coordination sites for the four-electron donor cyclobutadiene derivative (**1B** in Scheme I) but not for the five-electron donor cyclopentadienyl ring in a tricyclic cyclopentadienyl derivative (**1C** in Scheme I). Therefore the reactions of $C_5H_5Co(CO)_2$ with the macrocyclic alkadiynes I are relatively simple[1b] and always proceed relatively efficiently to form the tricyclic cyclobutadiene derivatives II.

The reactions of the macrocyclic alkadiynes I with iron carbonyls are considerably more complex since the $Fe(CO)_3$ groups in the intermediate metallacyclopentadiene derivative (**1A** in Scheme I) either have enough free coordination sites for the four-electron donor cyclopentadienyl ring in a tricyclic cyclobutadiene derivative (**1B** in Scheme I) or can generate enough free coordination sites for the five-electron donor cyclopentadienyl ring in a tricyclic cyclopentadienyl derivative (**1C** in Scheme I) by losses of a carbonyl ligand to form $Fe(CO)_2$ groups. In all cases studied some formation of a tricyclic cyclobutadiene–iron tricarbonyl derivative of type III corresponding to **1B** in Scheme I can be detected. However, in cases where the macrocyclic alkadiyne I contains a pentamethylene bridge (*i.e.*, $m = 5$ and/or $n = 5$) the alternative transannular cyclization to form a tricyclic cyclopentadienyl–iron carbonyl derivative of type V corresponding to **1C** in Scheme I predominates apparently because of the formation of a six-membered end ring in the tricyclic product of type **1C**. A further feature of the transannular cyclizations of macrocyclic alkadiynes I with iron carbonyls is the apparent need of at least one bridge of at least five methylene groups for collapse of the tricarbonylferrole–iron tricarbonyl derivatives IV (*i.e.*, **1A** in Scheme I)[5a] to form either the tricyclic cyclobutadiene derivatives III (*i.e.*, **1B** in Scheme I) or the tricyclic cyclopentadienyl derivative V (*i.e.*, **1C** in Scheme I). Apparently in the case of the iron carbonyl derivatives a bridge of four methylene groups is too inflexible for the molecular motions in the tricarbonylferrole–iron tricarbonyl derivatives (*i.e.*, **1A** in Scheme I) necessary for extrusion of the ferrole iron atom and formation of a new carbon–carbon bond.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for support of the early phases of this work (1968–1970) under Grant AF-AFOSR-1435-68 and to the National Science Foundation for subsequent support (1971–1972) of this work under Grant GP-31347X.

Vapor-Phase Charge-Transfer Complexes. VIII. Charge-Transfer and Blue-Shifted Bands of Complexed Iodine by the Constant Activity Method

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Abstract: The vapor-phase charge-transfer bands and blue-shifted bands of iodine complexed with diethyl sulfide, dimethyl sulfide, and diethyl ether have been determined by a recently proposed method of maintaining a constant activity of iodine between two tetramethylammonium polyiodide solids. Band positions and shapes of the charge-transfer bands and the blue-shifted iodine bands, the ratio of the extinction coefficients (ϵ) of the CT band and the blue-shifted iodine band, and the $K_c\epsilon$ products of these bands are obtained from absorbance measurements of only a single mixture of donor with polyiodide solids. For the conditions of these experiments, a slow reaction occurred with diethyl sulfide, but the systems with dimethyl sulfide and diethyl ether were stable. Results for dimethyl sulfide–iodine agree fairly well with a previous study based on the usual regression analysis of data at several donor–acceptor concentrations. The present study establishes the shape of the vapor-phase blue-shifted iodine band complexed with diethyl ether. This band undergoes a blue shift in *n*-heptane solvent which is greater than that for sulfide–iodine complexes.

Recently, it has been shown that a blue-shifted iodine band exists in the vapor phase when iodine is complexed with diethyl sulfide,[1] dimethyl sulfide,[2] and diethyl ether.[3] For the stronger sulfide complexes, a reliable determination of the equilibrium constant (K_c) and extinction coefficient (ϵ) is possible[4,5] based on the spectrophotometric equation

$$\frac{C_D^0 b C_A^0}{A'} = \frac{C_D^0 + C_A^0}{\epsilon'} + \frac{1}{K_c\epsilon'} - \frac{A'}{b\epsilon'^2} \qquad (1)$$

where C_D^0 and C_A^0 are the initial concentrations of donor and acceptor, respectively, b is the cell path, and A is the absorbance. The primes on A and ϵ signify corrected values taking into account the contributions of free donor and free acceptor.[3,5]

The separation of the total iodine absorbance in the visible region into free and complexed components is quite sensitively dependent on the value of K_c;[1,3] *i.e.*, the calculated band shape and position of the blue-shifted iodine band changes markedly when K_c is altered by a factor of 2 or 3. For the stronger diethyl sulfide–iodine[1] and dimethyl sulfide–iodine[2] complexes, where K_c seems reliable, it may be assumed that characterization of the blue-shifted iodine bands is reasonably good.

The diethyl ether–iodine complex is much weaker.

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[1] M. Tamres and S. N. Bhat, *J. Phys. Chem.*, **75**, 1057 (1971).

[2] M. Tamres and S. N. Bhat, *J. Amer. Chem. Soc.*, **94**, 2577 (1972).

[3] J. Grundnes, M. Tamres, and S. N. Bhat, *J. Phys. Chem.*, **75**, 3682 (1971).

[4] W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965).

[5] R. A. LaBudde and M. Tamres, *J. Phys. Chem.*, **74**, 4009 (1970).

