Arguing qualitatively, one can propose that, as the unpaired spin density becomes more localized at the nitro group due to solvation by the polar MeOH, the chlorine lone-pair electrons tend to back-bond into the π system. The net effect on the chlorine atom is greater unpaired electron density which is reflected in the larger hfs. Other literature values correlate with this view. Ayscough, *et al.*,[22] obtained a 0.24-G chlorine coupling in the photochemical reduction of *p*-ClNB in sodium ethoxide–ethanol solution. The increased coupling is reasonable if the sodium cations are seen as more effective in polarizing the spin density on the nitro group than MeOH. Further support for this hypothesis is given by Seo, *et al.*,[23] who reported couplings of 1.72 and 1.43 for Cl^{35} and Cl^{37}, respectively, in the electrochemical oxidation of tri-*p*-chlorotriphenylamine. This agrees with the above model since a full positive charge on the radical would be expected to cause a large increase in chlorine back-bonding. Nmr studies of *p*-fluoronitrobenzene also substantiate the model.[24]

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A Spectroscopic Study of the Ethanol–Iodine Complex

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Abstract: The spectroscopic properties of the charge-transfer band and the thermodynamic properties for the formation of the electron donor–acceptor complex between ethanol and iodine have been measured in solution in *n*-heptane and in methylene chloride. The measured absorbance of the complex in the ultraviolet region has been analyzed by the Liptay–Scott procedure to give K_f and ϵ_{ic}; measurements at different temperatures give $\Delta H_f°$ and $\Delta S_f°$. In this analysis there was a slight trend with wavelength; consideration of possible causes suggests that the most likely reason may be that the molar absorptivity of uncomplexed iodine changes as ethanol is added to the I_2 solution in *n*-heptane. The Liptay–Scott procedure is modified slightly to take this possibility into consideration and remove the trend in data, but the resulting values of K_f and ϵ_0 are not changed drastically. The formation constant of the ethanol–I_2 complex in *n*-heptane is about twice as large as that found for the same complex in methylene chloride solution, but the stability (as measured by ΔH_f) is about the same in both solutions. The complex is found to be more stable ($\Delta H_f = -4.5$ kcal/mol in *n*-heptane) than had been previously reported. The maximum of the charge-transfer absorption is observed at 233 mμ (or about 0.3 eV to higher energies than previously reported), and the intensity is greater by about a factor of 2 than that previously reported. Reasons for these discrepancies are presented.

Properties of the ethanol–I_2 complex are of considerable importance for the understanding of electron donor–acceptor complexes, because it is a representative example of a complex between an alcohol acting as an n donor and the aσ acceptor, I_2. The ultraviolet and visible spectrum and the thermodynamic properties of this complex have been studied previously by de Maine[3] and by Amako,[4] with results summarized by Briegleb.[5]

The study by de Maine[3] was made in solution in CCl_4 as a solvent and included both the visible "blue-shifted" iodine absorption band and the ultraviolet charge-transfer band. That by Amako[4] was of the complex in solution in *n*-hexane and included only the "blue-shifted" visible iodine absorption band. Brandon, Tamres, and Searles had pointed out that the thermodynamic properties reported from these two studies were inconsistent with each other,[6] even allowing for the use of different solvents. Thus Amako[4] reported that the formation constant, K_x (296°K) = 6.99, and the enthalpy of formation, $\Delta H_f = -3.53$ kcal/mol, while de Maine[3] reported K_x (298°K) = 4.00, with $\Delta H_f = -2.10$ kcal/mol. Furthermore, de Maine reported that the maximum absorption for the ultraviolet band occurred at 243 mμ, with a very unusual shape for the band (falling off sharply on the high-frequency side; see curve III of our Figure 4), while Amako reported that the ultraviolet absorption band was broad with a maximum near 235 mμ, without giving further details.

Although the differences between these two studies were not excessive—especially the differences in K_x—further examination revealed additional inconsistencies. These include (1) comparison of the wavelength of maximum absorption reported by de Maine[3] with that found earlier by Ham[7] for the similar complex between

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iodine and *t*-butyl alcohol ($\lambda_{\max}$ 233 mμ); (2) the rather anomalously low value of $-\Delta H_x$ reported by de Maine,[3] which seems inconsistent with the large "blue shift" of the visible I_2 band; and (3) the anomalously low value of the transition dipole, *D*, computed from the result given by de Maine[3] and reported in Table III of the paper by Tsubomura and Lang.[8]

Thus, these several inconsistencies, even though each one is by itself not significant, suggested a need for repeating and extending the earlier studies,[3,4] of the ethanol–I_2 system especially in view of its importance as one of the simplest representatives of alcohol–halogen complexes.

Experimental Section

Chemicals. Mallinckrodt analytical reagent grade iodine was resublimed according to the procedure given by Kolthoff and Sandell.[9] Ethanol (95%) was purified[10] by distillation, twice in a nitrogen atmosphere over dried calcium oxide, and once in a nitrogen atmosphere over magnesium and iodine. Pure grade *n*-heptane (Phillips Petroleum Co.) was purified as recommended by Potts.[11] Methylene chloride (Baker analyzed reagent grade) and carbon tetrachloride (Fisher certified reagent grade) were purified as recommended by Wiberg.[12] The criterion for purity of the solvents was the ultraviolet absorption spectrum, as described by Potts[11] for aliphatic hydrocarbons.

