Physical and Inorganic Chemistry

Vapor-Phase Charge-Transfer Complexes.   IV.   Aliphatic Hydrocarbon–Iodine Contact Charge Transfer

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Abstract: Mixtures of iodine with He, N_2, air, n-pentane, n-hexane, n-heptane, cyclohexane, and methylcyclohexane were studied in the ultraviolet region in the vapor phase. The hydrocarbons generally produce an enhanced absorption with a broad tail, similar to that observed in solution. The tail is attributed to contact charge transfer (CCT). The enhancement in the steeper portion of the band is attributed to a pressure effect (shift and broadening of the V ← N band of I_2), because all gases added to iodine enhanced the absorption. The latter effect makes uncertain the characterization of the pure CCT band. The variation of absorbance with the concentration of donor and acceptor and with temperature is in accord with a model based on *very* weak complex formation or on collisions. The latter model is used to establish limiting values of K and ϵ for cyclohexane–iodine.

It seems well established that systems of electron donors and acceptors which do not exhibit a measurable extent of complexation can still give rise to charge-transfer (CT) absorption. One of the systems studied extensively, by Evans[1] and others,[2-7] is that of O_2 as the acceptor with various hydrocarbon donors (saturated, unsaturated, and containing heteroatoms) in which new, broad bands appear in the ultraviolet region. Dependence of the absorbance on the O_2 pressure[1c,2,4,6] and on the donor concentration[1g,3,5,6] led to the conclusion that the interaction is 1:1. Analysis of the data by the Benesi-Hildebrand[8] (BH) method indicates that the equilibrium constants must be quite small, i.e., $K_c \simeq 0$, and this is consistent with the lack of interaction observed using nonspectrophotometric

methods, e.g., the magnetic susceptibility of O_2[1b] and the solubility of aromatic hydrocarbons in compressed O_2.[7,9] Further, no temperature dependence of absorbance is observed, i.e., $\Delta H \simeq 0$, for such systems as N,N-dimethylaniline-O_2 and triethylamine-O_2.[3] These are the typical characteristics attributed to collisional or contact charge-transfer (CCT) complexes.[10,11]

Another well-studied acceptor is I_2 which, unlike O_2, is known to form CT complexes of measurable stability with π- and n-type donors.[12] But CCT absorption is observed for the system aliphatic hydrocarbons-I_2, and attempts have been made to characterize the CCT bands.[13-19] The thermodynamic properties are reported to be in the very weak[18] or contact[19] category.

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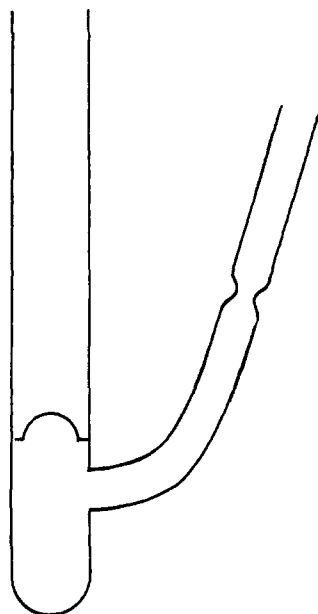(17) D. F. Evans, J. Chem. Soc., 4229 (1957).

Figure 1. Break-seal tube.

Other acceptors giving CCT spectra with hydrocarbons are $NO^{1d,g,4}$ (which is similar to O_2 in behavior), $C(NO_2)_4$,[17] and Br_2.[20] More recently, spectra and thermodynamic properties (low K_c and low ΔH) have been reported for WF_6, MoF_6, and IF_7 with aliphatic hydrocarbons as donors.[21]

Most of the studies to date on CCT systems have involved work in solution. There has been one report of interaction in an adsorbed phase, that of O_2 with organic molecules.[22] Relatively little has been done on CCT in the gas phase, and generally it is O_2 that has been involved.[1d,f,5,7] Studies with halogen vapors usually have been concerned with the effects on their visible spectra on adding "inert" gases,[20,23,24] including hydrocarbons.[25] There seems to have been no systematic vapor-phase study of CCT with the halogens.[26] This paper reports the results of such a study on aliphatic hydrocarbons-I_2.

Experimental Section

The spectrophotometric measurements were made using a Cary 14 spectrophotometer. The absorption cells were contained within an oven similar in construction to the one used by Kroll.[27] The oven could be operated over a range of 50–130° and the temperature controlled with a thermoregulator. Five iron–constantan thermocouples in contact with and spaced over the length of the absorption cell showed that the temperature along a cell of 1-m length was uniform to within ±0.5° at 70° and ±1.0° at 130°. A particular setting of the thermoregulator reproduced the temperature to better than ±0.5° on successive days. In this study, fused quartz cells, 75.0 cm long, from Amersil Inc., were used. The cell length was determined using a Wild cathetometer.

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(26) One such study is in progress in the laboratory of Professor C. N. R. Rao; private communication.
(27) M. Kroll, J. Amer. Chem. Soc., 90, 1097 (1968).

