Table V. The Constancy of the C–C Bond Length in Cyclobutane Rings

Compound	C–C (Å)	Reference
Bicyclo[2.1.1]hexane	1.544	This study, electron diffraction
Bicyclo[2.1.1]-2-hexene	1.549	Electron diffraction[a]
Cyclobutane	1.548	Electron diffraction[b]
Tricyclo[3.3.0.0^{2,6}]octane	1.558	Electron diffraction[c]
Bicyclo[3.1.1]heptane	1.553	Electron diffraction[d]
Biscyclobutyl	1.548	Electron diffraction[e]
Bicyclo[1.1.1]pentane	1.545	Electron diffraction[f]

[a] See ref 7. [b] See ref 9. [c] See ref 1b. [d] G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **88**, 185 (1969). [e] A. De-Meijere, *Acta Chem. Scand.*, **20**, 1093 (1965). [f] See ref 8.

obtained might not be the true ones. Owing to the above-mentioned reason, a comparison between the two structure determinations seems to be of little significance.

One may conclude that the C–C bond length (1.545 Å) in an unsubstituted cyclobutane ring and any substituted cyclobutane ring was constant, except for those rings with high electronegative substituents. Further support for this conclusion is shown in Table V. A surprisingly small ∠HCH (100.8°) at C_5, C_6 has been found for this molecule and some other strained hydrocarbons.[7,8]

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Molecular Complexes of Iodine with Alkyl- and Chloro-Substituted Phosphine Sulfides

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Abstract: Absorption spectrophotometric studies have been made in the near-ultraviolet and visible spectral regions on the iodine complexes of trioctylphosphine sulfide, diethylchlorophosphine sulfide, and trichlorophosphine sulfide, with *n*-heptane as solvent. For the iodine complexes with trioctylphosphine sulfide and diethylchlorophosphine sulfide the charge-transfer band was located in the near-ultraviolet and employed in the evaluation of the thermodynamic parameters for 1:1 complex formation. The spectral characteristics for both of these charge-transfer bands were determined. The charge-transfer band for the trichlorophosphine sulfide–iodine complex could not be located. For all three complexes a "blue shift" of the visible iodine band was observed and isosbestic points were obtained. Thermodynamic parameters were evaluated from the shifted visible iodine band data and the spectral characteristics for this band were determined.

During the past two decades, since Benesi and Hildebrand first determined an equilibrium constant for the benzene–iodine complex,[1] quantitative thermodynamic and electronic spectral data have been obtained for a great many iodine complexes involving a rather large variety of both n and π electron donors.[2] The strength of these iodine complexes, based on their standard enthalpies of formation, varies from about −1 kcal/mol[3] to −12 kcal/mol.[4] Attempts have been made to correlate the electronic spectral properties with complex stability, for both the charge-transfer (CT) band and the "blue-shifted" visible iodine band.[5]

In order to establish trends and to obtain a meaningful correlation between theory and the thermodynamic and electronic spectral properties of molecular complexes, it would be most useful to have experimental data involving the greatest range of complex stability for a series of structurally similar molecular complexes. One method of obtaining such data would be to investigate a series of complexes involving a common electron acceptor interacting with several different electron donors each containing the same electron donor site. This has been done, for example, with the iodine complexes of a series of aliphatic amines.[4] However, the donor strength range of this series varied only from the strongest of known iodine complexes to those of intermediate strength and, consequently, did not include the relatively weak iodine complexes, with $K_c < 1.0$. To cover a more complete range of iodine-complex stability, three phosphine sulfides containing alkyl and chloro substituents were selected: trioctylphosphine sulfide, diethylchlorophosphine sulfide, and trichlorophosphine sulfide.

Another reason for the present study was to clarify some ambiguity with regard to the strength of trialkylphosphine sulfide–iodine complexes. For example, a

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[1] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 71, 2703 (1949).

[2] R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, pp 396–404.