For the conditions at which this complex was studied in the vapor phase, separation of K_c and ϵ from the $K_c\epsilon$ product is so sensitive to small experimental errors that such values cannot be considered as giving anything much better than the order of magnitude.[3] The blue-shifted iodine band estimated from the spectrophotometric value of K_c at 60° did show a maximum at ~475 mμ, but this result certainly has to be questionable.[3] No maximum below 498 mμ is found based on a K_c determined recently by an isopiestic method,[6] a value which at 60° is about three times as large as the one estimated from the recent spectrophotometric experiment.[3]

In the reported isopiestic method,[6] a constant activity of iodine is maintained between two solid polyiodides,[7] *e.g.*

$$\tfrac{1}{2}(CH_3)_4N\cdot I_9(s) \rightleftarrows \tfrac{1}{2}(CH_3)_4N\cdot I_5(s) + I_2(g)$$

or

$$(CH_3)_4N\cdot I_5(s) \rightleftarrows (CH_3)_4N\cdot I_3(s) + I_2(g)$$

Addition of a donor to the system establishes a second equilibrium

$$D(g) + I_2(g) \rightleftarrows D\cdot I_2(g)$$

and the concentration of iodine in the second equilibrium is determined by the loss in weight of the polyiodide mixture. Precise temperature control is necessary in such an experiment (and was maintained in the above study[6] to 0.01°).

The constant activity method also has been applied to spectrophotometric studies in solution,[7] but not yet to the vapor phase. In the latter phase, because of the longer cell paths, temperature control is more difficult. However, by using a differential procedure, *i.e.*, donor vapor plus polyiodide mixture in the sample cell and a polyiodide mixture in the reference cell, the problem of temperature control can be minimized. This procedure also allows the positions and shapes of the charge-transfer (CT) bands and the blue-shifted iodine bands to be obtained directly.[7] Furthermore, when the same sample is run in both the uv and visible regions, the ratio of the ϵ's of the CT band (ϵ_{CT}) and blue-shifted iodine band (ϵ_{bs}) is determined directly.

In this study, the applicability of the constant activity method to the vapor phase was explored. Specifically, the CT and blue-shifted bands of iodine complexed with diethyl sulfide, with dimethyl sulfide, and with diethyl ether were investigated.

Experimental Section

Materials. Tetramethylammonium iodide was prepared by dropping a solution of trimethylamine (Eastman) in dry ether into an equimolar amount of methyl iodide (Matheson Coleman) in dry ether cooled to Dry Ice temperature. The salt was washed with ether and recrystallized from 50% ethanol.

Tetramethylammonium pentaiodide ($TMAI_5$, mp 129–131°, lit.[8] 129–130°) and tetramethylammonium enneaiodide ($TMAI_9$, mp 109°, lit.[8] 110°) were prepared and recrystallized as described in the literature.[8,9]

Diethyl and dimethyl sulfides (Eastman) were fractionally distilled through a 20-cm Vigreux column packed with glass helices, and the middle cuts were taken. Fresh diethyl ether (Mallinckrodt) was used without further purification. Analysis by vpc showed the samples to be better than 99.9% pure.

Procedure. The method for sealing samples in the breakseal tubes and introducing the samples into the cells was described previously.[1] Cell lengths were measured with a Wild cathetometer (precision to 0.02 mm). Cell volumes were determined to within a few tenths of a per cent by filling the cells with a measured quantity of water. Donor concentrations were calculated from the known weights of samples and the volume of the cells. Weighings read to ±0.1 mg were made with a Mettler H15 balance. The weight of diethyl sulfide used was of the order of ~0.6 g, and that for the smallest quantity of diethyl ether was 3.583 g. Therefore, the errors in the concentrations of these donors are considered to be well below 1%. The weight used for dimethyl sulfide was ~0.15 g and, since this is a rather volatile compound, a small correction was made for the displacement of air in the breakseal tube (amounting to ~2 mg). The error in concentration here may be of the order of 1–2%.

The concentration of iodine was controlled by the temperature of the experiment. In order to select the desired concentration it was necessary first to establish the vapor pressure curves for the $TMAI_3$-$TMAI_5$ and $TMAI_5$-$TMAI_9$ equilibria. These data were obtained from spectral measurements using a Cary 14 spectrophotometer and are given in Tables I and II. The absorbances were taken at 480 mμ because there is very little temperature dependence of absorbance at this wavelength.[1]

Table I. Spectrophotometric Data for the Equilibrium[a]

$$\tfrac{1}{2}TMAI_9(s) \rightleftarrows \tfrac{1}{2}TMAI_5(s) + I_2(g)$$

T, °C	Cell path, cm	Absorbance at 480 mμ Obsd[b]	Absorbance at 480 mμ Calcd[c]
39.0	100.0	0.290	0.290
45.0	100.0	0.435	0.439
49.8	100.0	0.608	0.605
55.0	100.0	0.852	0.848
60.2	100.0	1.180	1.175
63.8	100.0	1.479	1.464
65.5	100.0	1.598	1.622
69.8	50.0	1.045	1.046
75.3	50.0	1.438	1.435
79.0	50.0	1.762	1.765
89.8	10.0	0.648	0.631
96.7	10.0	0.910	0.898
101.7	10.0	1.173	1.150
106.8	10.0	1.490	1.471

[a] These data are described by the equation $\log A/b = -(2983.34/T) + 7.01938$. The errors in the slope and intercept, at the 95% confidence level, are ±20.01 and ±0.06015, respectively. [b] $\epsilon_{I_2} = 350 \pm 2$ l. mol^{-1} cm^{-1} at 480 mμ. [c] Calculated from the equation in footnote *a*.