For the spectral determinations, the oven was placed between the cell compartment of the instrument and the photomultiplier. The diverging beams from the monochromator were collimated by a pair of fused-quartz lenses placed within the oven in front of the absorption cells. After passing through the cells, the beams were focused by another set of lenses on to the photomultiplier. With this arrangement, it was necessary to ascertain that reliable optical readings were obtained. The spectrum of gaseous iodine was used for this purpose. The measured extinction coefficients between 350 and 220 mμ over the temperature range 60–120° were in excellent agreement with the values obtained previously in this and other laboratories. It was also observed that the absorbance of a liquid sample placed in the ordinary cell compartment of the instrument was the same with or without the oven. The presence of the oven increased the slit width to some extent, but a value of 0.08 mm at 230 mμ and 0.20–0.25 mm at 210 mμ was considered satisfactory.

The volume of the absorption cell ($\sim$1.3 l.) made it feasible to determine the concentration of the iodine by direct weighing, employing the break-seal technique described by Kroll.[27] The break-seal shown in Figure 1 was found to be more convenient than that commercially available. It was easier to evacuate and seal the sample in the tube. A critical feature was blowing the break wall quite thin. After breaking, the larger opening allowed for more rapid transfer of the reagent into the main part of the absorption cell. In the case of iodine, this was done by gentle heating, or by washing it out with the hydrocarbon liquid. For the experiments with nitrogen and helium, the iodine break-seal tube was first sealed onto the cell. High-purity N_2 or He was then flushed through the cell to remove the air, and the cell was then quickly sealed off at atmospheric pressure. For this case, rather strong heating of the iodine break-seal tube was necessary to bring the iodine into the main body of the absorption cell. In the experiments with air at reduced pressure, the cell was attached to a vacuum line, the system evacuated, air admitted to a known pressure, and the cell then sealed off from the line.

The concentration of the iodine varied between 3.5 × 10^{-5} and 1.4 × 10^{-4} M, corresponding to weights between 11 and 46 mg. In addition, the iodine concentration was checked spectrophotometrically using an extinction coefficient for iodine vapor at 100° of 350 ± 2 l. mol^{-1} cm^{-1} at 480 mμ.[28] The visible band of iodine is temperature dependent,[29] but it is not sensitive to small temperature changes in the vicinity of 480 mμ, nor is it sensitive to the presence of the gases added.[24,28] The two methods of determining iodine concentration, spectrophotometric and weighing, agreed to within 1%. The hydrocarbons were pumped on to remove air before sealing and weighing. Their concentrations varied between 1.5 × 10^{-2} and 5.4 × 10^{-2} M, corresponding to weights between 1 and 7 g.

The details of handling the samples, determining the volume of the absorption cell, and recording the spectra have been described.[27] After temperature equilibration, the spectra of the gaseous mixtures did not change with time. In the temperature-dependence studies, the initial temperature was always rerun at the end of the experiment. No significant change in absorbance was found, demonstrating the absence of irreversible chemical reactions and also that the absorbance base line did not change as a result of varying the temperature.

The source and purification of the iodine has been given before.[30] The hydrocarbons were all Matheson Coleman and Bell spectrograde quality. The low absorbance at wavelengths >210 mμ and the absence of irreversible reactions with iodine suggested use without further purification.

Results

Vapor-phase spectra were taken of iodine alone and in the presence of (1) the gases He, N_2, and air, and (2) the vapors of the saturated hydrocarbons n-pentane, n-hexane, n-heptane, cyclohexane, and methylcyclohexane. Data at 110° are shown in Figure 2. An amount of iodine was weighed out in the break-seal tube to give as close as possible the concentration of

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(29) P. Sulzer and K. Wieland, Helv. Phys. Acta, 25, 653 (1952).
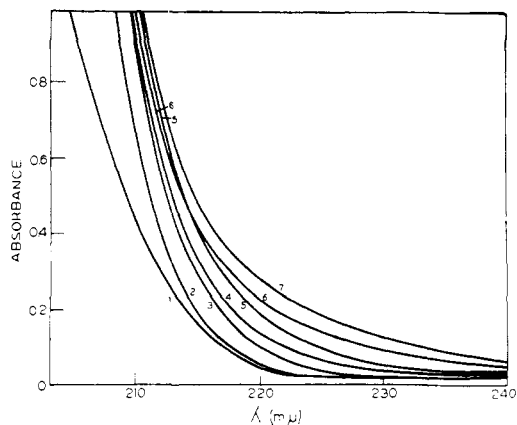(30) M. Brandon, M. Tamres, and S. Searles, J. Amer. Chem. Soc., 82, 2129 (1960).

Figure 2. Vapor-phase ultraviolet spectra of I_2, of He–I_2, and of aliphatic hydrocarbon–I_2 mixtures at 110° in a 75.0-cm cell: $I_2 = 6.50 \times 10^{-5}$ M and (1) no added gas, (2) He $= 3.93 \times 10^{-2}$ M, (3) n-pentane $= 3.50 \times 10^{-2}$ M, (4) n-hexane $= 3.50 \times 10^{-2}$ M, (5) n-heptane $= 3.50 \times 10^{-2}$ M, (6) cyclohexane $= 3.50 \times 10^{-2}$ M, (7) methylcyclohexane $= 3.50 \times 10^{-2}$ M. Curves 3–7 corrected for small hydrocarbon absorption.