[3] (a) T. M. Cromwell and R. L. Scott, *J. Amer. Chem. Soc.*, 72, 3825 (1950); (b) R. M. Keefer and L. J. Andrews, *ibid.*, 77, 2164 (1955).

[4] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jap.*, 33, 1660 (1960).

[5] H. Tsubomura and R. P. Lang, *J. Amer. Chem. Soc.*, 83, 2085 (1961).

Table I. The Thermodynamic Characteristics of the Trioctylphosphine Sulfide–Iodine and the Diethylchlorophosphine Sulfide–Iodine Complexes

Donor	K_c, l./mol (20°)	$\Delta H°$, kcal/mol	$\Delta S°$, eu
	(a) From Uv Data		
Trioctylphosphine sulfide	8500 ± 200	−11.4 ± 0.1	−21 ± 2
Diethylchlorophosphine sulfide	2.9 ± 0.4	−3.6 ± 0.4 (−4.0 ± 0.6)[a]	−10 ± 1
	(b) From Visible Data		
Trioctylphosphine sulfide	8800 ± 400	−11.5 ± 0.5	−21 ± 5
Diethylchlorophosphine sulfide	3.1 ± 0.2	−4.4 ± 0.1 −(4.4 ± 0.1)[b]	−13 ± 1

[a] Based on $K_c\epsilon_c$ *vs.* $1/T$ data. [b] Based on $K_c(\epsilon_c - \epsilon_I)$ *vs.* $1/T$ data.

K_c value of 59 l./mol was reported for the tributylphosphine sulfide–iodine complex to be compared with a K_c value of 1820 l./mol for the tricyclohexylphosphine sulfide complex with iodine.[6] Furthermore, both of these iodine complexes were reported to have their blue-shifted visible iodine band maxima at the same wavelength. Consequently, it was considered to be of some value to determine both K_c and $\Delta H°$ for a trialkylphosphine sulfide–iodine complex and to obtain the spectral parameters for the shifted visible iodine band.

Experimental Section

Materials. Matheson Coleman and Bell spectroquality *n*-heptane and resublimed iodine were used without further purification. Eastman reagent grade trioctylphosphine sulfide was dried over Drierite and distilled under reduced pressure. Diethylchlorophosphine sulfide (diethylthiophosphoryl chloride), obtained from City Chemical Corp., was dried over Drierite, treated with alumina, and then distilled under reduced pressure. Trichlorophosphine sulfide (thiophosphoryl chloride), obtained from K & K Laboratories, Inc., was also treated with Drierite and alumina and distilled under reduced pressure. However, the trichlorophosphine sulfide, based on spectral studies of the visible iodine band, was observed to react with iodine, producing spectra that came below the expected isosbestic point. Consequently, the trichlorophosphine sulfide was further treated with alumina for several weeks with daily shaking, resulting in solutions of the donor and iodine that gave the expected isosbestic point.

Spectrophotometric Determinations. Absorption spectra in the visible and near-ultraviolet spectral regions were measured by a Beckman double-beam (DB) ratio-recording spectrophotometer equipped with a Sargent linear–log (SRL) recorder. A pair of matched Beckman 1-cm silica "U" rectangular cells with ground-glass stoppers was employed for all the spectroscopic measurements. The Beckman DB spectrophotometer has a thermostatable cell compartment through which thermostated water was circulated from a WACO (Wilkins-Anderson Co.) heating and cooling constant-temperature bath. Measurements were made at 10, 20, 30, and 40° with the sample temperatures maintained constant to better than ±0.5°. Temperatures lower than 10° could not be employed because of the condensation of water vapor on the cell windows (a dry nitrogen purge kit cannot be used with the DB spectrophotometer).

The spectrophotometer wavelength scale was calibrated with a holmium oxide standard (Arthur H. Thomas Co.). For all the equilibrium constant determinations a series of solutions with a constant initial iodine concentration and variable initial donor concentrations was employed. The donor and acceptor concentrations were chosen so that all absorbance readings were in the range 0.30–0.95.