Instrumentation. A Beckman Model DK-2A far-ultraviolet ratio recording spectrophotometer was used for all spectrophotometric measurements. A Beckman temperature-regulated cell holder was controlled to a constant arbitrary cell temperature over a range from −12 to 60° (±0.2°) by circulating a solution of ethylene glycol in water (1:1 by volume) from a thermostated Haake circulator and, for low temperatures, a Sargent water bath cooler.

Oxygen (and other undesirable vapors) was removed from the instrument by purging with high purity dry nitrogen. A slow purge was maintained continuously, and the purge rate was increased during the study—especially for the low temperature studies—in order to prevent condensation of water.

A pair of matched, stoppered, 1.00-cm Beckman cells with far-ultraviolet silica windows were used when *n*-heptane was the solvent. Another pair of matched, stoppered, 1.00-cm Beckman cells with standard silica windows were used with 0.95-cm standard silica fillers to obtain 0.05-cm pathlengths when methylene chloride was the solvent.

Procedure. Previous work[3,4] indicated that side reactions leading to formation of triiodide ions were a serious complication for this system in the interpretation of the experimental results to obtain spectroscopic and thermodynamic constants for the complex. In order to minimize these effects, solvents were purified and handled under a dry nitrogen atmosphere at all times. The presence of I_3^- ions in solution is indicated by strong ultraviolet absorption at 290 and 350 mμ.[13,14] With these precautions in handling, no absorbance (*i.e.*, <0.005) was observed in our solutions in these regions.

A stock solution of iodine in *n*-heptane (or methylene chloride) was prepared by weighing solid iodine into a 100-ml volumetric flask on a semimicro Mettler balance. The flask and iodine were then placed in a nitrogen-filled drybox, and the flask was filled to the mark with *n*-heptane (or methylene chloride). The concentrations of the stock solutions were checked by titration with standard thiosulfate solutions and by measurement of the visible absorption spectrum of I_2 before and after an experiment. The concentrations of the stock solutions obtained from titration usually agreed with those calculated from the visible I_2 absorption within 2 or 3%.

Sample solutions were prepared by dilution of the stock solutions and the addition of donor using microburets to measure donor and stock solution aliquots. The absorption spectrum of the sample solution, with respect to a reference solution consisting of donor and solvent, was recorded at 24°. The spectrum was then recorded after adjusting the temperature of the cell holder to a new value, allowing 30 min or more for the cell compartment to reach equilibrium. In this way, spectra of each I_2 solution were recorded at the following approximate temperatures: 24, 10, −10, and 40°, in the order of measurement. The measured absorbances were then plotted for each solution as a function of temperature so that the absorbance at any arbitrarily selected temperature could be read from the graph. In order to check on possible irreversible reactions during the time needed to go through this cycle the spectra of randomly chosen solutions were recorded again at 24° at the end of the cycle. No changes were observed between the first and last recordings. The changes in molar concentrations of the solution due to the changes in volume with temperature were calculated using data for the solvent density from Timmermans.[15]

Analysis of Data

Here we attempt only a brief summary of the procedure followed in analyzing the data, presenting selected results that we believe to be correct. Additional data and considerable discussion of the details of the analysis are given by Julien.[16]

Liptay–Scott Analysis. To obtain the formation constant, K_f, and the molar absorptivities, ϵ_{ic}, for the complex (indicated by the subscript "c") at wavelength λ_i, we have used the Liptay procedure,[17] in conjunction with Scott's modification[18] of the Benesi–Hildebrand[19] equation. Because the charge-transfer (CT) absorption band of this complex overlaps the absorption by uncomplexed I_2 in the region of our measurements (220–260 mμ), we corrected the measured absorbance by computing the concentration of uncomplexed I_2 in solution, using an estimated value of K_f. The absorbance by uncomplexed I_2 was then computed using values for ϵ_{i3} (the molar absorptivity of uncomplexed I_2) measured in the solvent, with no ethanol added. The interfering absorption by the ethanol was not a problem because of the compensation by the ethanol solution in the reference beam.

After estimating the corrected absorbances of the complex, as just described, we computed the value of K_f and of ϵ_{ic}, using a program[16] (in FORTRAN IV, for the IBM 7040/7044 computer) of the Liptay–Scott procedure. The new value of K_f thus obtained was used to recompute the corrected absorbances of the free I_2 and the procedure repeated until successive values of K_f agreed to within one-half of the standard deviation in K_f.