Figure 4. Vapor-phase ultraviolet spectra of methylcyclohexane–I_2 at 110° in a 75.0-cm cell: $I_2 = 6.50 \times 10^{-5}$ M and (1) methylcyclohexane (MCH) $= 1.174 \times 10^{-2}$ M, (2) MCH $= 2.550 \times 10^{-2}$ M, (3) MCH $= 3.534 \times 10^{-2}$ M, (4) no added gas, (5) He $= 3.93 \times 10^{-2}$ M. Curves 1–3 corrected for small MCH absorption.
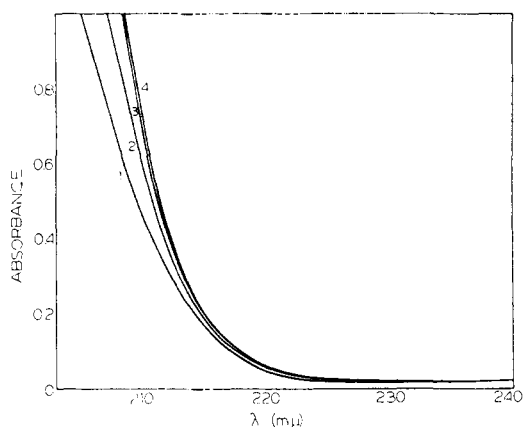

Figure 3. Vapor-phase ultraviolet spectra of air–I_2 mixtures at 110° in a 75.0-cm cell: $I_2 = 6.50 \times 10^{-5}$ M and (1) no added gas, (2) air $= 0.084$ atm, (3) air $= 0.88$ atm, (4) air $= 1.25$ atm.

Figure 5. Vapor-phase ultraviolet spectra of methylcyclohexane–I_2 at 110° in a 75.0-cm cell: (7) methylcyclohexane (MCH) $= 3.50 \times 10^{-2}$ M, (5) $I_2 = 13.97 \times 10^{-5}$ M, (6) 5 + 7, (3) $I_2 = 6.98 \times 10^{-5}$ M, (4) 3 + 7, (1) $I_2 = 3.50 \times 10^{-5}$ M, (2) 1 + 7. Curves 2, 4, 6 corrected for small MCH absorption (curve 7).

6.50×10^{-5} M. The weight corresponds to only 21.4 mg and could be reproduced from one run to another to within 5%. In order to compare the effects of added gases, the absorption curves of all the iodine samples were adjusted to the same iodine concentration of 6.50×10^{-5} M by assuming a linear dependence on absorbance with iodine concentration. The basis for this will be mentioned in the discussion of Figure 5. The hydrocarbon samples in Figure 2 were measured out in the break-seal tubes to give to within 1% a concentration of 3.50×10^{-2} M, which corresponds to a pressure of 1.10 atm at 110°. For all the hydrocarbons (curves 3 to 7, Figure 2), there is an enhanced absorbance in the ultraviolet region similar to that which has been observed in solution.[13–19] The curves have been corrected for the contribution to the absorbance of the hydrocarbon alone, which is small.

It is apparent that even helium produces an enhancement in absorbance of the iodine vapor, but not as great as the hydrocarbons, even though helium is at the slightly higher pressure of 1.25 atm at 110°. A similar curve was observed for the same pressure of nitrogen or air, with the absorbance being very slightly greater. The absorbance is dependent on the pressure of added
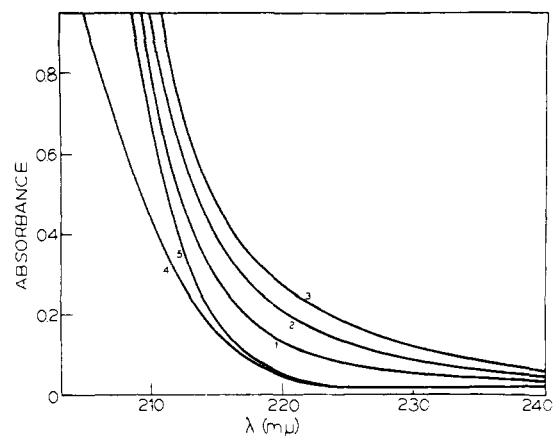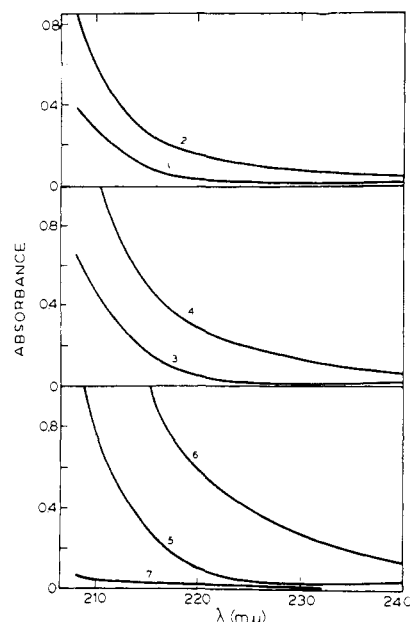
gas, as may be seen in Figure 3, where there is progressively smaller absorbance with decreasing pressure of air.

