is reasonable to assume that the simplest model is represented by an interaction involving donation of the σ electron pair from the thiophosphoryl sulfur to the electronegative halogen. This would result in a decrease in the electron density about the sulfur atom and a concurrent net decrease in sulfur to phosphorus $p\pi_s \rightarrow d\pi_p$ back-bonding. This has been discussed elsewhere.[4]

Recent crystallographic studies[9] on the structure of the $(C_6H_5)_3PS \cdot 1.5I_2$ complex are pertinent to this discussion. For every two donor molecules there is present a third mole of acceptor which, it was believed, could be π bonded to the aromatic rings. The iodine–sulfur bond distance shows that two iodine molecules are bonded to the sulfur atoms of the thiophosphoryl groups of two donor molecules and the S–I–I arrangement is essentially linear. The third molecule of iodine is too distant from the aromatic rings and can have no interaction with them. Rather, it is coplanar and collinear with the terminal iodine atoms of two of the halogen molecules bonded to the sulfur atoms.

What previously appeared to be a doublet in the region of $\tilde{\nu}_s$(P–S) was observed[6] in the infrared spectra of tri-1-naphthyl-, di-1-naphthylphenyl-, and diphenyl-1-naphthylphosphine sulfide. It has now been observed that upon halogen complexing only the longer wavelength component of the apparent doublet is shifted to a lower frequency. This suggests that the splitting previously observed was due to a combination of the P–S fundamental with some other vibration and that the P–S vibration in these molecules is not itself a doublet. The C–P vibration in triphenylphosphine

TABLE I

PHYSICAL DATA FOR PHOSPHINE SULFIDE–HALOGEN CRYSTALLINE COMPLEXES

	Analytical data								P–S freq, $\tilde{\nu}$ (cm^{-1})		
Compound		%C	%H	%P	%S	%I	Color	Mp, °C	Phosphine sulfide	Halogen complex	$-\Delta\tilde{\nu}$, cm^{-1}
Tris(4-methylnaphthyl)phosphine sulfide·I_2	Calcd	53.53	3.68	4.18	4.33	34.28	Light brown	233–245	600	583	17
	Found	53.26	3.66	4.03	4.26	34.54					
Bis(4-methylnaphthyl)phenylphosphine sulfide·I_2	Calcd	49.72	3.43			37.53	Brown	177–180	604	591	13
	Found	49.64	3.41			37.38					
Diphenyl-4-methylnaphthylphosphine sulfide·I_2	Calcd	45.12	3.13	5.06	5.24	41.46	Reddish brown	161–166	605	595	10
	Found	45.27	3.12	5.11	5.05	41.58					
Tris(1-naphthyl)phosphine sulfide·I_2	Calcd	51.60	3.03			36.34	Light brown	174–176	621	589	32
	Found	51.08	2.98			36.17					
Bis(1-naphthyl)phenylphosphine sulfide·I_2	Calcd	48.17	2.95			39.15	Dark brown	117–120	613	590	23
	Found	47.63	3.32			38.41					
Diphenyl-1-naphthylphosphine sulfide·I_2	Calcd	44.17	2.87	5.18	5.36	42.43	Reddish purple	157–160	608	596	12
	Found	43.93	2.91	5.21	5.50	42.23					
Bis(1-naphthyl)phenylphosphine sulfide·IBr	Calcd	51.93	3.18	Br:	13.29	21.10	Pale yellow	137–140	613	584	29
	Found	51.68	3.33		13.07	20.92					
Diphenyl-1-naphthylphosphine sulfide·IBr	Calcd	47.93	3.11	Br:	14.50	23.03	Yellow	155–156	608	588	20
	Found	47.91	3.28		14.25	22.96					

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(8) J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961); L. S. Singer and J. Kommandeur, *ibid.*, **34**, 133 (1961).

(9) E. A. Meyers, Texas A&M University, personal communication.

TABLE II

EQUILIBRIUM QUOTIENTS AND EXTINCTION COEFFICIENTS FOR 1:1 PHOSPHINE SULFIDE–IODINE COMPLEXES IN CHLOROFORM

Phosphine sulfide deriv	T, °C	λ_{max}, blue-shift band, mμ	$\Delta\tilde{\nu}_{1/2}$, cm^{-1}	ϵ_c	K, l./mole	$-\Delta H$, kcal/mole	$-\Delta F°_{298}$, kcal/mole	$-\Delta S$, eu
Tri-4-methylnaphthyl-	25	426	5520	3331 ± 102	144 ± 9			
	35	427	6030	3358 ± 114	95 ± 7	6.12	2.94	10.67
	45	428	6126	3272 ± 56	73 ± 2			
Di-4-methylnaphthylphenyl	25	430	4938	3026 ± 54	210 ± 6			
	35	430	5275	3205 ± 40	127 ± 4	6.12	3.17	9.90
	45	431	5741	3018 ± 19	104 ± 2			
Diphenyl-4-methylnaphthyl	25	432	5008	3067 ± 24	128 ± 3			
	35	435	5191	3010 ± 44	89 ± 5	5.71	2.87	9.53
	45	435	5655	2916 ± 67	72 ± 4			
Tri-1-naphthyl-	25	430	5347	3101 ± 57	96 ± 5			
	35	432	5743	3007 ± 64	69 ± 5	4.66	2.70	6.58
	45	436	6255	2755 ± 63	58 ± 2			
Di-1-naphthylphenyl	25	433	5150	3086 ± 46	108 ± 3			
	35	434	5668	3167 ± 61	70 ± 4	6.80	2.77	13.52
	45	433	6340	3198 ± 109	55 ± 4			
Diphenyl-1-naphthyl-	25	437	4796	2668 ± 41	109 ± 4			
	35	438	5105	2712 ± 44	69 ± 2	6.00	2.78	10.81
	45	440	5707	2592 ± 98	58 ± 4			