Absorbances from 12 solutions of I_2 in *n*-heptane with different ethanol concentrations (ranging from 0.34 to 2.70 *M* at 24°) were read at 5-mμ intervals from 225 to 250 mμ. Absorbances from six solutions of I_2 in methylene chloride with ethanol concentrations ranging from 2.05 to 7.50 *M* at 24° were read over the same wavelength range. The Liptay–Scott analysis was carried out to obtain K_f and ϵ_{ic} at 10° intervals (and at

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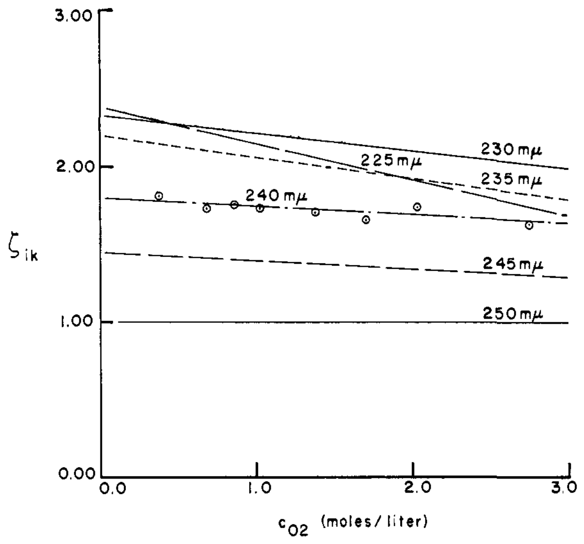

Figure 1. Trends in ζ_{ik} as a function of wavelength and of the total ethanol concentration, c_{02}, for the ethanol–I_2 system in *n*-heptane at 24°. The data points are shown only for the values of ζ_{ik} at 240 mμ in order to illustrate the experimental scatter, which is comparable for data at other wavelengths.

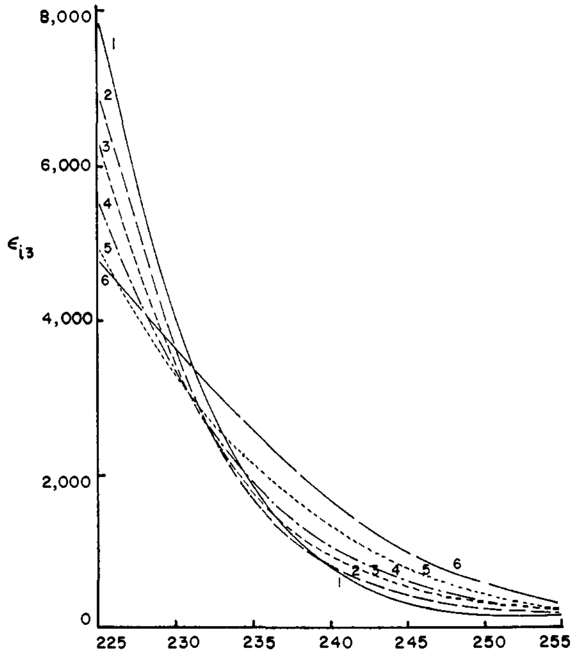

Figure 2. Molar absorptivities measured for I_2 solutions in methylene chloride as *n*-heptane is added. The concentration of *n*-heptane in methylene chloride is: curve 1, 0.00 *M;* curve 2, 1.36 *M;* curve 3, 2.71 *M;* curve 4, 4.06 *M;* curve 5, 5.42 *M;* and curve 6, 6.77 *M.*

24°) from −10 to +40° for the *n*-heptane solutions and for the methylene chloride solutions from −10 to +30°.

Trends in Data. The straightforward application of the Liptay–Scott procedure, described above, led to results showing a trend with wavelength, which we believe to be somewhat greater than the experimental error, and hence significant. These trends can be illustrated by examining the values of ζ_{ik}, computed in the Liptay–Scott procedure,[17] which vary systematically with wavelength, rather than remaining constant or scattering about an average value. The values of ζ_{ik} as a function of wavelength are shown for a typical set of data in Figure 1.

Such trends in data raise questions concerning the interpretation to obtain formation constants. Plausible explanations for the trends include the possibility that ethanol dimers complex with I_2 to give a CT band at a slightly different frequency from that for the complex with monomeric ethanol. The trend in results with changing concentration of ethanol might then be due to the changing relative concentration of monomer to dimer. We have examined this possibility,[16] but we do not believe it is in quantitative agreement with our experimental results, especially with the observation that the trends in data at different temperatures are the same.

Instead, we prefer an alternative explanation for the trend in data; namely, that the molar absorptivity (ϵ_{i3}) of uncomplexed I_2 in the *solution* is different from the molar absorptivity of I_2 in pure *solvent* (ϵ_{i3}') and that it varies as a function of ethanol concentration. This explanation is consistent with the observed temperature independence in the trends. It seems more acceptable when we notice that the ethanol concentration is quite high in these solutions (approaching 50% by volume).

We believe that the reason that ϵ_{i3} may change as a function of the ethanol concentration is that the *contact* CT band of I_2 in the *n*-heptane solvent may be affected by the added ethanol. This effect is potentially quite a bit larger than an "ordinary" solvent shift of the locally excited I_2 absorption at 180 mμ, for example. It is expected to be especially important for this system (ethanol–I_2 in *n*-heptane) because the CT band of ethanol–I_2 overlaps the contact CT band of I_2 in *n*-heptane.