Table II. Spectrophotometric Data for the Equilibrium[a]

$$TMAI_5(s) \rightleftarrows TMAI_3(s) + I_2(g)$$

T, °C	Cell path, cm	Absorbance at 480 mμ Obsd[b]	Absorbance at 480 mμ Calcd[d]
68.0	100.0	0.0857[c]	0.0850
80.6	100.0	0.200[c]	0.199
85.3	100.0	0.265[c]	0.268
101.1	100.0	0.675	0.699
108.1	100.0	1.077	1.042

[a] The data are described by the equation $\log A/b = -(3529.24/T) + 7.27445$. The errors in the slope and intercept, at the 95% confidence level, are ±165.71 and ±0.45913, respectively. [b] $\epsilon_{I_2} = 350 \pm 2$ l. mol^{-1} cm^{-1} at 480 mμ. [c] Reading made using a 0–0.2 absorbance scale. [d] Calculated from the equation in footnote *a*.

The cells were housed in a large box which also was designed for temperature control. For the longer cells, there was a temperature gradient along the length of the cell which got progressively larger as the temperature was raised. This gradient between the ends of a 100.0-cm cell, as measured with constantan thermocouples,

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(6) S. D. Christian and J. Grundnes, *J. Amer. Chem. Soc.*, **93**, 6363 (1971).

(7) J. D. Childs, S. D. Christian, J. Grundnes, and S. R. Roach, *Acta Chem. Scand.*, **25**, 1679 (1971).

(8) *Inorg. Syn.*, **5**, 172 (1957).

(9) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

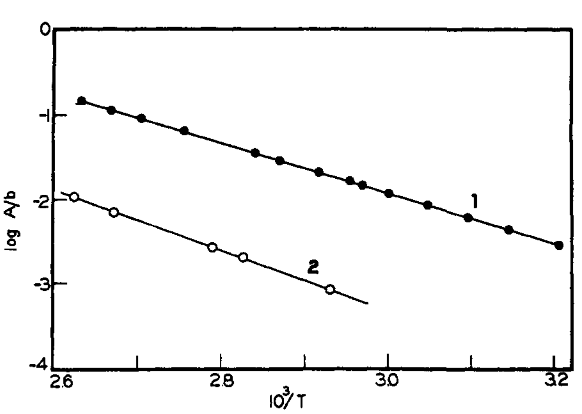

Figure 1. Temperature dependence in the vapor phase of absorbance (at 480 mμ)/cell path for the polyiodide equilibria: (1) $\frac{1}{2}TMAI_9(s) \rightleftarrows \frac{1}{2}TMAI_5(s) + I_2(g)$ and (2) $TMAI_5(s) \rightleftarrows TMAI_3(s) + I_2(g)$

was only 0.2 at 64° but rose to about 0.8 at 108°. To ensure precise knowledge about the cancellation of the free iodine absorbance in the sample and reference cells, and to obtain the concentration of iodine, the following sequence of steps was made: (1) running a base line of the evacuated sample cell *vs.* evacuated reference cell at room temperature; (2) running a base line of the evacuated reference cell *vs.* air at room temperature (by removing the sample cell from the light path and changing the direction of the absorbance by flipping the beam interchange switch on the Cary 14 from "normal" to "reverse"); (3) opening the breakseal tubes containing the polyiodide mixtures of the sample and reference cells, raising the temperature to the selected setting, and running a base line when the system reached equilibrium; (4) cooling the breakseal tube containing the donor (to reduce its vapor pressure) by swabbing with cotton dipped in liquid nitrogen, breaking the tube, equilibrating the system again at the selected temperature, and recording the spectra in the uv and visible regions; (5) removing the sample cell from the path of the light beam again, allowing equilibration at the selected temperature, and recording the spectrum of the reference cell *vs.* air (with the beam interchange switch in the "reverse" position). Steps (2) and (5) permit direct calculation of the concentration of iodine from its known ϵ_{I_2} values and, in these experiments, the concentration always checked (to ~1%) that determined from the log A/b *vs.* $1/T$ plot (Figure 1).

That the temperature differential between the sample and reference cells was not serious was determined from steps (1) and (3) above. In 100.0-cm cells at 65°, the base lines for the empty cells and for the equilibrated $TMAI_9$–$TMAI_5$ system were virtually the same. At 105°, there was a small differential; *e.g.*, for the $TMAI_5$–$TMAI_3$ system in 10.0-cm cells the difference in absorbance increased from ~0.003 at 400 mμ to 0.015 at ~500 mμ. This would not affect determination of the positions or shapes of the CT and blue-shifted iodine bands which were determined from steps (3) and (4).

Two slide-wire scales were used, 0–2.0 and 0–0.2 absorbance unit. In a few cases, the absorbance near the band maximum extended beyond the scale range. These spectra were determined by adjusting the balance knob to lower the absorbance by a fixed amount at a selected wavelength and then recording the band peak region.

The absorbances of the pure donors in the vapor phase were determined at the temperatures at which their iodine complexes were studied. For the donor concentrations used, the absorbances are quite small in the region of their respective CT band maxima. These small corrections were made where appropriate.

The temperature region at which each complex was studied was higher than the boiling point of the respective donor involved. Consequently, the breakseal tubes containing the donors were tested in a bath at higher temperatures to ensure they could withstand the pressures prior to sealing them to the cells.

In the initial experiments, the breakseal tubes containing the polyiodide mixtures in both the reference and sample cells were positioned as close together as possible to ensure their being at a common temperature. After opening the breakseal tubes, the polyiodide mixtures were left in the tubes. When donor was added, it was found that diffusion was so slow through the narrow tubing connecting the breakseal tube to the cell that it took many days to reach equilibrium. In subsequent experiments, the polyiodide mixtures were shaken from the opened breakseal tubes into the body of the cells (sample and reference) and the time for equilibration was reduced considerably. Specific results will be given for the dimethyl sulfide–iodine system.

