Another point deriving from the CD experiments is the near doubling of the nucleoside B_{2u} molecular ellipticities in DMSO relative to water (Figures 8 and 9). Although the carbonyl chromophore is far less complex than the pyrimidine chromophore at issue here, the same hypothesis offered to explain anomalous solvent effects on chiroptical spectra of some selected ketones[20] may be involved in the DMSO solvent effect on the present 5-halouridine ellipticities. Kirk, Klyne, and Wallis suggested two general solvent effects: (1) changes in perturbation of the chromophore by asymmetric solvation and (2) solvent-dependent vicinal effects. In the present case, an additional phenomenon must be considered, (3) induced optical activity of the solvent. This last is plausible for DMSO because its absorption maximum[21] is in the vicinity of the pyrimidine B_{2u} transition. Although the contribution to the total molecular ellipticity by an extrinsic DMSO Cotton effect induced by specific nucleoside binding is an intriguing possibility, there is no evidence that allows either its rejection or acceptance. In view of the conclusion that the conformations of the series in water and in DMSO are quite similar, the second possibility is of minor importance. Thus solvational change without significant conformational change is implicated.

Little differential H_2O–DMSO solvent effect is seen on the ellipticity of syn nucleosides,[4] and only a moderate enhancement of the uridine ellipticity is seen on going from H_2O to DMSO solvent (Table IV). If, as noted above, uridine may be characterized by some proportion of the anti conformer, the DMSO ellipticity enhancement may be operative in proportion to the amount of anti conformer present.

Conclusion

The important result of this work is the separation of substituent from conformational effects on the CD of a series of nucleosides by means of an independent and more intimate probe, the nuclear Overhauser effect. Future work will be directed toward more extensive characterization of substituent effects.

Acknowledgment. Financial support of this work was provided by the Wisconsin Alumni Research Foundation and by a National Institutes of Health General Research Support Grant. The assistance of Richard A. Wood and the National Science Foundation Undergraduate Research program that supported him is acknowledged. We thank the University of Wisconsin Chemistry department for use of the HA-100 spectrometer. The sample of 5-fluorouridine was graciously supplied by Professor Charles Heidelberger.

[20] D. N. Kirk, W. Klyne, and S. R. Wallis, *J. Chem. Soc. C*, 350 (1970).

[21] U. Quintily and G. Scorrano, *J. Chem. Soc. D*, 260 (1971).

Vapor-Phase Charge-Transfer Complexes. VII. Iodine Complexes with Diethyl Sulfide and Dimethyl Sulfide[1]

Milton Tamres* and S. N. Bhat

Contribution from the Chemistry Department, University of Michigan, Ann Arbor, Michigan 48104. *Received July 19, 1971*

Abstract: A spectrophotometric study in the vapor phase of the dimethyl sulfide–iodine and diethyl sulfide–iodine complexes has been made. The equilibrium constants are lower and the oscillator strengths of the charge-transfer bands are higher than previously reported in the literature. In comparison with solution data, these results indicate a smaller solvent influence than had been believed. Further, the relative oscillator strengths of these two complexes are found to follow their relative strengths of complexation, in contrast to an earlier report. The blue-shifted iodine band for dimethyl sulfide–iodine in the vapor phase also has been characterized.

Sulfides are relatively strong donors toward iodine, and the complexes formed have CT bands located in a region comparatively clear of absorbance by the components. These are desirable characteristics for spectrophotometric study, particularly in the vapor phase, where the concentration range is necessarily small because of pressure limitations.[2]

Results from two laboratories on the vapor-phase study of diethyl sulfide–iodine[3–5] are in agreement on the $K_c\epsilon_{max}$ product (*i.e.*, equilibrium constant times extinction coefficient at λ_{max}). However, they differ in the separated K_c and ϵ_{max} values by a factor of ~3.5. This is rather disconcerting, considering that this system ought to be among the more favorable ones to study. Resolving this difference is important in order to determine the extent of solvent influence on these properties when comparison is made with solution data. Further, as has been reported, a reliable value for K_c is needed for characterization of the blue-shifted iodine band.[6]

---

[1] Presented before the Division of Physical Chemistry at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971.