We can estimate the position expected for the contact CT band of I_2 with different solvents. For I_2 in *n*-heptane the maximum of the contact band is found to be at 227 mμ;[20] for I_2 in C_2H_5OH, we predict a shift to 210 mμ, so it is reasonable to expect the value of ϵ_{i3} to decrease from *n*-heptane to ethanol solution for λ greater than about 230 mμ and for it to increase at wavelength less than that value. In order to investigate the credibility of the hypothesis that ϵ_{i3} changes as another solvent (ethanol, here) is added to the I_2 solution in *n*-heptane, we investigated the change in ϵ_{i3} from I_2 solutions in mixed solvents of *n*-heptane with varying amounts of added "inert" polar solvent, CH_2Cl_2. We estimated that the wavelength for the maximum of the contact CT band of I_2 in CH_2Cl_2 would be at about 183 mμ, so the spectral changes in I_2 in this mixed solvent might be expected to be similar to those for ethanol–*n*-heptane, but more exaggerated. The apparent molar absorptivity ϵ_{i3} of I_2 solutions in mixed CH_2Cl_2–*n*-heptane solvent is shown in Figure 2. We note that ϵ_{i3} at 225 mμ decreases as the concentration of *n*-heptane increases, in contrast with the behavior of ϵ_{i3} in the wavelength region between 230 and 260 mμ where ϵ_{i3} increases as the *n*-heptane concentration increases, as expected if the change in the change in the contact CT

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[20] (a) D. F. Evans, *J. Chem. Phys.*, 23, 1424 (1955); (b) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 79, 4839 (1967); (c) L. M. Julien and W. B. Person, *J. Phys. Chem.*, 72, 3059 (1968).

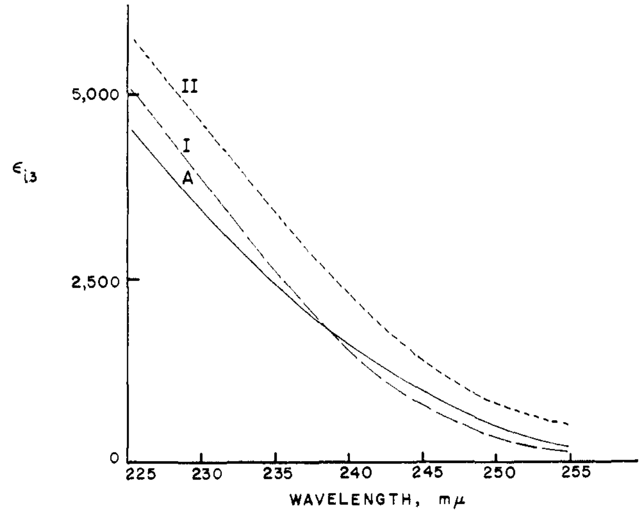

Figure 3. Plots of calculated and measured molar absorptivities of I_2 in *n*-heptane. Curve A was measured for a solution of iodine dissolved in pure *n*-heptane (ϵ_{i3}'). Curve I was calculated from first iterative method. Curve II was calculated from the second iterative method (see text).

absorption band[16,20] of iodine is indeed the correct explanation for the change in ϵ_{i3} with changing solvents, and for the resulting trends we have observed in the ζ_{ik} values (Figure 1).

With this possibility (of changing ϵ_{i3}) in mind, we have used two different iterative procedures[21] to compute from the experimental data values of ϵ_{i3}, treating them as additional parameters. These values may then be used in the Liptay-Scott analysis to obtain the corrected absorbance of the complex. The first method consisted of fitting a set of calculated absorbances (from assumed molar absorptivities and concentrations for the complex and for the uncomplexed iodine) by least squares to the observed absorbances, D_{ik}, making use of the material balance for the total iodine concentration with the assumption that only a 1:1 donor-acceptor complex forms. The second procedure was expected to be better. It was similar to the first, except that the least-squares fitting was made to give a consistent value of K_f, rather than to give the best agreement between the calculated and observed absorbances, D_{ik}. These two procedures are described by Julien[16] in more detail.

In order to compare the resulting average molar absorptivity of iodine in ethanol–*n*-heptane solutions (ϵ_{i3}) calculated from these two procedures, we show in Figure 3 the computed results compared with the measured molar absorptivity of iodine in pure *n*-heptane (ϵ_{i3}'). Note that the first procedure (curve I) predicts that ϵ_{i3} in solutions containing ethanol is expected to be very similar to ϵ_{i3} for iodine solutions in CH_2Cl_2–*n*-heptane mixtures (Figure 2). Because we believe the values for ϵ_{i3} from the second iterative procedure (curve II in Figure 3) are less reasonable, we are inclined to prefer the results from the first procedure even though it is expected to be less rigorous than the second procedure. However, the results for the molar absorptivity values ϵ_{ic} from the first procedure depended somewhat upon the initial guesses for these molar absorptivities. The second iterative procedure converged to the same results for ϵ_{ic} each time, independent from the initial guesses.

In spite of these minor differences from the different iterative procedures, use of either set of the ϵ_{i3} values in the Liptay-Scott analysis removed the trends in the ζ_{ik} matrices for the ethanol-iodine system in *n*-heptane. The formation constants, K_f, computed using ϵ_{i3} values from the first iterative procedure were identical, within experimental error, with those computed from the Liptay-Scott procedure assuming that $\epsilon_{i3} = \epsilon_{i3}'$. These results are shown in Table I, where we see also that the values of K_f calculated using the ϵ_{i3} values from the second iterative procedure differ somewhat from the other values. However, we do not find that the results from the different methods of analysis for the thermodynamic and spectroscopic properties of the complex are very different from each other, justifying our belief that the complications causing the trend in data are not an important source of error in our results.