Results

The vapor pressure study of the polyiodide equilibria ranged from the lowest temperature which permitted a reasonable absorbance reading in a 100.0-cm cell to a temperature several degrees below the melting point of the lower melting component where the solid phase of the mixture still persisted. Since absorbance/cell path is directly proportional to concentration, the temperature dependence of log A/b (Figure 1) permits determining the change in internal energy (ΔE_{sat}). Our result at the 95% confidence level for the system $TMAI_9$–$TMAI_5$ over the temperature range 39–107° is 13.65 ± 0.09 kcal mol^{-1}, which is a little lower than that of 14.6 ± 0.3 (or ΔH = 15.2 ± 0.3) kcal mol^{-1} reported by Childs, Christian, Grundnes, and Roach[7] at 35°. For the less volatile $TMAI_5$–$TMAI_3$ system over the range 68–108°, ΔE_{sat} = 16.14 ± 0.76 kcal mol^{-1}.

Based on the previous vapor-phase data for the iodine complexes,[1-3] conditions were selected which were considered optimum for the study of the same complexes by the constant activity method. The more volatile $TMAI_5$–$TMAI_9$ system was used to provide the desired iodine concentration for the dimethyl sulfide and diethyl ether experiments because these donors and their iodine complexes, being more volatile, could be studied at lower temperatures. For the less volatile diethyl sulfide–iodine complex, higher temperature must be reached, and, therefore, the less volatile $TMAI_3$–$TMAI_5$ system was used to limit the iodine concentration.

Initial experiments with the constant activity method were made with the polyiodide solids kept in the opened breakseal tubes. In the first study, using dimethyl sulfide, the quantity of donor introduced into the 100.0-cm cell was such that there should have resulted an absorbance at 60° of 2.30 at the CT maximum (285 mμ), according to the data obtained previously.[2] After 3 days of a continuously increasing absorbance, a reading of only 1.82 was obtained, and the change of absorbance with time had become so slow that it was not expected to reach a reading of 2.30. Apparently the dimethyl sulfide–iodine complex was not completely in the vapor phase. The reading, therefore, affords a direct spectrophotometric determination of the vapor pressure of the complex. Calculation of the dimethyl sulfide–iodine concentration, based on the absorbance of 1.82 and using the ϵ_{CT} determined earlier,[2] gave a vapor pressure at 60° of ~0.027 mm, which indicates the rather low volatility of the complex.

The above experiment was repeated using a smaller quantity of donor which was calculated to give a CT absorbance at 285 mμ of 1.58 at 60°. Equilibration was quite slow; the CT band increased in absorbance to 1.41 (1 day), 1.53 (2 days), 1.56 (3 days), and, finally, 1.59 (6 days). The absorbance in the region of the blue-shifted iodine band started out negative at the longer wavelengths because of the over compensation from the free iodine in the reference cell. The ratio $\epsilon_{CT}/\epsilon_{bs}$ continually decreased on approaching equilibration, and after 6 days the ratio was 20.6. These obser-

Table III. Temperature-Dependence Study[a] of Dimethyl Sulfide[b]–Iodine by the Constant Activity Method

T, °C	$[I_2]$, $M \times 10^5$	Corrected absorbance[c] CT band	Corrected absorbance[d] blue-shifted iodine band	$10^{-5}K_c\epsilon_{CT}$,[e] $l.^2$ mol^{-2} cm^{-1}	$10^{-5}K_c\epsilon_{CT}$ (lit.),[f] $l.^2$ mol^{-2} cm^{-1}	$\epsilon_{CT}/\epsilon_{bs}$
55.1	2.44	1.35_1	0.070_5	3.79	3.62	19.2
60.2	3.37	1.62_5	0.086_5	3.30	3.10	18.8
65.5	4.65	1.89_3	0.099_5	2.79	2.62	19.0
70.8	6.35	2.18_8	0.114	2.36	2.23	19.2

[a] In a 100.0-cm cell. [b] $[(CH_3)_2S] = 1.46 \times 10^{-3}$ M. [c] Using a 0–2.0 absorbance scale. [d] Using a 0–0.2 absorbance scale; readings probably good to 0.002 absorbance unit. [e] Calculated using eq 4. [f] Reference 2.

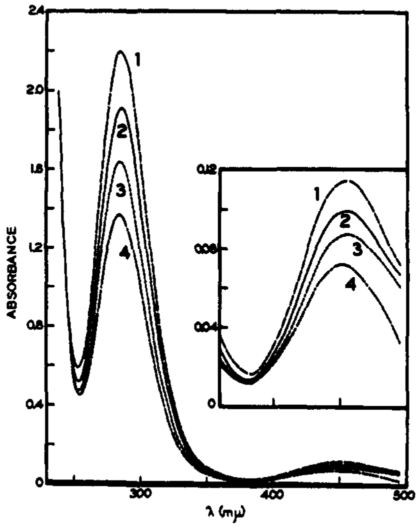

Figure 2. CT band and blue-shifted iodine band for dimethyl sulfide–iodine in the vapor phase: 100.0-cm cell; $[(CH_3)_2S] = 1.44 \times 10^{-3}$ M; (1) 70.8°, $[I_2] = 6.39 \times 10^{-5}$ M; (2) 65.5°, $[I_2] = 4.58 \times 10^{-5}$ M; (3) 60.2°, $[I_2] = 3.38 \times 10^{-5}$ M; (4) 55.1°, $[I_2] = 2.44 \times 10^{-5}$ M; insert recorded with 0-0.2 absorbance scale. These are difference spectra with $TMAI_9$–$TMAI_5$ in the sample and reference cells.