appears at 663 cm^{-1}.[10] In highly condensed aromatic groups it should be located at slightly lower frequencies because of the heavier masses of the substituents and could very easily fall into the range of the P–S vibrations. It appears, therefore, that what originally seemed to be a P–S doublet is in fact a combination of the C–P and P–S vibrations.

Phosphine Sulfide–Iodine Equilibria.—When a trisubstituted phosphine sulfide was added to a dilute solution of iodine in chloroform, the visible iodine absorption band at 512 mμ was shifted to 433 ± 10 mμ (depending upon the particular donor).

The molar extinction coefficients (ϵ_c) and concentration equilibrium quotients (K) at 25, 35, and 45° (all ±1°) for six phosphine sulfide–iodine charge-transfer complexes have been measured. The thermodynamic functions were estimated from the temperature dependence of the equilibrium quotients in the usual manner. The results are summarized in Table II.

The excellent isosbestic point present in the spectral curves of Figure 1 and which was observed in all systems reported herein suggests the formation of a well-defined 1:1 complex between the trisubstituted phosphine sulfides and iodine according to the reaction

$$R_3PS + I_2 \rightleftarrows R_3PS \cdot I_2$$

The equilibrium quotient, K, for this reaction is defined as

$$K = \frac{[R_3PS \cdot I_2]}{[R_3PS][I_2]}$$

The charge-transfer theory[11] predicts that the magnitude of the blue shift should increase as the donor becomes more electron-releasing in character. The blue-shift absorption maxima for the complexes studied were correspondingly graded from 426 to 437 mμ in the order tris(4-methylnaphthyl)-, bis(4-methylnaphthyl)phenyl-, diphenyl-4-methylnaphthyl-, tris(1-naphthyl)-, bis(1-naphthyl)phenyl-, diphenyl-1-naphthylphosphine sulfide. This suggests a corresponding order of donor strengths contrary to that expected since the 4-methylnaphthyl group should be more basic than either the 1-naphthyl or phenyl group. That the correlation between blue shift and stability is not good is further supported by the values of the equilibrium quotients and free energies of formation of the complexes, which indicate that the stabilities of the six complexes are about equal.

The values of ΔH for all the complexes investigated were found to be apparently temperature dependent as was evident from the curvature obtained in plots of log K *vs.* $1/T$ if the average values of K were used. The average values were experimentally reproducible, as was done in independent sets of experiments carried out in four of the six donors. Such behavior can best be interpreted in one of two ways:[12] more than one complex is formed or only one is formed, but its enthalpy varies with temperature. In the former case the effective extinction coefficient will vary with temperature, but as can be seen from Table II there is no significant change in ϵ_c with temperature in this series of complexes. Thus, it is reasonable to conclude that there is only one complex present. In fact, there is no theoretical basis for *not* expecting ΔH to be temperature dependent. However, reference to Figure 3 shows that a straight line can be drawn through points which are within the maximum deviations from the arithmetical mean of the experimental values. Therefore, the apparent curvature may be due simply to experimental scatter.

Keefer and Andrews[13] have reported that there exists a linear relationship between the enthalpies and the free energies or entropies of formation for complexes

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[10] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[11] R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956).

[12] L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

[13] R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

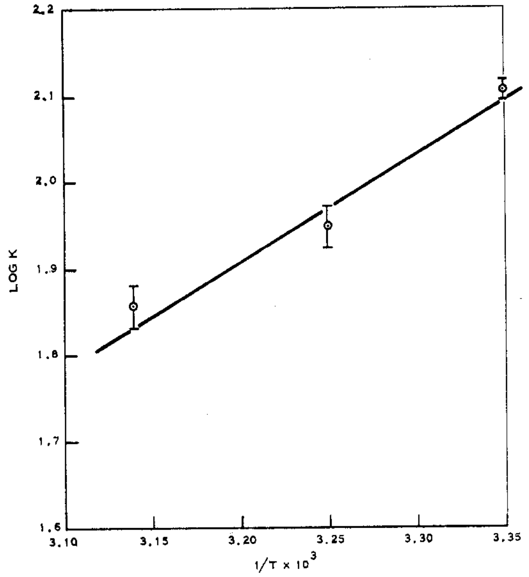

Figure 3.—Plot of log K *vs.* $1/T$ for the system diphenyl-4-methylnaphthylphosphine sulfide–iodine.

of iodine with aromatic and oxygenated donors. Such a linear relationship was observed in the case of the present donors, although the free energies of formation are virtually invariant.