Table I. Formation Constants, K_f, and Molar Absorptivities, ϵ_{ic}, of the CT Band[a] for the Ethanol–I_2 Complex in *n*-Heptane at 24°, Computed by the Liptay–Scott Procedure[a]

Wave-length, mμ	A[a] K_f,[b] l./mol	A[a] ϵ_{ic}[b]	"First iterative procedure" I[a] K_f[b]	"First iterative procedure" I[a] ϵ_{ic}[b]	"Second iterative procedure" II[a] K_f[b]	"Second iterative procedure" II[a] ϵ_{ic}[b]
250	1.33	6,070	0.99	6,380	0.72	7,050
245	1.13	8,400	0.98	8,610	0.65	9,470
240	1.02	10,410	0.90	10,660	0.66	11,500
235	0.84	12,190	0.87	11,980	0.59	13,060
230	0.84	12,660	0.89	12,370	0.64	13,200
225	0.73	12,200	0.85	11,680	0.62	12,360
Av K_f =	0.94		0.92		0.64	

[a] The results in the columns labeled A are from the Liptay–Scott analysis, assuming $\epsilon_{i3} = \epsilon_{i3}'$ (see text). The other two results (I and II) are obtained from the Liptay–Scott procedure using the two iterative procedures described in the text to obtain ϵ_{i3} and then obtain D_{ik}. [b] From the scatter in data the standard deviation of each K_f value was estimated to be about ±0.06, and for ϵ_{ic} it is estimated to be about ±4%.

Results

The results for the ethanol–I_2 complex in *n*-heptane are summarized in Table II. We have listed there the values obtained from the Liptay-Scott analysis of our data, using ϵ_{i3} obtained from the first iterative procedure. Again we emphasize that the results using the other procedures are not markedly different.

The corresponding results found for the ethanol–I_2 complex in methylene chloride solution are listed in Table III. For this system, however, we found that the ζ_{ik} values in the usual Liptay-Scott analysis did not show any trend with the concentration of added ethanol. Hence, the results shown in Table III for that system are obtained from the unmodified Liptay-Scott analysis. We believe, incidentally, that the absence of a trend in ζ_{ik} (or in K_f with wavelength) for the data from CH_2Cl_2 solution is added support for the validity of our explanation for the system in *n*-heptane, since the contact CT band of I_2 is shifted to shorter wavelengths in CH_2Cl_2 and so changes in it would not be expected as ethanol is added.

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(21) W. E. Bennett, unpublished program.

Table II. Results for K_f and ϵ_{io} for the Ethanol–I_2 Complex in *n*-Heptane Solution, from the Liptay–Scott Analysis of the Data, Using ϵ_{is} Values from the "First Iterative Procedure"[a,b]

Wavelength, mμ	ϵ_{io}						
250	6,670	6,530	6,430	6,620	6,380	6,710	6,860
245	9,130	8,910	8,750	8,940	8,610	8,720	9,080
240	11,470	11,240	10,960	11,150	10,660	11,110	11,170
235	13,960	12,650	12,290	12,450	11,980	12,270	12,010
230	13,260	13,010	12,700	12,860	12,370	12,660	12,460
225	12,350	12,200	11,950	12,060	11,680	11,850	11,830
K_f, l./mol	2.32 ± 0.16	1.74 ± 0.11	1.26 ± 0.13	0.94 ± 0.05	0.92 ± 0.06	0.72 ± 0.04	0.54 ± 0.03
Temp, °C	−10	0	10	20	24	30	40

[a] These data are selected from the other possible sets of results listed by Julien[16] as being most probably correct. [b] See column II of Table I, and see text.

Table III. Results for K_f and ϵ_{io} for the Ethanol–I_2 Complex in Methylene Chloride Solution from the Liptay–Scott Analyses (See Text)

Wavelength, mμ	ϵ_{io}					
250	7,070	7,010	7,080	7,210	7,350	7,510
245	8,990	8,900	8,990	9,120	9,380	9,650
240	10,610	10,540	10,650	10,800	11,110	11,390
235	11,570	11,500	11,590	11,700	12,010	12,310
230	11,520	11,410	11,370	11,390	11,560	11,750
225	10,730	10,540	10,220	9,920	9,830	9,620
K_f, l./mol	0.56 ± 0.03	0.43 ± 0.02	0.33 ± 0.02	0.26 ± 0.02	0.23 ± 0.02	0.20 ± 0.03
Temp, °C	−10	0	10	20	24	30

We note from Tables II and III that ϵ_{ic} is relatively independent of temperature, as expected. The differences shown there at the different temperatures are believed to be a measure of our experimental scatter. We note, furthermore, that the molar absorptivity of the CT band of the complex is relatively independent of solvent, as expected. However, we note that the formation constant for the complex does change by about a factor of 2 as the solvent changes. Such solvent effects on stability have been recognized previously.[22]