The effects of varying the concentrations of the donor and the acceptor are shown in Figures 4 and 5 for the system methylcyclohexane–I_2. In Figure 4, the iodine concentration is constant, and the methylcyclohexane concentration is progressively increased in the sequence 0, 1.174×10^{-2}, 2.550×10^{-2}, 3.534×10^{-2} mol l.$^{-1}$ (curves 4, 1, 2, 3, respectively). The absorbance curves are corrected for the small contribution from the methylcyclohexane absorption.

In Figure 5, the methylcyclohexane concentration is held constant at 3.50×10^{-2} mol l.$^{-1}$. The absorbance at this concentration in the absence of iodine is shown as curve 7. With increasing iodine concentration of
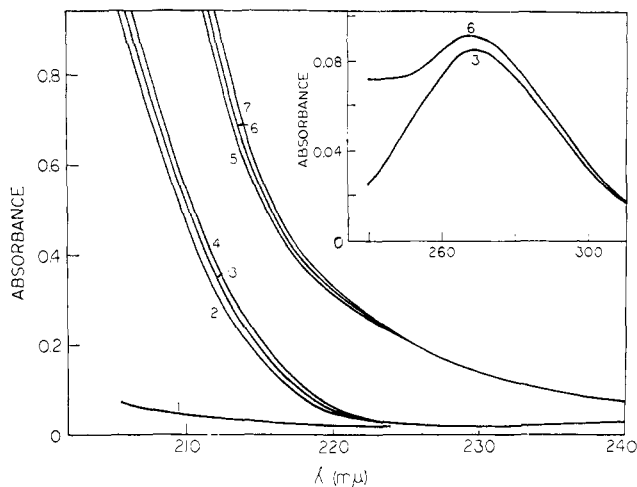
Figure 6. Temperature dependence of I_2 and of methylcyclohexane-I_2 in a 75.0-cm cell: $I_2 = 6.50 \times 10^{-5}\,M$, methylcyclohexane (MCH) = $3.50 \times 10^{-2}\,M$, (1) MCH at 110–130°, (2) I_2 at 110°, (3) I_2 at 120°, (4) I_2 at 130°, (5) 1 + 2, (6) 1 + 3, (7) 1 + 4.

3.50×10^{-5}, 6.98×10^{-5}, and 13.97×10^{-5} mol l.$^{-1}$ (curves 1, 3, and 5, respectively) there is a corresponding increase in absorbance (curves 2, 4, and 6, respectively, which has been corrected for the small absorbance of free methylcyclohexane, curve 7).

In both figures, it is clear that there is an increase in absorbance with an increase in concentration of either the donor or the acceptor. Similar behavior, but smaller in magnitude, was observed for iodine with cyclohexane and with n-pentane.

The temperature dependence of the absorbance for methylcyclohexane-I_2 is shown in Figure 6. For the concentrations used, the absorbance of methylcyclohexane is temperature independent, while the iodine begins to show a temperature broadening below 226 mμ. The bands above 240 mμ are continued in the insert (with expanded ordinate and condensed abscissa scales) showing the I_2 absorption band at 268 mμ.[31,32] The temperature dependence of absorbance for the mixture matches that of the temperature broadening of the iodine alone, within experimental limits. Therefore, no apparent temperature dependence of the CCT is observed. This was observed also for n-pentane-I_2 from 60 to 110° and for cyclohexane-I_2 from 80 to 120°.[33]

Discussion

Spectral Characteristics. Many features of the vapor-phase CCT spectra are similar to those observed in solution. There is an extended tail in the spectra of most of the hydrocarbon-I_2 mixtures, and the absorbance rises rapidly at lower wavelengths down to 210 mμ without going through a maximum (Figure 2). At wavelengths longer than $\sim$220 mμ the enhancement in absorption is in the order n-pentane < n-hexane < n-heptane < cyclohexane < methylcyclohexane, which follows the trend of decreasing ionization potential.[34] This sequence is not maintained at low wavelengths;

(31) M. Tamres, W. K. Duerksen, and J. M. Goodenow, *J. Phys. Chem.*, 72, 966 (1968).
(32) A. A. Passchier and N. W. Gregory, *ibid.*, 72, 2697 (1968).
(33) In preliminary studies with M. Kroll, similar observations were made for I_2 mixtures with n-heptane and n-perfluoroheptane.
(34) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc., Radiat. Transfer*, 2, 369 (1962).
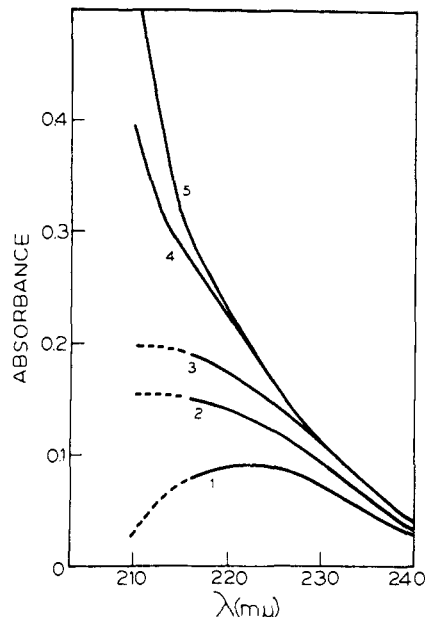