Calculation of K_c and ϵ_c. Three modifications of the following general equation for 1:1 molecular complex formation[7] were employed for the calculation of the molar concentration equilibrium constant, K_c, and the molar extinction coefficient of the complex, ϵ_c

$$\frac{D_0 I_0 b}{A'} = \left(D_0 + I_0 - \frac{A'}{b\epsilon_c'}\right)\frac{1}{\epsilon_c'} + \frac{1}{K_c\epsilon_c'} \qquad (1)$$

where D_0 and I_0 are the initial molar concentrations of the donor and iodine, respectively, b is the path length of the spectrophotometer cell in centimeters, and A' and ϵ_c' depend on the experimental conditions. $A' = A - b\epsilon_I I_0$ and $\epsilon_c' = \epsilon_c - \epsilon_I$, where A is the total experimental absorbance and ϵ_I is the molar extinction coefficient of uncomplexed iodine.

For both the ultraviolet and visible spectral studies of the trioctylphosphine sulfide–iodine complex $A' = A$ and $\epsilon_c' = \epsilon_c$.[8] In the case of the diethylchlorophosphine sulfide and trichlorophosphine sulfide complexes with iodine, where $D_0 \gg I_0$, the last two terms in the parentheses are dropped. In addition, for the ultraviolet studies $A' = A$ and $\epsilon_c' = \epsilon_c$,[9] whereas for the visible studies $A' = A - b\epsilon_I I_0$ and $\epsilon_c' = \epsilon_c - \epsilon_I$.[10]

Results

Trioctylphosphine Sulfide. Solutions containing a constant initial iodine concentration and variable initial trioctylphosphine sulfide concentrations showed an isosbestic point at about 496 nm in the visible spectral region. The iodine concentration was in the range (4.2–6.1) × 10^{-4} *M* and the trioctylphosphine sulfide concentrations varied from 2.8 × 10^{-4} to 12.7 × 10^{-4} *M*. The blue-shifted visible iodine band peak of the complex occurs at 440 nm, and this wavelength was chosen for the determination of K_c. At this wavelength there was no absorption by the colorless trioctylphosphine sulfide and, because of the small concentration employed, there was also no significant absorption by iodine. The standard enthalpy and entropy of complex formation was evaluated from a plot of log K_c *vs.* $1/T$. The results are presented in Table I.

In the near-ultraviolet the intense charge-transfer band of the trioctylphosphine sulfide–iodine complex has a maximum at 300 nm. For spectral studies using this band the initial iodine concentration was maintained in the range (4.2–6.1) × 10^{-5} *M*, a factor of 10 less than for the visible spectral studies, and the initial donor concentration was in the range (1.0–12.8) × 10^{-5} *M*. The charge-transfer band peak was employed for the determination of K_c and ϵ_c. At this wavelength, with the concentrations employed, there was negligible absorption due to either the donor or the acceptor. The standard enthalpy and entropy were also determined from the charge-transfer band data and are also listed in Table I. The values for the thermodynamic parameters of the trioctylphosphine sulfide–iodine complex obtained from both visible and ultraviolet spectral data agree very well.

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(6) R. A. Zingaro, R. E. McGlothin, and E. A. Meyers, *J. Phys. Chem.*, **66**, 2579 (1962).

(7) M. Tamres, *ibid.*, **65**, 654 (1961); see eq 25.

(8) R. P. Lang, *J. Amer. Chem. Soc.*, **84**, 1185 (1962).

(9) R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, **75**, 787 (1956).

(10) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *ibid.*, 71, 1104 (1952).