As a test of the consistency of our data, we have analyzed them by the Liptay–Scott procedure expressing the concentrations *both* in molarities and in mole fraction units. Thus, we have obtained from our experimental data both K_x and $(\epsilon_c)_x$ (from mole fraction units) and K_c and $(\epsilon_c)_c$ (from molarities). The relationship between these quantities has been given by Andrews and Keefer[23]

$$K_c = K_x\bar{V}_s + (\bar{V}_s - \bar{V}_D) \qquad (1)$$

and

$$(\epsilon_c)_x/(\epsilon_c)_c = 1 + (\bar{V}_s - \bar{V}_D)/K_x\bar{V}_s \qquad (2)$$

Here $\bar{V}_i$ is the molar volume of solvent (s) or of donor (D); x represents mole fraction units and c molarities. The comparison between the values from experiment with those calculated from eq 1 and 2 is shown in Table IV. Although such agreement is to be expected, we believe that it does measure to some extent the consistency of our experimental procedure.

In order to visualize better the molar absorptivity results listed in Tables II and III for the CT band of the ethanol–I_2 complex, we have plotted them as a function of wavelength in Figure 4. We see a slight blue shift of the CT band on changing solvents from methylene chloride to *n*-heptane, consistent with the solvent effect expected on changing from the less polarizable solvent, *n*-heptane (with refractive index $n = 1.39$) to the slightly more polarizable CH_2Cl_2 ($n = 1.42$).[24] However, the observed solvent shift may possibly be due to stabilization of the vertical dative state by solvation in the more polar solvent, CH_2Cl_2.[25]

Table IV. Comparison between $(\epsilon_c)_x$ and $(\epsilon_c)_c$ and between K_x and K_c for the Ethanol–I_2 System in *n*-Heptane and Methylene Chloride at 20.0°[a]

	n-Heptane	Methylene chloride
K_x	5.97 ± 0.34	3.65 ± 0.33
K_c(calcd),[b] l./mol	0.96	0.24
K_c(obsd), l./mol	0.96 ± 0.05	0.26 ± 0.02
$\frac{(\epsilon_c)_x}{(\epsilon_c)_c}$(calcd)[b]	1.101	1.022
$\frac{(\epsilon_c)_x}{(\epsilon_c)_c}$(obsd)[c]	1.071 ± 0.050	1.022 ± 0.050

[a] The molar volumes ($\bar{V}$(*n*-heptane) = 0.1465 l./mole, $\bar{V}$ (ethanol) = 0.0584 l./mol and $\bar{V}$ (methylene chloride) = 0.0635 l./mol) were taken from Timmermans, ref 15. [b] Calculated on the basis of eq 1 and 2. [c] Averaged over all the wavelengths listed in Tables III and IV.

We have also plotted in Figure 4 the molar absorptivities reported by de Maine.[3] We see that they agree very well with ours up to his apparent "peak" at 243 mμ. We have repeated de Maine's work,[3] and we found that his solvent (CCl_4) in the reference cell becomes totally absorbing at this wavelength. With our

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[22] For example, see R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Amer. Chem. Soc.*, **88**, 2717 (1966).

[23] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

[24] N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1958).

[25] See, for example, R. S. Mulliken and W. B. Person, "Molecular Complexes: A Lecture and Reprint Volume," John Wiley & Sons, Inc., New York, N. Y., 1969.

Table V. Thermodynamic and Spectral Properties of the Ethanol–I_2 System

Solvent	Standard state	K_f, 298 °K	$-\Delta F_{298}°$, kcal/mol	$-\Delta H_f°$, kcal/mol	$-\Delta S_f°$, eu	λ_{max} mμ	ϵ_{max}	$\Delta\nu_{1/2}$, cm^{-1}	f	D, D	Ref
n-Heptane	Unit molarity	K_c = 0.92 ±0.05	−0.09 ±0.05	4.56 ±0.03	15.6 ±0.7	230	12,660	6800	0.37	4.26	*a*
n-Heptane	Unit mole fraction	K_x = 5.81 ±0.4	0.98 ±0.18	5.24 ±0.18	14.3 ±0.7	230	13,600	6860			*a*
CH_2Cl_2	Unit molarity	K_c = 0.23 ±0.02	−0.89 ±0.14	4.09 ±0.14	16.7 ±0.7	234	12,100	6500	0.34	4.11	*a*
CH_2Cl_2	Unit mole fraction	K_x = 3.1 ±0.4	0.66 ±0.07	4.65 ±0.16	13.4 ±1.2	234	12,000	6570			*a*
n-Hexane	Unit mole fraction	K_x = 6.99	1.15	3.53[d]	8.03[d]						*b*
CCl_4	Unit mole fraction	K_x = 4.00	0.83	2.10	4.09	243	10,802				*c*

[a] This work. [b] From Amako.[4] [c] From de Maine.[3] [d] We believe these values are incorrect, and should be considered to be in agreement with ours with the experimental error. See text.

Beckman DK-2A, the apparent absorbance decreases abruptly when that happens, causing a resulting apparent "maximum" by this instrumental artifact. We conclude that this same effect occurred unrecognized in de Maine's work.