Figure 7. Vapor-phase CCT of methylcyclohexane-I_2 at 110° in a 75.0-cm cell: $I_2 = 6.50 \times 10^{-5}\,M$ and methylcyclohexane (MCH) = $3.50 \times 10^{-2}\,M$. These are absorbance difference curves between (5) MCH-I_2 and I_2, (4) MCH-I_2 and He-I_2, (3) MCH-I_2 and n-pentane-I_2, (2) MCH-I_2 and n-hexane-I_2, (1) MCH-I_2 and n-heptane-I_2.

some of the curves apparently cross, e.g., n-heptane and cyclohexane at $\sim$215 mμ. A similar result for the same system in solution can be found in the data of Julien and Person.[19] It is possible that other curves in Figure 2 cross at still shorter wavelengths. However, in this region, the steep rise in absorbance and the accompanying opening of the slit makes quantitative comparison of absorbance less reliable.

The usual procedure for characterizing a CT band has been to correct the total absorbance of an electron donor–acceptor mixture for the contributions from the free donor and free acceptor. For the case of CCT spectra of aliphatic hydrocarbons-I_2 *in solution*, the hydrocarbons absorb very little down to 200 mμ (provided O_2 has been removed[1]), and the main correction made has been for the contribution of the same concentration of I_2 in some reference solvent. The choice of a reference has been based on convenience and on relative "inertness"; *i.e.*, a solvent in which the iodine is sufficiently soluble, is easy to handle, and its I_2 solution has a smaller absorbance in the uv relative to the other hydrocarbon-I_2 systems whose interaction is being studied. n-Heptane[15,18,19] often has been selected. It has been suggested that n-perfluoroheptane, in spite of poorer solvating power, might be a better reference solvent because the spectrum of iodine in n-perfluoroheptane is most similar to that of iodine vapor itself.[16]

If the same view were to be applied to vapor-phase studies, it would suggest that CCT bands could be characterized by subtracting the absorbance of free gaseous donor and free gaseous acceptor from the absorbance of the mixture. When this is done for methylcyclohexane-I_2 and for cyclohexane-I_2 (for which there are more solution data[15,18,19]) using the data in Figure 2, the result is curve 5 in Figure 7 and curve 4 in Figure 8, respectively. It is evident that *no* band maximum is obtained in either case, the absorbance rising sharply

at ~215 mμ. However, this procedure to obtain CCT bands is questionable since even He enhances the iodine absorbance below ~222 mμ, and this certainly cannot be attributed to CCT because of the high ionization potential of He. Further, N_2 (or air) has very nearly the same effect as He in spite of a much lower ionization potential. Thus the change in I_2 absorption in the presence of He, N_2, or air must be attributed to a pressure effect. The change in absorbance for different pressures of air (Figure 3) shows that the effect is dependent on the pressure of the added gas. Qualitatively, a low pressure of air seems to have a disproportionately large effect; but quantitative comparison of the absorbance differences among the curves in Figure 3 is difficult because of the steep slopes and opening up of the slit, as mentioned previously.

At the concentrations used for the iodine mixtures in Figure 2, the absorbances of I_2 alone, He–I_2, and n-pentane–I_2 are essentially the same at wavelengths longer than ~227 mμ. There is, however, a residual absorbance for each of the other hydrocarbon–I_2 pairs which appears as a broad tail in the spectrum. In this region, a plot of absorbance vs. the concentration of donor for a fixed I_2 concentration is linear and extrapolates at zero donor concentration to the absorbance of I_2 vapor alone, within experimental limits. This is seen in the data for methylcyclohexane–I_2 in Figure 4. Similar results, although with smaller absorbance changes, were obtained with cyclohexane–I_2 and, at lower wavelength, even with n-pentane–I_2.

The same plot made at shorter wavelengths still appears essentially linear, if allowance is made for the larger error in taking absorbance differences in steeper portions of the curves. Extrapolation to zero donor concentration comes much closer to the absorbance corresponding to the He–I_2 curve than it does to that for I_2 vapor (curves 5 and 4, respectively, in Figure 4). Actually, the He–I_2 absorbance is expected to be dependent upon the pressure of the He gas, just as is observed for different pressures of air (Figure 3). But it should be noted that even with a ~15-fold variation in the pressure of air (from 0.084 to 1.25 atm) the difference in absorbance is small at a wavelength as low as 214 mμ. The donor pressure in methylcyclohexane–I_2 (Figure 4) is varied by only a factor of 3.

Subtracting the He–I_2 absorbance from the methylcyclohexane–I_2 and cyclohexane–I_2 curves in Figure 2 gives the bands shown as curve 4 in Figure 7 and curve 3 in Figure 8, respectively. Again, no well-defined maximum is observed, although in the former case the shape of the curve suggests the presence of an inflection point.