Table II. The Spectral Characteristics of the Iodine Complexes with Trioctylphosphine Sulfide, Diethylchlorophosphine Sulfide, and Trichlorophosphine Sulfide

Donor	λ_{max}, nm	ϵ_{max}, l./(mol cm)	$\Delta\bar{\nu}_{1/2}$, cm^{-1}	f	D, D
(a) The Charge-Transfer Band					
Trioctylphosphine sulfide	300	36,000	5200	0.80	7.1
Diethylchlorophosphine sulfide	277	26,000	5100	0.58	5.8
(b) The Shifted Visible Iodine Band					
Trioctylphosphine sulfide	440	2,260	4300	0.042	2.0
Diethylchlorophosphine sulfide	470	1,330	3800	0.022	1.5
Trichlorophosphine sulfide	505	1,180	3500	0.018	1.4
n-Heptane. solvent	522	897	3200	0.012	1.2

The spectral data for both the position and the intensity of the charge-transfer band are listed in Table II. The oscillator strength, f, and the transition dipole moment, D, were calculated from the following equations[11]

$$f = (4.32 \times 10^{-9})\epsilon_{max}\Delta\bar{\nu}_{1/2} \tag{2}$$

$$D = 0.096\sqrt{\epsilon_{max}\Delta\bar{\nu}_{1/2}/\bar{\nu}_{max}} \tag{3}$$

where $\bar{\nu}_{max}$ is in reciprocal centimeters. In order to obtain the integrated intensity data for the shifted visible iodine band of the complex, a correction was made, using K_c, for the overlap of the visible iodine band of the uncomplexed iodine with the long-wavelength side of the shifted visible iodine band. The results for the shifted visible iodine band of the complex are also listed in Table II.

Diethylchlorophosphine Sulfide. The visible absorption spectra of solutions with constant initial iodine concentration and variable initial diethylchlorophosphine sulfide concentrations showed an isosbestic point at about 510 nm. These solutions exhibited an absorption maximum for the shifted visible iodine band in the wavelength range between about 470 and 480 nm, depending on the initial iodine and donor concentrations. Owing to the great overlap of the uncomplexed iodine band with the shifted complexed iodine band, a resolution of the experimental spectra was required to determine the exact absorption maximum of the shifted iodine band and to evaluate the integrated absorption intensity parameters for this band. The spectral data for the shifted visible iodine band of the diethylchlorophosphine sulfide–iodine complex are listed in Table II, where f and D were calculated from eq 2 and 3, respectively.

The determination of K_c was made from spectral data at 470 nm, where there was no significant absorption by the donor at the concentrations employed. The concentration range for iodine was (5.0–7.0) × 10^{-4} *M*, while the diethylchlorophosphine sulfide concentration range was (0.1–0.6) *M*. The thermodynamic parameters for the diethylchlorophosphine sulfide–iodine complex, determined from visible spectral data, are listed in Table I. The standard enthalpy change was determined from the variations of both K_c and $K_c(\epsilon_c - \epsilon_I)$ with temperature, with the same results being obtained from both methods.

The charge-transfer band of this complex was located in the near-ultraviolet in a spectral region where there was strong absorption by diethylchlorophosphine sulfide. For the determination of K_c from the CT band, the initial iodine concentration was about 1.0 × 10^{-4} *M* while the initial donor concentration varied from 0.02 *M* to 0.29 *M*, with the lower concentrations being used for the 10° studies and the higher concentrations for the 40° measurements. Since the initial donor concentrations were much greater than the initial iodine concentration, only a very small per cent of the donor was involved in complex formation. Consequently, the ultraviolet absorption due to the donor could be directly subtracted from the experimental absorption to obtain the charge-transfer band of the complex, showing a peak at about 277 nm. However, for the K_c determination it was experimentally more convenient to have the donor in the reference cell at the same concentration as in the sample cell containing both iodine and donor.

The thermodynamic parameters for the diethylchlorophosphine sulfide–iodine complex, determined from the peak of the charge-transfer band, are listed in Table I. The standard enthalpy change was determined from both the variation of K_c and of $K_c\epsilon_c$ with temperature, with about a 10% difference being obtained from these two methods. The spectroscopic parameters of the charge-transfer band are listed in Table II.