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

[3] J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965).

[4] M. Tamres and J. M. Goodenow, *J. Phys. Chem.*, **71**, 1982 (1967).

[5] M. Kroll, *J. Amer. Chem. Soc.*, **90**, 1097 (1968).

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

Table I. Concentration and Spectral Data for Diethyl Sulfide–Iodine and Dimethyl Sulfide–Iodine in the Vapor Phase

Run	$[I_2] \times 10^5$, M	[Sulfide] $\times 10^3$, M	Cell path, cm	Corrected absorbance[a]						
				Diethyl Sulfide[b]						
				105.2°	110.0°	115.1°	122.0°	127.1°		
1	5.77	2.016	100.0	1.882	1.657	1.440	1.202	1.037		
2	3.25	4.538	75.0	1.764	1.567	1.352	1.116	0.987		
3	3.21	7.348	50.0	1.853	1.625	1.420	1.185	1.040		
4	1.82	13.36	50.0	1.790	1.588	1.384	1.160	1.036		
5	5.86	19.38	10.0	1.564	1.393	1.219	1.024	0.929		
6	6.07	22.75	10.0	1.872	1.660	1.475	1.252	1.128		
7	5.98	25.83	10.0	2.050	1.854	1.634	1.386	1.226		
8	4.71	30.06	10.0	1.835	1.630	1.473	1.251	1.105		
9	3.90	34.20	10.0	1.689	1.512	1.344	1.134	1.026		
				Dimethyl Sulfide[c]						
				90.0°	95.0°	100.0°	105.0°	110.0°	115.0°	120.0°
1	2.90	2.658	100.0	1.016		0.777		0.615		0.486
2	3.10	5.164	100.0	2.028	1.790	1.587	1.385	1.238	1.099	0.983
3	1.54	10.22	100.0	1.927	1.667	1.486	1.282	1.163	1.033	0.920
4	1.73	14.55	50.0	1.473	1.293	1.135	1.001		0.808	0.722
5	1.72	20.04	50.0	1.925	1.720	1.517	1.341	1.187	1.061	0.962
6	6.09	24.77	10.0	1.648		1.320	1.170	1.047		0.855
7	5.81	29.59	10.0	1.797	1.617	1.430	1.294	1.153	1.036	0.939
8	3.69	34.45	10.0	1.284	1.154	1.036	0.923	0.823	0.738	0.677

[a] Error limit ~0.005 unit. [b] λ_{max} 290 mμ. [c] λ_{max} 285 mμ.

Solution studies[7-11] have established the order of donor strength of several sulfides toward iodine, *e.g.*, thiacyclopentane > diethyl sulfide > dimethyl sulfide. The same sequence in the vapor phase was reported by Kroll.[5] A point of concern, however, is the finding that ϵ_{max} apparently increases with decreasing donor strength, which is not expected for stronger complexes.[12,13] A similar problem persists in the data for the aromatic hydrocarbon complexes with tetracyanoethylene in the vapor phase.[5]

The present study was undertaken to try to resolve the discrepancies. Complete spectral and thermodynamic data have been obtained for the iodine complexes with diethyl sulfide and with dimethyl sulfide. This includes characterization of the blue-shifted iodine band for the latter. A study of thiacyclopentane–iodine also was attempted. The complex was observed to have a maximum at 293 mμ, as reported previously by Kroll.[5] However, the procedures and conditions which were satisfactory for the studies with the two open-chain sulfides did not seem to be suitable to thiacyclopentane. Reaction with iodine apparently occurred, which led to nonreproducible results and prevented quantitative study.

Experimental Section

The apparatus for spectral measurements and temperature control already has been described.[14] To extend the sensitivity of the measurements, a recording scale of 0–0.2 absorbance unit was used in addition to the previous one of 0–2.0 absorbance units.