The equilibrium quotients and thermodynamic constants for a number of iodine complexes with various donors are reported in the literature, from which are taken the values shown in Table III. Comparison of these values with those measured for donors studied in this paper suggests that the triarylphosphine sulfides are weaker donors toward iodine than triethylamine, stronger than benzene, and about equal in donor strength to pyridine and the trialkylphosphine sulfides. In the case of the thioethers, the donor strength appears to be about equal to that of the phosphine sulfides. This general behavior further emphasizes the n-type donor action of these molecules and the lack of any significant correlation with the nature of the organic substituent on the phosphorus atom. That the donor ability of the sulfur atom is only slightly affected by substituents on the phosphorus atom is further demonstrated by the values of the equilibrium quotient and enthalpy of formation of the $(C_2H_5O)_3PS–I_2$ complex.

One consistency is apparent, and this is that in the G_3PX compounds, where X is a group VI atom, there is a progressive increase in the equilibrium quotient as X changes from O to S to Se. The tris(cyclohexyl)-series supports this observation, as well as the following pairs of donors: diethyl ether and diethyl sulfide, dimethyl sulfide and dimethyl selenide, triphenylphosphine sulfide and triphenylphosphine selenide, and triethyl phosphate and triethyl phosphorothionate (Table III). From the data available it is apparent that the equilibrium quotient of the iodine complex formed with the molecule bearing the most electropositive group VI atom is always greater. No exception to this regularity has been noted, and since the complexing abilities of the triarylphosphine sulfides studied here are very similar to that of triphenylphosphine sulfide, these donor molecules apparently follow this same order.

TABLE III

EQUILIBRIUM QUOTIENTS AND HEATS OF FORMATION FOR 1:1 IODINE COMPLEXES AT 25°

Donor	Solvent	K, l./mole	$-\Delta H$, kcal/mole	Ref
Triethylamine	Heptane	4,690	12.0	*a*
Pyridine	Heptane	290 (17°)	7.8	*b*
Benzene	Hexane	1.55	1.3	*c*
Tris(n-octyl)phosphine oxide	Heptane	588		5
Tris(cyclohexyl)phosphine oxide	$CHCl_3$	39		5
Tris(cyclohexyl)phosphine sulfide	$CHCl_3$	1,820		5
Tris(cyclohexyl)phosphine selenide		46,600		5
Triphenylphosphine sulfide	$CHCl_3$	106		5
Triphenylphosphine selenide	$CHCl_3$	3,370		5
Trimethylphosphine sulfide	$CHCl_3$	604		5
Tris(n-butyl)phosphine sulfide	$CHCl_3$	59		5
Triphenylarsine oxide	$CHCl_3$	41.2		2
Triphenylarsine	CCl_4	1,400	9.4	*d*
Diethyl ether	CCl_4	8.7	4.3	*e*
Diethyl sulfide	Heptane	210	7.82	*e*
Dimethyl sulfide	CCl_4	71		*f*
Dimethyl selenide	CCl_4	472		*f*
Diphenyl selenide	CCl_4	28		*f*
Triethyl phosphate		6.2	3.2	*g*
Triethyl phosphorothionate		10	5.9	*g*

[a] S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958). [b] C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954). [c] R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955). [d] E. Augdahl, J. Grundes, and P. Klaboe, *Inorg. Chem.*, **4**, 1475 (1965). [e] H. Tsubomura and R. B. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961). [f] N. W. Tideswell and J. D. McCullough, *ibid.*, **79**, 1031 (1957). [g] T. Gramstad and W. J. Fuglevik, *Acta Chem. Scand.*, **16**, 2368 (1962).

The simplest explanation of the stability of the phosphine chalcogenide complexes in the order Se > S > O can be made on the basis of the ionization potentials of the chalcogenides. Selenium, having the lowest ionization potential, has the most loosely bonded pair of electrons, which are in turn most readily available for donation to the acceptor molecule. Similarly, the ionization potential of sulfur, being lower than that of oxygen, makes sulfur a stronger donor.

An alternative explanation, in terms of simple molecular orbital concepts, is as follows. Consider the R_3PX molecule, where X = O, S, or Se. The X atom is bonded to the phosphorus by an sp hybrid σ bond and by partial overlap of a $p\pi$ bond with an empty $d\pi$ orbital of the phosphorus atom. In addition, the X atom has two lone-pair orbitals, an sp hybrid σ and a $p\pi$ orbital, which are available for overlap with the lowest energy unfilled orbital of the acceptor molecule (the $\sigma_u^*(5p_z)$ level in the case of iodine). Of the two lone-pair orbitals, the σ_{sp} orbital is the better donor, because of its more favorable orientation with respect to