Trichlorophosphine Sulfide. For the trichlorophosphine sulfide–iodine complex an isosbestic point was obtained at about 524 nm for solutions containing a constant initial iodine concentration and a variable donor concentration. The isosbestic point for this complex is, therefore, located at the peak of the uncomplexed visible iodine band spectrum. Consequently, there was a very great overlap of absorption by the complexed and the uncomplexed iodine, requiring a resolution of the experimental spectrum in order to obtain the spectral parameters for the shifted visible iodine band of this complex.

For the determination of K_c from the shifted visible iodine band the initial iodine concentration was in the range (6.0–7.0) × 10^{-4} *M*, while the initial concentration of trichlorophosphine sulfide varied from 0.4 to 1.2 *M*. There was no absorption by the donor in the wavelength range employed for the K_c determinations.

The difficulties involved in the determination of concentration equilibrium constants for very weak complexes have been discussed previously.[12] In the present study the donor concentrations could only be varied by a factor of 3 because at concentrations greater than about 1.2 *M* the plots for the appropriate form of eq 1 began to deviate from linearity. Furthermore, the value of K_c is very important for the resolution of the experimental visible iodine band spectrum into complexed and uncomplexed components. Consequently, K_c was determined at each of five wavelengths and the average value employed for the spectral resolution. If there is only one complex, and K_c is a reliable molar concentration equilibrium constant for 1:1 complex formation, there should be a random deviation or scatter in the K_c values determined at each of

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(11) R. S. Mulliken and W. B. Person, *Annu. Rev. Phys. Chem.*, **13**, 107 (1962).

(12) W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965).

the five wavelengths located on the short-wavelength side of the complexed visible iodine band, whereas there should be a systematic decrease in the ϵ_c values down the side of the absorption band of the complex. The five K_c values seem to deviate randomly with an average value of 0.41 ± 0.04 l./mol at 20°, whereas there is a systematic decrease in the ϵ_c values on the short-wavelength side of the shifted visible iodine band of the complex between 480 and 500 nm. The spectral characteristics for the shifted visible iodine band of the trichlorophosphine sulfide–iodine complex are listed in Table II.

In order to determine the standard enthalpy change for this complex, spectrophotometric studies were made at 10 and 30°, in addition to the 20° measurements. At 30° a side reaction occurred, as indicated by a decrease in the visible iodine band absorption and the absence of the isosbestic point. For the 10° studies the isosbestic point was maintained and K_c and ϵ_c were determined at the same five wavelengths as were employed in the 20° studies. Again the K_c values were found to deviate randomly while there was a systematic decrease in the ϵ_c values. However, the deviation was rather large, with an average K_c value of 0.51 ± 0.13 l./mol.

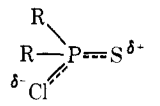
Using the average K_c values at 10 and 20°, the standard enthalpy change becomes −3.6 kcal/mol. When the experimental uncertainties in the K_c values are considered, one can see that the 10 and 20° values overlap. Consequently, the associated experimental uncertainty in the standard enthalpy change would be relatively very large so that the standard enthalpy change calculated from the average K_c values at 10 and 20° should not be considered very reliable. To obtain a better estimate of the standard enthalpy change the $K_c(\epsilon_c - \epsilon_I)$ product data were employed. Using the 10 and 20° $K_c(\epsilon_c - \epsilon_I)$ data for each of the five wavelengths in the 480 nm to 500 nm range, five values of the standard enthalpy change were obtained with an average value of −1.1 ± 0.6 kcal/mol.

An attempt was made to locate the charge-transfer band for this complex. The visible and near-ultraviolet spectral regions were investigated down to about 235 nm, where the iodine "contact-charge-transfer" absorption band[13] is very intense. However, the experimental absorbance for solutions of iodine and trichlorophosphine sulfide was always equal to the sum of the iodine and the donor spectra, at the same concentrations as in the mixture, measured separately.