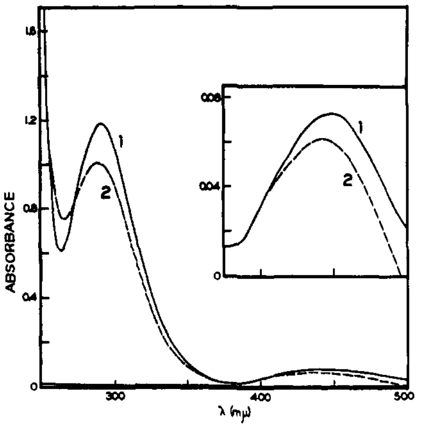

Figure 3. CT band and blue-shifted iodine band for diethyl sulfide–iodine in the vapor phase: 10.0-cm cell, 104.9°, $[(C_2H_5)_2S] = 3.54 \times 10^{-2}$ M; $[I_2] = 2.48 \times 10^{-5}$ M; (1) 2 hr after adding donor and (2) 14 hr after adding donor. Insert recorded with 0–0.2 absorbance scale. These are difference spectra with $TMAI_5$–$TMAI_3$ in the sample and reference cells.

vations over such an extended period show that the system is quite stable.

In the final experiment on dimethyl sulfide–iodine, the polyiodide solids were shaken from the open breakseal tubes into the main body of the cells, which reduced the equilibration process from days to hours. Results of a temperature-dependence study are shown in Figure 2. The range, from 55.1 to 70.8°, is rather limited, being a compromise for obtaining sufficiently high absorbances of the CT band on the 0–2.0 absorbance scale and of the blue-shifted iodine band on the 0–0.2 scale. The latter recording is shown in the insert of Figure 2 with background noise smoothed out and corrected to a base line of 0. The data are summarized in Table III. The $\epsilon_{CT}/\epsilon_{bs}$ ratio is consistent at the several temperatures, the differences being within experimental error (considering that the base line has to remain unchanged for the duration of the experiment, and this is all the more critical when using the 0–0.2 scale). The average value of $\epsilon_{CT}/\epsilon_{bs}$ is 19.0, which is in reasonable accord with the previous result[2] of ~17.2.

The absorption spectrum of the diethyl sulfide–iodine complex at 104.9° is shown in Figure 3. It is evident that the spectrum undergoes a slow change with time; curve 1 was taken 2 hr and curve 2 was taken 14 hr after adding the donor. Such change was not observed in a previous study of this complex in which all reagents were completely in the vapor phase,[1,2] even at higher temperatures, and it must be assumed that the presence of the solid polyiodides enhances chemical reaction. The diethyl sulfide, being present in appreciable excess, could consume sufficient iodine so that the $TMAI_3$–$TMAI_5$ equilibrium is no longer maintained. If so, the reference cell could become more strongly absorbing in the visible region, and the reading would become negative. This is the trend observed. It should be noted that, for the period of time shown in Figure 3, the ratio $\epsilon_{CT}/\epsilon_{bs}$ remained at 16.0, which is in very good agreement with that determined in the earlier study,[1,2] *i.e.*, ~15.3. The visible region is shown more clearly in the insert in Figure 3 as recorded using a 0–0.2 absorbance scale with background noise smoothed out and corrected to a base line of 0. Five studies of the diethyl sulfide–iodine complex were attempted, with reaction being observed each time. Because of the slow reaction, the CT band and the blue-shifted iodine band are less well characterized here than in the previous study.[1,2]

Two studies on the diethyl ether–iodine complex were made in a similar temperature region: one at 60.5° using a donor concentration of 5.014×10^{-2} M and the other at 63.6° using a donor concentration of 2.870×10^{-2} M. The spectrum for the former is shown in Figure 4. The system was found to be stable for the duration of the experiment. (The diethyl ether–iodine complex has been observed to undergo reaction in the vapor phase at somewhat higher temperature, ~90°.)[3,10] Unlike the sulfide–iodine system, *no* maxi-

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(10) F. T. Lang and R. L. Strong, *J. Amer. Chem. Soc.*, **87**, 2345 (1965).

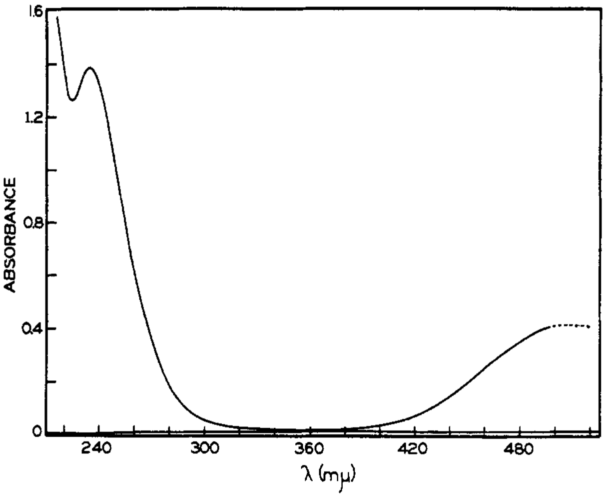

Figure 4. CT band and blue-shifted iodine band for diethyl ether–iodine in the vapor phase: 100.0-cm cell, 60.5°, $[(C_2H_5)_2O]$ = 5.014 × 10^{-2} *M*, $[I_2]$ = 3.43 × 10^{-5} *M*. Dotted line is an extrapolation of the blue-shifted band. These are differential spectra with $TMAI_9$–$TMAI_5$ in the sample and reference cells.

mum for the blue-shifted iodine band is observed in the region from 400 up to 498 mμ. At wavelengths just longer than this the absorbance rises rather abruptly. This is the region where the vibrational band structure of iodine appears. The presence of an added gas (diethyl ether in this case) enhances and smooths out the absorbance which accounts for the large difference compared to the reference cell.[11] In order to estimate both the band position and absorption at the maximum, the procedure of Gordus and Bernstein[12] was followed in which a parabolic shape around the region of the band maximum is assumed. The result of this calculation is shown in Figure 4 as the dotted line extension of the blue-shifted iodine band. The band maximum is at ~509 mμ. The $\epsilon_{CT}/\epsilon_{bs}$ ratio from analysis of the spectrum in Figure 4 came out to be 3.34. This result matched very well the value of 3.26 from the duplicate study at the lower donor concentration. The agreement is better than could be expected from the error inherent in reading such relatively low absorbances.