The type of break-seal tube used to introduce known weights of reagent into the cell also has been described.[14] Cells of different path length were used: 10.0, 50.0, 75.0 and 100.0 cm, determined with a Wild cathetometer. The volumes of the cells ranged from ~200–1700 ml, determined to within ±2 ml by filling with water after each run. Weighings to ±0.1 mg were made using a Mettler H15 balance. In the study with diethyl sulfide the weight of iodine ranged from 1.9 to 24.7 mg, and with dimethyl sulfide from 1.9 to 13.1 mg. However, the concentrations actually were determined spectrophotometrically by always introducing iodine first into the cell and measuring the absorbance in the visible region using the appropriate recording scale. The extinction coefficient of free iodine in the visible region, ϵ_{I_2}, had been determined previously over a temperature range from 60 to 120°.[6] It was extended in this study to 45°. The concentration of iodine in the various cells ranged from 1.82×10^{-5} to 5.86×10^{-5} M in the diethyl sulfide study and 1.54×10^{-5} to 6.09×10^{-5} M in the dimethyl sulfide study. The error is estimated to be $\leq 1\%$. The concentrations of the sulfides were determined from their weights and the volumes of the cells. In the case of the more volatile dimethyl sulfide, a small correction was made for the displacement of air in the break-seal bulb when determining the weight of the sulfide. Since the weights ranged from ~0.3 to ~1.1 g (2.016×10^{-3}–2.583×10^{-2} M for diethyl sulfide and 2.634×10^{-3}–3.409×10^{-2} M for dimethyl sulfide), the errors in concentration are considered to be under 1%.

The source and purification of iodine have been described.[15] Diethyl sulfide and dimethyl sulfide (Eastman Kodak Co.) were fractionally distilled through a 20-cm Vigreux column packed with glass helices, and the middle cuts used. Analysis by vapor-phase chromatography showed the absence of impurities.

Results

Concentration and spectral data for diethyl sulfide–iodine and dimethyl sulfide–iodine are given in Table I. A typical vapor-phase spectrum of the former system showing the absorbance of donor, acceptor, and complex has been published.[4] Figures 1 and 2 show the temperature dependence of the CT band of each complex for a given concentration of donor and acceptor. There is a small, but systematic broadening of each CT band as the temperature is raised, the half-width increasing by just a little less than 2% per 10° rise in temperature. The average value of the half-width of the CT band over the temperature range studied is 5400 cm^{-1} for dimethyl sulfide–iodine and 5800 cm^{-1} for diethyl sulfide–iodine. These results

---

(7) N. W. Tideswell and J. D. McCullough, *J. Amer. Chem. Soc.*, **79**, 1031 (1957).

(8) J. D. McCullough and D. Mulvey, *ibid.*, **81**, 1291 (1959).

(9) J. D. McCullough and I. C. Zimmerman, *J. Phys. Chem.*, **66**, 1198 (1962).

(10) M. Tamres and S. Searles, *J. Amer. Chem. Soc.*, **66**, 1099 (1962).

(11) E. T. Strom, W. I. Orr, B. S. Snowden, Jr., and D. E. Woessner, *J. Phys. Chem.*, **71**, 4017 (1967).

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

(13) R. S. Mulliken, *ibid.*, 74, 811 (1952).

(14) M. Tamres and J. Grundnes, *ibid.*, **93**, 801 (1971).

(15) M. Brandon, M. Tamres, and S. Searles, *ibid.*, **82**, 2129 (1960).

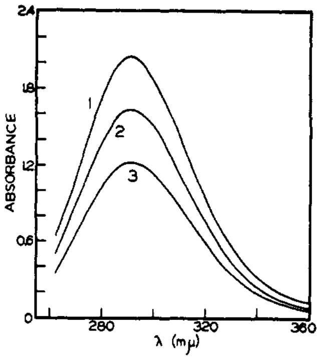

Figure 1. Temperature dependence of vapor-phase charge-transfer spectrum of diethyl sulfide (2.58×10^{-2} M) and iodine (5.97×10^{-5} M) in a 10.0-cm cell: (1) 105°, (2) 115°, (3) 127°.