Discussion

The values for both the molar concentration equilibrium constant and the standard enthalpy change show that the trioctylphosphine sulfide–iodine complex is one of the strongest known iodine complexes, being comparable in donor strength to trialkylamines,[4] dialkyl selenides,[14] and thioamides.[15] The thermodynamic parameters also indicate that a trialkylphosphine sulfide is a stronger electron donor toward iodine than dialkyl thio ketones[16] and much stronger than dialkyl sulfides.[5] The sulfur atom of a thiophosphino group might be expected to be a better electron donor than the sulfur atom of a thiocarbonyl group, since phosphorus is less electronegative than carbon by 0.4.

A comparison of the thermodynamic data for the triethyl phosphorothionate–iodine complex[17] with that of the trioctylphosphine sulfide–iodine complex shows a marked reduction in donor strength when three alkyl groups are replaced by three alkoxy groups, which can be attributed to the greater electron-withdrawing inductive effect of an alkoxy group relative to an alkyl group. The substitution of a chlorine atom for an alkyl group in a trialkylphosphine sulfide would also be expected to produce a reduction in donor strength due to the electron-withdrawing inductive effect of chlorine relative to the alkyl group. However, the great reduction in donor strength toward iodine of diethylchlorophosphine sulfide compared to trioctylphosphine sulfide seems to indicate that a conjugation effect might be contributing to the reduction in donor strength in addition to the inductive effect. This conjugation effect could be due to the partial overlap of a vacant 3d chlorine atomic orbital with the dπ phosphorus atomic orbital that is involved in π bonding with the pπ atomic orbital of sulfur, *i.e.*



The standard enthalpy change values for the trichlorophosphine sulfide–iodine complex may not be too reliable as a criterion for a comparison of donor strength because of their relatively large experimental uncertainties and in view of the difference between the values obtained from the temperature variation of the K_c and the $K_c(\epsilon_c - \epsilon_I)$ data. However, the K_c values for this complex indicate that it is a weaker electron donor toward iodine, by about a factor of 10 in terms of K_c, than diethylchlorophosphine sulfide.

The thermodynamic data indicate a much greater reduction in the donor strength of the thiophosphino group due to the replacement of the first alkyl group by a chlorine atom than by the subsequent substitution of the second and third alkyls by chlorine atoms. This disproportionate reduction in donor strength may be due to a relatively much greater role being played by conjugation for the first chlorine atom substitution than for the subsequent chlorine substitutions. In other words, the π electrons of the thiophosphino group may be so extensively delocalized by the first chlorine atom that the second and third chlorine atom substitutions produce a relatively much smaller electron delocalization of the thiophosphino group, resulting in a relatively much smaller reduction in donor strength.

According to theory,[11] the frequency of the absorption maximum of the charge-transfer band should increase with the ionization potential of the donor so that the weaker of two electron donors, with the greater ionization potential, would be expected to have its charge-transfer band absorption maximum at a shorter wavelength than that of the stronger donor when both form complexes with the same acceptor. Experimentally,

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

[14] J. D. McCullough and A. Brummer, *Inorg. Chem.*, 6, 1251 (1967).

[15] R. P. Lang, *J. Phys. Chem.*, 72, 2129 (1968).

[16] K. R. Bhaskar, S. N. Bhat, A. S. N. Murthy, and C. N. R. Rao, *Trans. Faraday Soc.*, 62, 788 (1966).

[17] T. Gramstad and W. J. Fuglevik, *Acta Chem. Scand.*, 16, 2368 (1962).

this is observed for structurally similar pairs of iodine complexes such as diethyl ether–diethyl sulfide,[5] tetramethylurea–tetramethylthiourea,[15] and, from the present study, trioctylphosphine sulfide–diethylchlorophosphine sulfide.