Discussion

The equilibrium constant for the interaction between an electron donor (D) and an acceptor (A) to form a complex (C) is

$$K_c = \frac{[C]}{(C_D{}^0 - C)(C_A{}^0 - C)} \tag{2}$$

The spectrophotometric equivalent of this equation is eq 1. In the usual treatment, the determination of the $K_c\epsilon$ product is based on a regression analysis of eq 1.

The constant activity method permits determination of the $K_c\epsilon$ product by measuring the absorbance of only a single mixture of donor–polyiodide. For the condition of constant activity, the saturation concentration of the acceptor at a fixed temperature *T* is $(C_A{}^0)_T$. Therefore, the spectrophotometric equivalent of eq 2 is

$$K_c b\epsilon = \frac{[A]}{(C_D{}^0 - C)(C_A{}^0)_T} \tag{3}$$

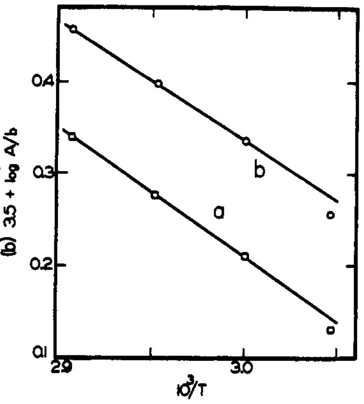

Figure 5. Temperature dependence in the vapor phase of log absorbance (at band maximum)/cell path for dimethyl sulfide–iodine: $[Me_2S]$ = 1.46 × 10^{-3} *M*, I_2 source from $TMAI_9$–$TMAI_5$, (a) CT band, (b) blue-shifted iodine band.

Now, provided that $C_D{}^0$ is in large excess (*i.e.*, ≫ *C*), then

$$K_c b\epsilon = \frac{[A]}{C_D{}^0(C_A{}^0)_T} \tag{4}$$

from which $K_c\epsilon$ is readily obtained.

Taking the logarithm of eq 4 gives

$$\log K_c\epsilon + \log b + \log C_D{}^0 + \log (C_A{}^0)_T = \log [A] \tag{5}$$

Since *b* and $C_D{}^0$ (in the vapor phase) are temperature independent, then

$$\frac{d \log K_c\epsilon}{d(1/T)} + \frac{d \log (C_A{}^0)_T}{d(1/T)} = \frac{d \log [A]}{d(1/T)} \tag{6}$$

The middle term represents a saturation pressure curve. It corresponds to the data in Tables I and II from which ΔE_{sat} was calculated. Therefore, eq 6 offers a means of determining the internal energy of complexation (ΔE_{comp}) from a temperature-dependence study of the absorbance of either the CT band or the blue-shifted iodine band, using only a single mixture of donor–polyiodide. This method should be applicable to stronger complexes than is permitted in the previous technique where all components are in the vapor phase.[2,3,13] The value calculated from the data at ϵ_{max} represents an upper limit for ΔE_{comp} because of the contribution from the expected temperature broadening of bands with increasing temperature.[3]

The data recorded in Figure 2 for dimethyl sulfide–iodine were taken to test the feasibility of obtaining ΔE_{comp} in this way. It should be noted in the figure that, unlike the usual study in the vapor phase, the absorbance *increases* with increasing temperature. This is due to the fact that the increase in the second term in eq 6 more than compensates for the decrease in the first term.

A plot of the data in Table III of log *A vs.* 1/*T* for both the CT band and the blue-shifted iodine band for the dimethyl sulfide–iodine complex is shown in Figure 5. Good straight lines are obtained through the three points at the higher temperature. That at the lowest temperature falls a little off the line, probably due to the complex not being completely in the vapor phase.

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[11] See curves 1 and 2 in Figure 3 of ref 3, and curves 1 and 2 in Figure 1 of ref 1.

[12] A. A. Gordus and R. B. Bernstein, *J. Chem. Phys.*, **22**, 790 (1954).

[13] M. Tamres in "Molecular Complexes," R. Foster, Ed., Paul Elek Ltd., London, 1973.

There is some indication for this in the different shape of the blue-shifted iodine band at the lowest temperature (Figure 2). However, comparison of the data in Table III of the currently and previously obtained values of $K_c\epsilon_{CT}$ does not indicate an apparent discrepancy; the agreement at all temperatures is good (within ~6%).

Equation 6 can be written in the simplified notation

$$\Delta E_{\text{comp}} + \Delta E_{\text{sat}} = \Delta E_{\text{total}} \qquad (7)$$

The values of ΔE_{total} based on three temperatures[14] are $+6.4 \pm 0.6$ and $+6.0 \pm 0.3$ kcal mol^{-1} for the CT band data and the blue-shifted iodine band data, respectively. The error limits, for the 95% confidence level, are remarkably small considering that there are only three data points covering the very limited temperature range of less than 11°. The result of the study in the CT region leads to a value for ΔE_{comp} of -7.3 ± 0.8 kcal mol^{-1}, which compares very favorably with that of the previous CT study,[2] *i.e.*, -7.1 ± 0.4 kcal mol^{-1}.