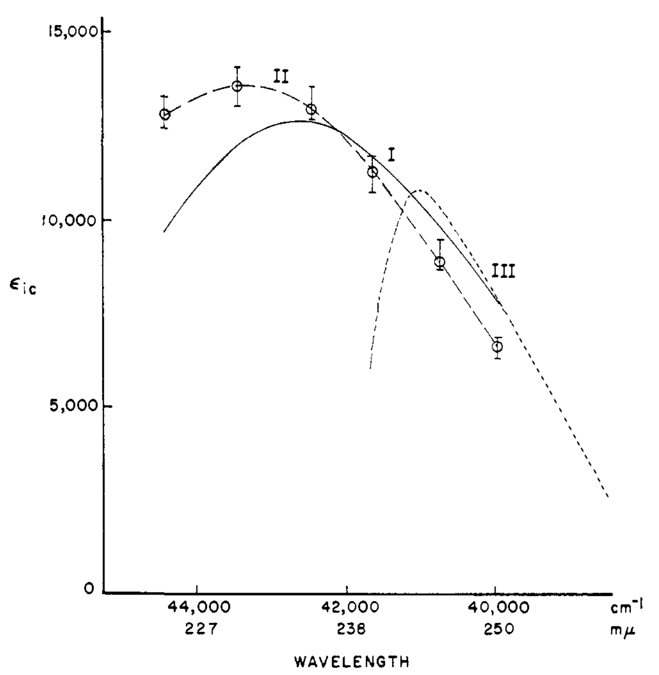

Figure 4. The charge-transfer absorption band of the ethanol–I_2 complex. Curve I is for the solution in methylene chloride; curve II is for the solution in *n*-heptane, using data from Table III; and curve III is replotted from de Maine, ref 3.

We have recalculated f, the oscillator strength, and D, the transition dipole for the CT band, using our data, according to the following approximate equations[25]

$$f = 4.32 \times 10^{-9}[\epsilon_{max}\Delta\nu_{1/2}] \quad (3)$$

and

$$D = 0.0958[\epsilon_{max}\Delta\nu_{1/2}/\nu_{max}] \quad (4)$$

We were not able to measure the high-frequency side of the CT band due to interference from overlapping absorption by the ethanol; hence, we have assumed that $\Delta\nu_{1/2}$ is just twice the difference in cm^{-1} from ν_{max} to the frequency of the half-intensity point on the long-wavelength side of the band. As discussed elsewhere,[5,25] this estimate for $\Delta\nu_{1/2}$ (and thus of the values of f and D) is probably too low. These estimates for the spectral properties of the CT band for the ethanol–I_2 complex in the two solvents are summarized, together with the thermodynamic properties, in Table V.

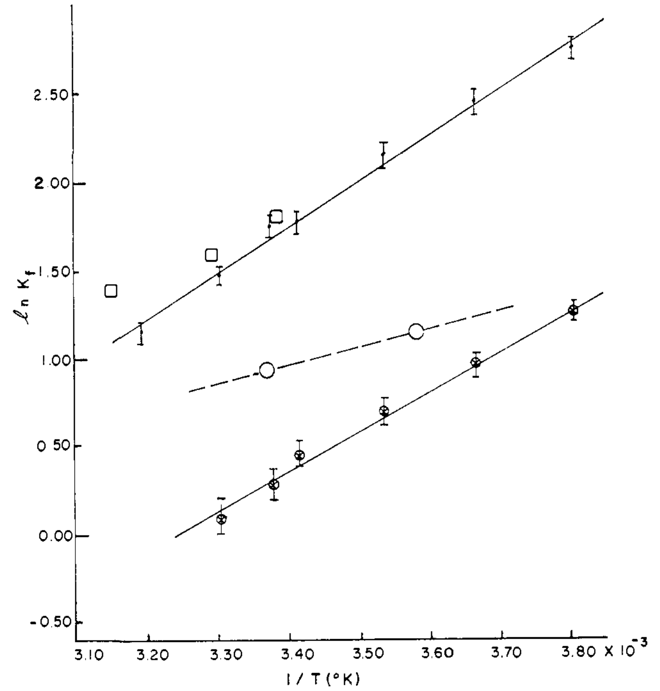

Figure 5. van't Hoff plots for the ethanol–I_2 complex. Here the symbol □ refers to points from a *n*-hexane solution (Amako, ref 4); ⫯ refers to our points in *n*-heptane solution with experimental uncertainty indicated; ○ refers to points in CCl_4 solution (de Maine, ref 3); and ⊗ refers to our points in CH_2Cl_2 solution. Here we have plotted $\ln K = \ln [K_x(\text{solvent}) (\bar{V}_s/\bar{V}_{n\text{-hep}})]$ as the ordinate where K_x (solvent) is the measured value of K_x in a solvent; $\bar{V}_s$ is the molar volume of that solvent; and $\bar{V}_{n\text{-hep}}$ is the molar volume of *n*-heptane. This factor of the molar volumes is an attempt to correct K_x values to a common basis for comparison. The value of $-\Delta H_f$ is obtained by multiplying the slopes of the lines on this graph by R.