Consequently, one would expect the charge-transfer band of the trichlorophosphine sulfide–iodine complex to be located at a somewhat shorter wavelength than that of the diethylchlorophosphine sulfide–iodine complex. Unfortunately, the charge-transfer band for the trichlorophosphine sulfide–iodine complex could not be located, probably because of overlapping iodine–solvent contact charge transfer and donor spectral absorption at wavelengths below about 235 nm. It will probably be very difficult to locate the charge-transfer band for most weak iodine complexes involving n donors (a weak iodine complex being defined as one having a K_c value less than 1.0) because the relatively large ionization potential of such an electron donor will most likely cause the charge-transfer band to be located in a spectral region where either, or both, iodine–solvent contact-charge-transfer absorption and donor absorption occurs.

For the two iodine complexes in the present study whose charge-transfer bands could be studied, the stronger complex has the more intense band, both in terms of the molar extinction coefficient at the absorption maximum and the integrated intensity parameters. This increase in intensity of the charge-transfer band with increasing strength of complex formation is predicted by theory.[18] It is experimentally also verified for iodine complexes with such pairs of structurally related n donors as tetramethylurea–tetramethylthiourea[15] and diethyl ether–diethyl sulfide.[5] Furthermore, for iodine complexes with n donors in general, the charge-transfer band intensity is greater for the relatively strong complexes ($K_c > 100$) than for the intermediate and weak complexes ($K_c < 100$).[5]

For the phosphine sulfide–iodine complexes the results of the present study show an increase in both the magnitude of the blue shift and the intensity of the shifted visible iodine band with increasing donor strength. These results for the shifted visible iodine band are in general agreement with the values reported for other iodine complexes with n donors.[5] An explanation for both the wavelength shift and the intensity change for this band has been proposed by Mulliken.[19]

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(18) R. S. Mulliken, *J. Amer. Chem. Soc.*, 74, 811 (1952).

(19) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969, pp 158–161.

Chemistry of Transition Metals. I. Reactions of *n*-Alkyl Halides with Titanium[1a]

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Abstract: The reactions of *n*-alkyl halides on clean titanium metal and on hydrohalided titanium surfaces have been studied. With the exception of alkyl fluorides, the *n*-alkyl halides react stoichiometrically with titanium at a conveniently measurable rate in the temperature range 150–250°, yielding olefin and a minor amount of paraffin in the gas phase, and a titanium hydride–halide phase at the surface. These latter reactions all followed a half-order rate law for disappearance of reactant. The reactivity of *n*-propyl fluoride was several orders of magnitude greater than that of the other *n*-propyl halides, and the reaction was first order in reactant. The activation energies for the reactions of *n*-propyl fluoride, chloride, bromide, and iodide were 20.5, 23.5, 27.5, and 29.5 kcal/mol, respectively. A mechanism is proposed to explain these experimental observations.

The point of departure for much organometallic chemistry is the reaction of an electropositive metal with an organic halide to yield a product containing a metal–carbon bond. As a general rule such reactions, in order to be useful, must yield a product which is either soluble or at least sufficiently easily detached from the surface of the metal to allow complete reaction. No transition metal has been so treated because of the intrinsic instability of organo(transition metal) halides in the absence of stabilizing ligands. However, the generally high reactivity of the surfaces of transition metals toward other molecules leads to the expectation that they should react readily with organic halides and that the transient organo species should have chemistry resembling, in many respects, that of unstable organo(transition metal) halides in solution.

The present study was originally undertaken to understand in part the mechanism of the reported polymerization of ethylene on metallic titanium subjected to ball milling.[2] A reasonable hypothesis as to the origin of such polymerization activity was that the ball milling

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(1) (a) This work was done in partial fulfillment of the requirements for a Ph.D. thesis (W. R. S.); (b) National Research Council of Canada Scholar, 1969–1970.

(2) A. S. Matlack and D. S. Breslow, *J. Polym. Sci., Part A*, 3, 2583 (1965).