For diethyl sulfide–iodine at 104.9°, application of eq 4 to calculate $K_c\epsilon_{CT}$ for the higher absorbance in Figure 3 gave a value of 1.36×10^5 l.^{2} mol^{-2} cm^{-1}. For the same system at the same temperature in the previous study, where all reagents were in the vapor phase, $K_c\epsilon_{CT}$ was 1.67×10^5 l.^{2} mol^{-2} cm^{-1}. The lower value in the present study is a further indication that reagents have been consumed.

An interesting result of the application of the constant activity method to the diethyl ether–iodine system is that it resolves the previously posed question[3] whether the blue-shifted iodine band has a maximum at wavelengths shorter than 498 mμ. It is apparent in Figure 4 that it does not. The band does not resemble that which had been calculated based on the uncertain spectrophotometric value of K_c;[3] rather it is quite similar to that based on the K_c obtained by Christian and Grundnes by their isopiestic method.[6] Therefore, the differential spectrum in Figure 4 supports their value.

The position and shape of the blue-shifted iodine band complexed in the vapor phase with diethyl sulfide, with dimethyl sulfide, and with diethyl ether are shown in Figure 6. The uncomplexed iodine band at 90° (curve 1) is included for comparison. Figure 6 is a composite of the results obtained in the present and previous spectral studies. Curve 4 for the diethyl sulfide–iodine complex is taken from the data in the previous study[1,2] because of the slow reaction observed for this system under the conditions of the constant activity method. It was shown previously[1] that curve 1, the continuum region of the iodine spectrum, is unaffected by the presence of ~1 atm of "inert" gases or vapors, *e.g.*, air or *n*-heptane. (Such gases do affect the band structure of iodine, the region below 2.0×10^4 cm^{-1}, due to broadening of band lines.)

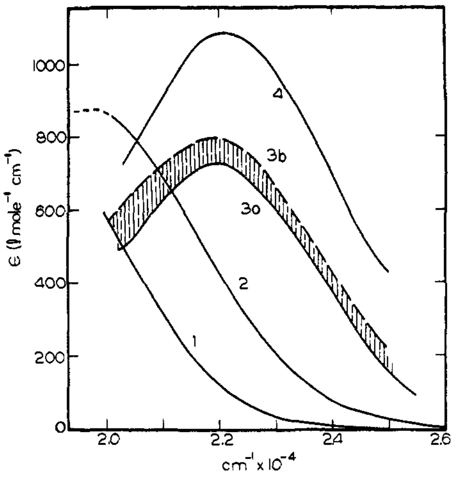

Figure 6. Blue-shifted iodine band in the vapor phase: curves 2 and 3a by constant activity method, curves 3b and 4 by conventional method, (1) iodine alone at 90°, (2) diethyl ether–iodine, (3) dimethyl sulfide–iodine, (4) diethyl sulfide–iodine.

Curve 3a in Figure 6 is for the dimethyl sulfide–iodine complex as obtained by the constant activity method. Its characterization is based on the value $\epsilon_{CT} = 1.375 \pm 0.331$ l. mol^{-1} cm^{-1} previously determined,[2] the ratio of 19.0 for $\epsilon_{CT}/\epsilon_{bs}$ found in the present study, and the shape of the curve in Figure 2. The blue-shifted iodine band taken from the earlier conventional study[2] is shown as curve 3b. The agreement between the two methods is quite good; the shaded region in the figure is within the error limits of the determination of ϵ_{CT}.

Curve 2 in Figure 6 is for the diethyl ether–iodine complex. It was determined by combining the data for K_c at 35°, ΔE, $K_c\epsilon_{CT}$ at 63.6°, and $\epsilon_{CT}/\epsilon_{bs}$ for this complex. The K_c at 35° obtained by the isopiestic study[6] is 4.35 ± 0.30 l. mol^{-1}. From the reported[3] ΔE value of -4.5 ± 0.2 kcal mol^{-1}, the K_c at 63.6° is calculated to be 2.33 l. mol^{-1}. The $K_c\epsilon_{CT}$ product at 63.6° obtained in the present study, using eq 4, is 6.7×10^3 l.^{2} mol^{-2} cm^{-1}, which is a little higher than the value of 6.2×10^3 l.^{2} mol^{-2} cm^{-1} at 59.8° determined previously.[3] (The absorbance corrections for donor and acceptor in the present study were assumed to be the same as in the previous study because the concentrations are so similar.) Therefore ϵ_{CT} is calculated to be ~2850 l. mol^{-1} cm^{-1}. Since the ratio of $\epsilon_{CT}/\epsilon_{bs}$ determined from the band maxima in Figure 4 is 3.3, this makes $\epsilon_{bs} \simeq 870$ l. mol^{-1} cm^{-1}. Based on the lower result for $K_c\epsilon_{CT}$ at 59.8° obtained previously,[3] the corresponding values for ϵ_{CT} and ϵ_{bs} are ~2500 and ~750 l. mol^{-1} cm^{-1}, respectively. The magnitude of ϵ_{bs} is similar to that obtained for the stronger dimethyl sulfide–iodine complex. Considering that such factors as geometry and mixing with excited states are not necessarily comparable, there seems no reason to expect a correlation of ϵ_{bs} with strength of complexation, except perhaps for a homologous series of donors.