But this procedure to characterize CCT bands also is subject to question because of the implication that different gases have comparable pressure effects on the spectrum of I_2. Although the difference apparently is small between He and N_2, this may not be the case with other gases. It is known that spectral properties are altered when gases are dissolved in a liquid or when foreign gases are added. In general, shifts, broadening, and asymmetry in the spectra are produced. These effects have been reported, for example, on the absorption lines of cesium vapor upon the addition of argon[35]
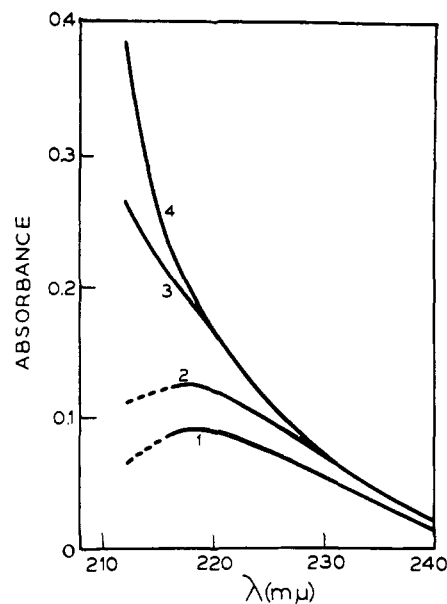
(35) S. Y. Ch'en and R. O. Garrett, Phys. Rev., 144, 59 (1966).

Figure 8. Vapor-phase CCT of cyclohexane–I_2 at 110° in a 75.0-cm cell: $I_2 = 6.50 \times 10^{-5}$ M and cyclohexane (CH) $= 3.50 \times 10^{-2}$ M. These are absorbance difference curves between (4) CH–I_2 and I_2, (3) CH–I_2 and He–I_2, (2) CH–I_2 and n-pentane–I_2, (1) CH–I_2 and n-hexane–I_2.

and helium,[36] with the effects of the two gases not being the same.

In the case of I_2 vapor, greater attention has been given to the effect of gases on the visible band.[20,23,24] The study by Luck[23] shows that the optical diameter is dependent on the nature of the foreign molecule–I_2 gas pair.

Unfortunately, in the present study, it was not possible to follow the spectral curves to much beyond just the onset of the intense V $\leftarrow$ N band of I_2. Consequently, little can be said about the effect of added gases on the general shape of this band other than there is a pressure effect which probably leads to broadening and a shift, and which may depend to some extent on the nature of the foreign gas. The data of Julien and Person[19] do show that the V $\leftarrow$ N band of I_2 at 182 mμ is broadened and red shifted in hydrocarbon solution.

If indeed the pressure effect as well as the CCT is dependent on the nature of the added gas, then separation of the total absorbance of the mixture into a purely CCT component is subject to some uncertainty. It is apparent in Figures 7 and 8 that the shape and height of the CCT bands are very much dependent on the choice of the reference system. CCT maxima are indicated for methylcyclohexane–I_2 and cyclohexane–I_2 when the reference system is another hydrocarbon–I_2. (The dashed sections of the curves are less well established as a consequence of taking small differences between large absorbance values.) It is of interest that this is precisely the condition used in reporting CCT maxima in solution.[14,15,18,19]

The n-pentane–I_2 CCT contribution is small relative to the other hydrocarbon–I_2 pairs, and if its CCT tail is as extended as it is for the other systems, then n-pentane would seem to be a preferable choice as a reference for the hydrocarbons. With this choice, the maxima of the CCT bands of I_2 with methylcyclohexane and with

(36) R. O. Garrett and S. Y. Ch'en, ibid., 144, 66 (1966).

cyclohexane lie in the region of $\sim$215 mμ. The band maxima are not fixed precisely, considering the uncertainty in the extrapolation and a possible small CCT contribution from n-pentane-I_2. However, as will be discussed in the last section, a λ_{max} of $\sim$215 mμ is not unreasonable. This position is blue shifted relative to that reported in solution.[15,18,19] Such blue shifts have been observed for very weak complexation, e.g., I_4.[31,32]

There seems to be no obvious reason to favor the selection of n-heptane as a reference system, as has been done in most solution studies involving CCT. Consequently, it would seem advisable to look with some caution at the characterization of such bands reported in the literature.

Thermodynamic Characteristics. There have been several studies to determine the thermodynamic properties of the aliphatic hydrocarbon-I_2 interactions, notably for the system cyclohexane-I_2 in n-heptane. Kortüm and Vogel[37] found no evidence for complexation from solubility data. From a spectrophotometric study, Bhat, Bhaskar, and Rao[18] obtained a rather small value for K ($=0.043$ l. mol^{-1} at 298°) and for ΔH ($= -1.6 \pm 0.5$ kcal mol^{-1}), which are in about the ranges that have been reported for many weak complexes. The authors point out that no clear distinction between contacts and weak complexes can be made. Julien and Person[19] consider the results of Bhat, et al.,[18] to represent upper limits for this system. Their own findings are closer to those expected for the contact pair model.