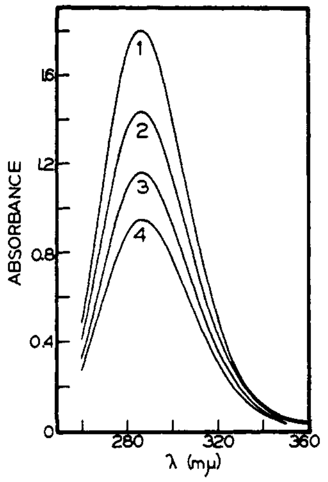

Figure 2. Temperature dependence of vapor-phase charge-transfer spectrum of dimethyl sulfide (2.91×10^{-2} M) and iodine (5.81×10^{-5} M) in a 10.0-cm cell: (1) 90°, (2) 100°, (3) 110°, (4) 120°.

agree quite well with those of Kroll.[5] There is agreement with previous work also on the position of the CT band maximum: 285 mμ for the former complex and 290 mμ for the latter.[3-5] The shifts in the CT bands from the vapor phase to solution have been tabulated and discussed by Kroll.[5]

Recently, evidence for the existence of a blue-shifted iodine band in the diethyl sulfide–iodine system has been presented.[6] Evidence now has been obtained for the dimethyl sulfide–iodine system as well, which supports the earlier finding. Figures 3 and 4 show the dependence of the iodine visible spectrum on the dimethyl sulfide concentration and on the temperature. Iodine vapor shows a band structure at wavelengths longer than ~500 mμ and a continuum at shorter wavelengths. The alteration in the region above 500 mμ on adding dimethyl sulfide, or any gas, is due to broadening of band lines. The enhanced absorbance in the continuum region, which increases with increased donor concentration and decreases with increasing temperature, is indicative of complex formation. Hydrocarbons at comparable pressures have no effect on the iodine spectrum in this region.[6]

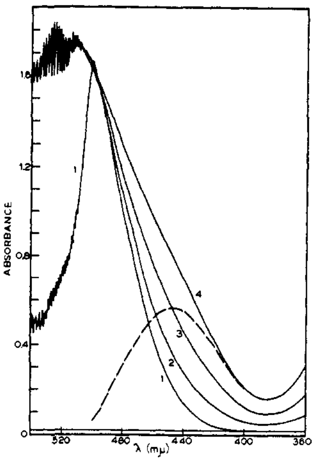

Figure 3. Donor concentration dependence of absorbance in visible region for dimethyl sulfide–iodine (5.60×10^{-5} M) at 90° in 50.0-cm cell: (1) iodine alone (at 45°); (2) iodine + sulfide (6.69×10^{-3} M); (3) iodine + sulfide (1.90×10^{-2} M); (4) iodine + sulfide (3.83×10^{-2} M). The dashed curve is the difference between curve 4 and curve 1 (corrected for temperature broadening to 90°).

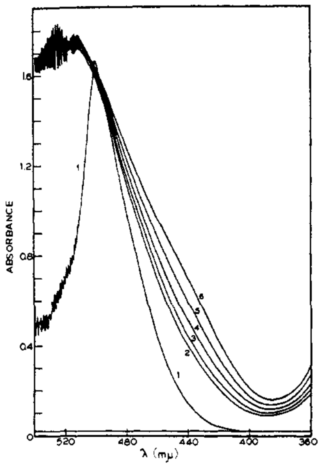

Figure 4. Temperature dependence of absorbance in visible region for dimethyl sulfide (3.83×10^{-2} M)-iodine (5.60×10^{-5} M) in a 50.0-cm cell: (6) 90°; (5) 100°; (4) 110°; (3) 120°; (2) 130°; (1) iodine alone at 45°.