The blue shift of the iodine band on complexation has been attributed by Mulliken[15] to the greater exchange repulsion between the antibonding σ_μ excited molecular orbital and the adjacent donor. It might be expected, therefore, that there should be a correlation between the magnitude of the blue-shifted iodine band (as measured by its $\lambda_{\max}$) and the strength of complexation. Such correlation, based on *solution* data, has been cited in the literature.[16-18] There are cases, how-

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[14] Based on all four temperatures, ΔE_{total} is $+6.9 \pm 1.1$ kcal mol^{-1} for the CT band data, and $+6.8 \pm 2.1$ kcal mol^{-1} for the blue-shifted iodine band data. The error limits here are much higher.

(15) R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956).

(16) M. Brandon, M. Tamres, and S. Searles, *J. Amer. Chem. Soc.*, **82**, 2129 (1960).

(17) R. P. Lang, *ibid.*, **84**, 1185 (1962).

(18) J. S. Ham, *ibid.*, 76, 3875 (1954).

Table IV. Spectral Characteristics[a] of the Visible Iodine Band

Donor	Phase	λ_{max}, mμ	ϵ_{bs}, l. mol^{-1} cm^{-1}	$\Delta\bar{\nu}_{bs}$,[b] cm^{-1}	$\Delta\bar{\nu}_{1/2}$,[c] cm^{-1}	f[d]	μ,[e] D	Ref
	Vapor	~498[f]	570					1
		480	350[g]					1
n-Heptane	*n*-Heptane	520	918		3200	0.0124	1.18	*l*
		522	897		3200	0.0124	1.17	19a, *m*
Diethyl ether	Vapor[j]	~509	~870[h]		4500[i]	0.0169	1.35	This work
	n-Heptane[j]	470	852	1630	3910	0.0144	1.20	*l*
	n-Heptane	469	890		3710	0.0143	1.19	*l*
	n-Heptane	462	950		4100	0.0168	1.29	19a, *m*
	CCl_4	468	873		4100	0.0155	1.24	*m*
Dimethyl sulfide	Vapor[j]	457	725		4350	0.0136	1.15	This work
	Vapor	~457	~800		4500	0.0155	1.23	2
	n-Hexane	437		1000				*n*
	CCl_4	437	1950[k]		4300[k]	0.036	1.8	*o*
Diethyl sulfide	Vapor[j]	452						This work
	Vapor	453	1080		4800	0.0224	1.47	2
	n-Heptane	437	1900	760				*p*
	n-Heptane	435	1960		4200	0.0352	1.80	19a, *m*
	n-Heptane	430	1900					*q*
	CCl_4	430	2320					*q*

[a] Study by conventional method unless otherwise specified. [b] Blue shift, taken as $\bar{\nu}_{max}$(soln) − $\bar{\nu}_{max}$(vapor). [c] Half-width: difference in $\bar{\nu}$ at half the maximum intensity on the high- and low-energy side of the CT band, or twice the difference between the band peak and half the maximum intensity on the high-energy side. [d] Oscillator strength (ref 19b), calculated from $f \simeq 4.32 \times 10^{-9}\epsilon_{max}\Delta\bar{\nu}_{1/2}$. [e] Transition moment (ref 19b), calculated from $\mu \simeq 0.0958[(\epsilon_{max}\Delta\bar{\nu}_{1/2})/\bar{\nu}_{max}]^{1/2}$. [f] Appearance of vibrational structure at $\lambda > 498$ mμ. [g] ϵ at 480 mμ practically temperature independent over the range 45–120°. [h] Could also be ~750 l. mol^{-1} cm^{-1} (see text). [i] Taken as twice the difference between the band peak and half the maximum intensity on the *high* energy side. [j] Study by constant activity method. [k] Estimated from figure in reference cited in footnote *o*, assuming no contribution from the tail of the CT band. [l] J. D. Childs, Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma, 1971. [m] H. Tsubomura and R. P. Lang, *J. Amer. Chem. Soc.*, **83,** 2085 (1961). [n] J. D. McCullough and I. C. Zimmerman, *J. Phys. Chem.*, **64,** 1084 (1960). [o] N. W. Tideswell and J. D. McCullough, *J. Amer. Chem. Soc.*, **79,** 1031 (1957). [p] M. Tamres and S. Searles, *J. Phys. Chem.*, **66,** 1099 (1962). [q] M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **83,** 4329 (1961).

ever, where the generality of this correlation apparently breaks down.[19a, 20]

One factor previously not considered in the correlation is the influence of the solvent on the blue-shifted iodine band. The present study shows that solvation effects can be large indeed. Available spectral characteristics of the complexed visible iodine band in the vapor phase and in solution are compared in Table IV. Apparently, the solvent causes an appreciably greater blue shift in the case of the weaker diethyl ether–iodine complex compared to the stronger dialkyl sulfide–iodine system. While overall solvation effects undoubtedly are not simple, one rationalization for the relatively large effect on a weak complex is the balance in energy between creation of a cavity in a liquid to accommodate the complex transferred from the vapor phase into a solvent and compression of the complex. Since energy is required to form a cavity, it will tend to be of minimum size. This would lead to a compression of the complex by the solvent cage, which should be larger for weak complexes because of the shallow minimum in their potential energy curves. The compression would be particularly pronounced for the excited iodine molecule because of the enhanced repulsion between the antibonding σ_μ iodine molecular orbital and the adjacent donor,[15] leading to a further blue shift.

It might be expected also that the increase in orbital overlap as a result of compression by the solvent cage should enhance the intensity of the absorption. While this seems to be the case for the sulfide–iodine system, it apparently does not hold for diethyl ether–iodine.

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(19) R. S. Mulliken and W. B. Person, "Molecular Complexes: A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969: (a) p 160; (b) p 26.

(20) M. Tamres and J. Yarwood in "Molecular Spectroscopy of Donor-Acceptor Complexes," J. Yarwood, Ed., Plenum Press London, 1973, Chapter 3.