In the present study, greater emphasis was given to methylcyclohexane-I_2 because this system was reported to give a larger CCT absorption[17-19] than cyclohexane-I_2. It has been discussed that the dependence of absorbance on either the methylcyclohexane or iodine concentration is linear. This means that a BH plot[8,16,18] would go through the origin or that a Scott-type[19] plot would have zero slope. Further, it was shown (Figure 6) that the absorbance is temperature independent. These findings are in accord with the conclusion that $\Delta E \simeq 0$, K is very small, and ϵ is large.

Comparison of the present vapor-phase study with an earlier one of benzene-I_2[38,39] does show that the methylcyclohexane-I_2 interaction definitely is weaker. A possible interpretation of the observations, therefore, is that this system forms a very weak complex which, because of experimental limitations, would be indistinguishable from zero complexation, thereby resulting in $\Delta E \simeq 0$ and $K \simeq 0$.[40]

An equally valid interpretation is based on the contact or collisional model. First, there is the direct relation of absorbance with the concentration of either component, to which the number of collisions is proportional. Second, the temperature independence of absorbance can be accounted for in the following way. Each of the randomly oriented collisions between iodine and hydrocarbon molecules can be considered to form a contact pair when the molecules are within the distance Δd, i.e., the distance within which electron transfer can occur. The concentration of such pairs is equal to the number of collisions per cubic centimeter per second

times the time spent within the average distance $\overline{\Delta d}$. Since the first part is directly proportional and the second part inversely proportional to velocity (or $T^{1/2}$), the concentration of contact pairs is independent of temperature. (Little change in closest approach of the molecules over a limited temperature range is expected.)

Thus, the vapor-phase study cannot distinguish between a contact pair and a very weak complex, although it does eliminate the solvent-environment factor which has been proposed as allowing, in principle, such distinction.[41] In fact, vapor study is less suited than solution study (assuming ideal behavior) to do so. This is because the concentration range in the vapor phase is much lower, which in the absence of special apparatus is necessitated by pressure limitations. Consequently, "complexation" is less favored.

Limiting Values for K and ϵ. There is a vast literature on the spectrophotometric study of weak CT complexes. Here, if the complex is the only absorbing species, the linear form of the spectrophotometric equation used to analyze the data is valid,[42] i.e.

$$\frac{D_0 A_0}{\text{OD}} = \frac{D_0 + A_0}{\epsilon} + \frac{1}{K\epsilon} \qquad (1)$$

where D_0 and A_0 are the initial concentrations of donor and acceptor, respectively, and OD is the observed optical density. K and ϵ usually are determined from a least-squares treatment of the data. Written as

$$D_0 A_0/\text{OD} = (1/\epsilon)[(D_0 + A_0) + 1/K] \qquad (2)$$

it is apparent from the terms within the brackets that $1/K$ eventually swamps out the concentration term as the value of K gets smaller, which is the basis for the statement that the $K\epsilon$ product for weak complexes can be determined precisely but the separation of the terms is difficult.[40,43]

For the aliphatic hydrocarbon-I_2 CCT systems the situation is even less favorable. First, in view of the earlier discussion with regard to choosing a reference system, even characterizing the $K\epsilon$ product is a problem. For example, for cyclohexane-I_2 in n-heptane, Bhat, Bhaskar, and Rao[18] found $K\epsilon \simeq 2.2 \times 10^2$ l.^{2} mol^{-2} cm^{-1}. Julien and Person's value for the same system is somewhat higher, 5.0×10^2 l.^{2} mol^{-2} cm^{-1}. The reason is that the latter authors corrected the n-heptane-I_2 solution curve based on the shape of the I_2 vapor curve which, in effect, reduced its CCT contribution. In the present vapor-phase study, the $K\epsilon$ value for cyclohexane-I_2 is of the same order ($\sim$8% higher) as that of Julien and Person if n-hexane-I_2 is used as the reference. With n-pentane-I_2 as the reference, the value obtained for $K\epsilon$ is higher, 7.6×10^2 l.^{2} mol^{-2} cm^{-1}.

Because CCT systems are completely unstable,[11,19] separation of K and ϵ by any of the standard procedures would hardly seem possible.[40,43] In their study, mentioned above, Bhat, et al.,[18] attempted the separation and obtained $K_{298} \simeq 0.043$ l. mol^{-1} and $\epsilon \sim$5000 l. mol^{-1} cm^{-1} (read from the figure in ref 18). Julien and Person[16] reported only the $K\epsilon$ product. They suggested that the results of Bhat, et al., represent limiting values, and made the intuitive guess that K should

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be in the range 0.02–0.001 l. mol^{-1} and ϵ should be of the order 2 × 10^4 to 5 × 10^5 l. mol^{-1} cm^{-1}.

It was pointed out by Prue[44] that random collisions in solution could lead to a value for K significantly greater than those cited above. His estimate, based on the ratio of the volume available for association between donor and acceptor to the remaining volume of the solution, was $K \simeq 0.2$ l. mol^{-1}.