Discussion

From the data in Table I, K_c and ϵ' were determined by the usual regression treatment of

$$\frac{D_0A_0}{\mathrm{OD}'} = \frac{1}{\epsilon'}\left[\frac{1}{K_c} + (D_0 + A_0) - \frac{\mathrm{OD}'}{\epsilon'}\right] \qquad (1)$$

where D_0 and A_0 are the initial concentrations of donor and acceptor, respectively, OD′ is the corrected optical density,[2] and ϵ' is the corrected extinction coefficient ($= \epsilon_{\mathrm{CT}} - \epsilon_{\mathrm{D}} - \epsilon_{\mathrm{A}})^2$. The corrections are small because the free donor and free acceptor contribute very little to the absorbance near the CT band maximum.

Results of the analysis at $\lambda_{\max}$ are given in Table II. The random variation of $\epsilon_{\max}$ with temperature is not in accord with the spectral curves in Figures 1 and 2 and is attributed to experimental error. It should be noted, however, that the maximum variation over the full temperature range is much smaller than that obtained in previous studies.[3-5] The improve-

Table II. Regression Analysis[a] of K_c and ϵ at λ_{max}

Temp, °C	$K_c\epsilon_{max} \times 10^{-4}$, $l.^2\ mol^{-2}\ cm^{-1}$	K_c, l. mol^{-1}	$\epsilon_{max} \times 10^{-4}$, l. mol^{-1} cm^{-1}	r[b]
		(A) Diethyl Sulfide–Iodine		
105.2	16.57 ± 0.33	9.41 ± 1.13	1.762 ± 0.181	0.993
110.0	14.58 ± 0.31	8.73 ± 1.17	1.670 ± 0.193	0.992
115.1	12.56 ± 0.29	7.37 ± 1.25	1.705 ± 0.254	0.986
122.0	10.42 ± 0.25	6.50 ± 1.28	1.602 ± 0.281	0.981
127.1	9.11 ± 0.13	5.48 ± 0.75	1.662 ± 0.208	0.990
		(B) Dimethyl Sulfide–Iodine		
90.0	13.38 ± 0.18	9.44 ± 0.75	1.417 ± 0.096	0.998
95.0	11.51 ± 0.22	7.74 ± 1.01	1.487 ± 0.170	0.996
100.0	10.20 ± 0.24	7.44 ± 1.29	1.371 ± 0.210	0.988
105.0	8.74 ± 0.30	5.71 ± 1.75	1.530 ± 0.421	0.972
110.0	8.00 ± 0.24	6.79 ± 1.60	1.180 ± 0.246	0.984
115.0	6.99 ± 0.22	5.87 ± 1.59	1.190 ± 0.290	0.985
120.0	6.26 ± 0.19	5.11 ± 1.61	1.224 ± 0.352	0.961

[a] Error limits for 95% confidence level. [b] Correlation constant.

ment in results is reflected in the smaller error limits (at the 95% confidence level) and in a value near unity for the correlation constant.

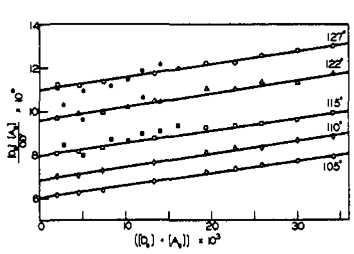

Figure 5. Plot of $[D_0][A_0]/OD'$ *vs.* $[D_0] + [A_0]$ from eq 1 for the diethyl sulfide–iodine complex at λ 290 mμ: open figures, this work; filled figures, Goodenow and Tamres.[3,4]

The main reasons for this improvement are: (1) the greater range in $(D_0 + A_0)^2$, which was achieved by using cells of various path lengths and recording scales of different sensitivity, and (2) the greater precision in determining iodine concentration,[2] which was achieved by direct spectrophotometric measurement. These features are evident in Figures 5 and 6, where the linear form of eq 1 is plotted for each of the complexes. The linear form is obtained by dropping the last term within the brackets (OD/ϵ') in eq 1. (Although this term makes a small contribution below room temperature where K_c is large,[10,16] it can be neglected at the higher temperature of this study.) Available earlier data of Goodenow and Tamres[3,4] for diethyl sulfide–iodine are included for comparison in Figure 5. The extension in the range of $D_0 + A_0$ (or the X coordinate) by a factor of 2 in the present study increases the overall change in D_0A_0/OD' (or the Y coordinate) by a corresponding factor. This gives an improved evaluation of the slope and intercept[2] and, hence, a better separation of K_c and ϵ'.