The values of K_f (in mole fraction units) at the different temperatures (*cf.* Tables II and III) are plotted in Figure 5 as $\ln K_f$ *vs.* $1/T$, and $\Delta H°$ evaluated from the slope.[25] Figure 5 also compares our data with those from de Maine[3] and Amako;[4] de Maine's data (from CCl_4 solution) do not agree either with our measurements in the nonpolar solvent, *n*-heptane, or with our measurements in the polar solvent, CH_2Cl_2. On the other hand, Amako's result[4] (in *n*-hexane) agrees quite well with ours in *n*-heptane. We believe that the larger temperature range covered in our work makes our resulting $\Delta H_f°$ somewhat more reliable than Amako's lower value,[4] and that the value of $\Delta H_f°$ is the same, within experimental error, in both *n*-heptane and *n*-hexane solvents.

Conclusion

Although the properties of the ethanol–I_2 complex are of basic importance for the understanding of complexes between alcohols (or other oxygen-containing donors) and halogens, we find on repetition of the earlier experiments[3,4] that the complex is considerably more stable (as measured by K_f, and especially by $-\Delta H_f°$) than indicated by the earlier work. We find no definite evidence indicating that competition between CT-complex formation between ethanol and I_2 and hydrogen-bond complex formation between two ethanol molecules affects these results. We do find some trends in the values of K_f (or in the ζ matrix of the Liptay method) using the simple Liptay–Scott analysis of the data in *n*-heptane. These trends can be eliminated by making reasonable assumptions concerning the change in ϵ_{13}, the molar absorptivity of free I_2, as the nature of the solvent changes due to the addition of the ethanol. However, the values of the molar absorptivity of the CT band of the complex, and the values of $\Delta H_f°$, do not depend very strongly upon how the corrections are made for these trends.

We have found, furthermore, that the frequency of maximum absorption of the CT band in a nonpolar solvent is higher (by about 3000 cm^{-1}, or 0.3 eV) than that reported earlier, and its intensity is much greater than that reported earlier (*f* and *D* are found to be about twice as large as those estimated earlier).

We find this evidence for much stronger interaction than was believed earlier to be more consistent with the large "blue shift" of the visible band and with other indications of stronger interaction. In general we believe our results are consistent with other ideas[25] about complexes and fit better with these than did the earlier indications[3,4] of only weak interaction.

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Electron Spin Resonance Studies of Steric Effects in Tetrakis(alkylthio)ethylene Cation Radicals[1a,b]

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Abstract: The temperature dependence of the esr spectra of cation radicals of the type $(RS)_2C^+{=}C(SR)_2$, I$^+$, has been investigated (R = methyl, ethyl, isopropyl, and phenyl). The radicals were produced by oxidation of the parent ethylenes with aluminum chloride in methylene chloride. The esr room-temperature spectrum of the methyl derivative, Ia$^+$, was attributed to interaction with 12 equivalent protons: $|a_H| = 2.70$ G. The spectrum observed at $-90°$ was analyzed in terms of interaction with two sets of six equivalent protons: $|a_H| = 0.93$ G, $|a_H| = 4.22$ G. At intermediate temperatures, the spectrum exhibited an alternating line-width effect. These results are in accord with a temperature-dependent intramolecular process which can be formally described as an interconversion of two identical conformers of Ia$^+$ (see eq A). The line-width variation was analyzed using the theory of Freed and Fraenkel to obtain *k*, the rate constant for the interconversion process, $E_a = (8.6 \pm 0.6)$ kcal mole^{-1}. A similar temperature dependence of the methylene proton coupling constant in the ethyl derivative, Ib$^+$, was observed and similarly interpreted. In addition, restricted rotation about two of the ethyl carbon–sulfur bonds is postulated to account for the low-temperature spectrum of Ib$^+$. It is suggested that the alkyl proton coupling constants in this type radical can be related to the sulfur spin density, ρ_S, by the following expression: $a_H = Q^H{}_{S-C-H}\rho_S\langle\cos^2\theta\rangle$. The ^{13}C coupling constant was observed in the esr spectrum of Ia$^+$ enriched in ^{13}C at the ethylenic position: at $+30°$, $a_C = +3.72$ G; at $-90°$, $a_C = +3.87$ G.

Few cation radicals of thioethers have been observed.[2,3] Zweig, *et al.*, have investigated the cation radicals of 1,4-bis(methylthio)benzene[2] and 1,2,4,5-tetrakis(methylthio)benzene and have suggested that the coupling constant of the methyl protons β to the sulfur is related to ρ_s by the expression $a_H = Q^H{}_{SCH_3}\rho_s$, $Q^H{}_{SCH_3} = 21$ G/e. In a reexamination of Zweig's work, Forbes and Sullivan concluded that the

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[1] (a) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) Abstracted from the Ph.D. Thesis of M. V. M., Cornell University, 1968. (c) Deceased, Dec 4, 1967. (d) Du Pont Teaching Fellow, 1966–1967, Cornell University Fellow, 1967–1968. Address correspondence to author at the Mellon Institute, 4400 Fifth Ave., Pittsburgh, Pa. 15213.

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[3] A. Zweig, W. G. Hodgson, W. H. Jura, and D. L. Maricle, *Tetrahedron Letters*, 1821 (1963).