Because of the random variation in ϵ_{max} with temperature, the change in internal energy, $\Delta E°$, was determined from the temperature dependence of log $K_c\epsilon_{max}$. It has been suggested[17-19] that, under certain conditions, $\Delta E°$ can be determined from a plot of log OD' *vs.* $1/T$ for a single electron donor–acceptor mixture. A necessary condition is that the per cent change in concentration of the lesser component (A_0 in this study) should be small over the temperature range.[19] Application of this method to runs 1 and 2 of the diethyl sulfide–iodine system (where the lowest donor concentrations were used) gave $\Delta E°$ values which were less by only 0.15 and 0.3 kcal mol^{-1}, respectively, from that determined by the conventional plot of log $K_c\epsilon_{max}$ *vs.* $1/T$. Similar application to runs 1–3 of the dimethyl sulfide–iodine system gave $\Delta E°$ values which were less by only 0.2 kcal mol^{-1}. These differences are within the experimental limits in determining $\Delta E°$.

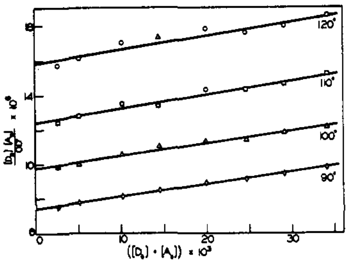

Figure 6. Plot of $[D_0][A_0]/OD'$ *vs.* $[D_0] + [A_0]$ from eq 1 for the dimethyl sulfide–iodine complex at λ 285 mμ.

The thermodynamic and spectral results from this study are presented in Table III, together with previous vapor-phase and solution data. The agreement in the vapor phase for the $K_c\epsilon_{max}$ product obtained in different laboratories is good, being within the specified error limits. The $\Delta E°$'s, although being a little higher in the present study, also are within the extremes of the error limits. On the other hand, K_c is lower and ϵ_{max} correspondingly higher than the previously reported values, particularly compared to those of Kroll.[5]

In comparison with solution studies, the present results indicate a smaller solvent influence on the sulfide–iodine system than had been believed. Observation of trends in other systems of the effect of

---

(16) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

(17) R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *J. Amer. Chem. Soc.*, **83**, 3572 (1961).

(18) E. A. Ogryzlo and B. C. Sanctuary, *J. Phys. Chem.*, **69**, 4423 (1965).

(19) M. Tamres in "Molecular Complexes," R. Foster, Ed., Paul Elek Ltd., London, in preparation.

Table III. Spectral and Thermodynamic Properties of Sulfide–Iodine Complexes[a,b]

	Diethyl sulfide–iodine				Dimethyl sulfide-iodine		
	Vapor (this work)	Vapor[c]	Vapor[d]	*n*-Heptane	Vapor (this work)	Vapor[d]	*n*-Heptane
λ_{max}, mμ	290	290	290	303[e]	285	285	299[d]
Half-width, cm^{-1}	5800 ± 150	~5700	5800 ± 150	5400 ± 150[d]	5400 ± 150	5600 ± 150	5300 ± 150[d]
ϵ_{max} (av), l. mol^{-1} cm^{-1}	16,800 ± 2230	11,200 ± 1900	3500 ± 1000	26,400 ± 1050[e]	13,750 ± 3310	5000 ± 2500	
f[f]	0.41	0.28	0.09 ± 0.03		0.33	0.13 ± 0.07	
μ_{mn},[g] D	5.1				4.5		
$K_c\epsilon_{max}$ (373°K), $l.^2$ mol^{-2} cm^{-1}	193,600 ± 3000	184,800 ± 9200	203,000 ± 22,900	248,200[e]	102,000 ± 3000	115,000 ± 1150	
K_c (373°K), l. mol^{-1}	11.5 ± 1.1	16.5	58 ± 20	9.4[e]	7.5 ± 1.3	23 ± 12	
K_c (298°K), l. mol^{-1}	191 ± 20	226	750 ± 250	180 ± 7[e] 180 ± 3[e] 210[h] 171 ± 23[i]	84 ± 15	220 ± 140	71 ± 2[j] 71 ± 5[i]
$-\Delta E°$, kcal mol^{-1}	8.3 ± 0.2	7.7 ± 0.4[k]	7.6 ± 0.5		7.1 ± 0.4	6.7 ± 0.5	
$-\Delta H°$, kcal mol^{-1}	9.0 ± 0.2	8.4 ± 0.4[k]	8.3 ± 0.5	8.9 ± 0.6[e,k] 8.3 ± 0.2[e,k] 7.8[h] 8.1[l] 9.0[l]	7.8 ± 0.4	7.4 ± 0.5	
$-\Delta S$, cal mol^{-1} deg^{-1}	17.3 ± 0.5	15.0 ± 1.1[k]	14.2 ± 1.9[k]	19.4 ± 2.0[e,k] 17.6 ± 0.5[e,k] 15.9[h] 12.0[l] 16.0[l]	15.1 ± 1.0	13.6 ± 2.4	

[a] Standard state of 1 *M*. [b] Error limits at 95% confidence level. [c] Reference 4. [d] Reference 5. [e] Reference 10. [f] Oscillator strength: R. S. Mulliken and W. B. Person "Molecular Complexes," Wiley, New York, N. Y., 1959, p 26. [g] Electronic transition dipole (same reference as in footnote *f*). [h] At 20° (ref 12). [i] In CCl_4 (ref 11). [j] In CCl_4: N. W. Tideswell and J. D. McCullough, *J. Amer. Chem. Soc.*, 79, 1031 (1957). [k] Standard error. [l] M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **83**, 4329 (1961).

solvation on the spectral and thermodynamic properties of complexes is hampered at present by several limitations.[19] First, the number of data available for comparison is not extensive. Second, the results in some cases are questionable. Third, the variation in results from different laboratories (often with accompanying large error limits) tend to mask trends. Nevertheless, a pattern does seem discernible if a wide range of complexes, weak to strong, is considered.

For the weak benzene-iodine complex,[20,21] a higher K_c and $\Delta E°$ and a much lower ϵ_{max} are found in the vapor phase compared to solution, even if activity in the latter phase is taken into account.[22] The situation is similar for diethyl ether-iodine,[23,24] which also is relatively weak. For the strong complex trimethylamine-sulfur dioxide,[25,26] K_c and $\Delta E°$ are *lower* in the vapor phase, with ϵ_{max} being about the same in the two phases.

The alkyl sulfide-iodine system is of intermediate strength. Hence, if the trend is valid, its spectral and thermodynamic properties ought to lie between the above extremes. Apparently, this is the case for the data from the present study. For the iodine complex with diethyl sulfide, ϵ_{max} in the vapor phase is *ca.* two-thirds that in solution and for the iodine complexes with both diethyl sulfide and dimethyl sulfides, the K_c's are the same in solution and the vapor phase, within experimental error. The variation in reported results for $\Delta E°$ and $\Delta H°$ for diethyl sulfide-iodine makes the absolute difference in the two phases uncertain. However, the *relative* magnitude of the $\Delta E°$'s for the two phases is intermediate between those for the weak and strong complexes. This result is in accord with a model developed by Christian, *et al.*,[27] based on the relative solvation effects on the donor, the acceptor, and the complex. The trend is rationalized on the basis that strong complexes, being polar, have greater polarization interaction with the solvent which more than compensates for the loss in solvation energy as a consequence of "squeezing out" several solvent molecules around the donor and acceptor when the complex is formed.

The present work resolves two important problems. First, in agreement with Kroll, the donor strength of diethyl sulfide is greater than that of dimethyl sul-

---

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

(21) D. Atack and O. K. Rice, *J. Phys. Chem.*, **58**, 1017 (1954).

(22) J. D. Childs, S. D. Christian, J. Grundnes, and S. R. Roach, *Acta Chem. Scand.*, **25**, 1679 (1971); J. D. Childs and S. D. Christian, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, No. PHYS 193.

(23) J. Grundnes, S. D. Christian, and W. Cheam, *Acta Chem. Scand.*, 24, 1836 (1970).

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

(25) S. D. Christian and J. Grundnes, *Nature (London)*, **214**, 1111 (1967).

(26) J. Grundnes and S. D. Christian, *J. Amer. Chem. Soc.*, **90**, 2239 (1968).

(27) S. D. Christian, J. R. Johnson, H. E. Affsprung, and P. J. Kilpatrick, *J. Phys. Chem.*, **70**, 3376 (1966).

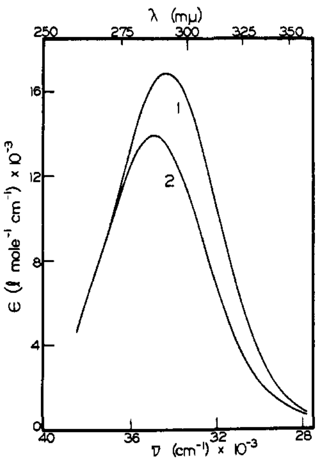

Figure 7. Vapor-phase CT spectra at 110°: (1) diethyl sulfide–iodine; (2) dimethyl sulfide–iodine.

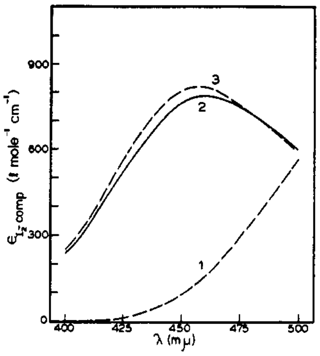

Figure 8. The blue-shifted iodine band for dimethyl sulfide–iodine in the vapor phase: (1) free iodine at 90°; (2) complexed iodine at 120°; (3) complexed iodine at 90°.

fide. However, as shown in Figure 7, the relative oscillator strengths are reversed from those reported by him, the order now being in accord with theory.[12,13] Correlation of oscillator strength with strength of complexation for a few aromatic hydrocarbon-tetracyanoethylene complexes also has been obtained,[28] which suggests that the earlier discrepancy[5] was due to experimental error. Second, characterization of the blue-shifted iodine band is sensitive to the value of K_c. This was shown for the diethyl sulfide-iodine system, where characterization was compared for different literature values of K_c, including the one obtained in this study, which was taken as being the most reliable.[6] Similar analysis of dimethyl sulfide-iodine, based on the present value of K_c and the spectral data of Figure 4, results in the blue-shifted iodine band shown in Figure 8. The band is not extended to wavelengths shorter than 400 mμ because of the probable small contribution to the absorbance in this region from the tail of the intense CT band.[6] The difference in the curves at 90 and 120° cannot be considered significant. The maximum for $\epsilon_{I_2\text{-comp}}$ is ~800 l. mol^{-1} cm^{-1} at ~457 mμ. By comparison, the maximum for $\epsilon_{I_2\text{-comp}}$ for the diethyl sulfide-iodine system is ~1100 l. mol^{-1} cm^{-1} at ~453 mμ. These numbers are subject to small variation because the separation of the total visible absorbance curve into free and complexed iodine components is sensitive to small changes in the values of K_c and of ϵ_{I_2}.[6] But the approximate magnitude of the shift seems established, and it would seem that the effect on the iodine visible band is somewhat less for dimethyl sulfide than for diethyl sulfide.

Acknowledgment. This research was supported by the National Science Foundation in part through Grant No. GP-9216, and in part through Grant No. GP-10367 to this department for the purchase of the Cary-14 spectrophotometer used in this study.

---

[28] I. Hanazaki, personal communication.