A more direct calculation for estimating limiting values of K and ϵ based on the contact or collisional model can be made from vapor-phase data. Here, the concentration of contact pairs can be calculated directly from collision theory. The number of collisions per cubic centimeter per second between two molecules is[45]

$$Z_{12} = \pi N_1 N_2 d_{12}{}^2 \bar{c} \qquad (3)$$

where N_1 and N_2 are the concentrations of the species in molecules per cubic centimeter, $d_{12} = (d_1 + d_2)/2$ is the mean molecular diameter of the pair, and $\bar{c}$ is the average velocity.

The time, t, in which the molecules stay in contact is

$$t = \frac{2\overline{\Delta d}}{\bar{c}} \qquad (4)$$

where $\overline{\Delta d}$ was defined previously.

The product $Z_{12}t$ gives the number of collisions (or contacts) per cubic centimeter. N_1 and N_2 are calculated from the known concentrations of donor and acceptor. The magnitude of d_{12} can be calculated from the equation[46]

$$h\nu_{\mathrm{CCT}} \simeq I_{\mathrm{D}}{}^{\mathrm{V}} - E_{\mathrm{A}}{}^{\mathrm{V}} - e^2/d_{12} \qquad (5)$$

where ν_{CCT} is the observed CCT frequency, $I_{\mathrm{D}}{}^{\mathrm{V}}$ is the vertical ionization potential of donor, $E_{\mathrm{A}}{}^{\mathrm{V}}$ is the vertical electron affinity of acceptor, and e is the electron charge. Equation 5 is essentially an equality for CCT in the vapor phase, in the absence of mixing of the CCT state with nearby excited states of donor or of acceptor.[47]

The calculations were applied to cyclohexane–I$_2$. With n-pentane–I$_2$ as the reference, the value of λ_{max} is ~215 mμ. Using the values of $I_{\mathrm{D}}{}^{\mathrm{V}} = 9.88$ eV[34] and $E_{\mathrm{A}}{}^{\mathrm{V}} = 1.7$ eV[48] gives $d_{12} \simeq 5.8$ Å. This is larger than the van der Waals sum (taking $d_1 = 2.0$ Å for a methyl group and $d_2 = 2.15$ Å for an iodine atom).[49] Accord-

ing to Mulliken,[10] the CT donor–acceptor molecular volume should be larger than that based on van der Waals radii. This is because, with I$_2$ as the acceptor, the MO involved is the strongly antibonding σ_{u} and is therefore large, which ought to increase the effective size of the molecule. Further, Luck[25] has reported from a study of the iodine visible band that the effective optical diameter of cyclohexane–I$_2$ gaseous pair is about 1.37 times that of the gas kinetic diameter.

The distance Δd ranges from zero for a grazing collision to several angströms for one that is head on. The average for all collisions, $\overline{\Delta d}$, probably is of the order 1–2 Å. Prue[44] has estimated a value of $\overline{\Delta d} \simeq 0.94$ Å for contacts in solution. The value used in the present calculation was 1 Å.

For an iodine concentration of 6.50 × 10^{-5} M and a cyclohexane concentration of 3.50 × 10^{-2} M, the concentration of contact pairs is 2.88 × 10^{-7} M. This gives a "collision" constant $K \simeq 0.13$ l. mol^{-1}. An absorbance of 0.13 was obtained at 215 mμ in a cell path of 75.0 cm; hence, $\epsilon \sim 5.9 \times 10^3$ l. mol^{-1} cm^{-1}.

While these values are subject to some uncertainty, they surely must be in approximately the correct range. The value of 5.8 Å for d_{12} must be correct within a factor of 2. In fact, from eq 5, the range $5 < d_{12} < 10$ Å would seem large. The smaller value corresponds to a λ_{max} ~233 mμ, which is too high a wavelength for the CCT maximum according to the data in Figure 2, and the larger value corresponds to a λ_{max} ~183 Å, which is about at the V ← N peak of I$_2$ vapor.[19]

The value of K calculated above is of the same magnitude as that estimated by Prue[44] for contacts in solution. The model assumed in both cases is that of noninteracting spherical molecules. Superposition of classical van der Waals interaction between donor and acceptor should increase K and thereby diminish the limiting value of ϵ. This would bring both K and ϵ closer in accord with the vapor-phase values reported for weak donor–acceptor interactions for which there is stronger evidence for complexation,[50] e.g., benzene–I$_2$[39,52] and diethyl ether–I$_2$.[39,51] The van der Waals forces should allow greater contribution from less favorable orientations of donor–acceptor pairs when solvent influence is absent.[53]

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(47) In the diagram of Mulliken and Person ("Molecular Complexes," Wiley, New York, N. Y., 1969, Figure 14.3), the CCT state of cyclohexane–I$_2$ is mixed with the higher energy $^1\Sigma_{\mathrm{u}}{}^+$ state of I$_2$ to bring the calculated and reported $h\nu_{\mathrm{CCT}}$ into closer agreement. Their calculation is based on a van der Waals distance of 4.4 Å, but with a larger distance the calculated and observed $h\nu_{\mathrm{CCT}}$ can be made to agree without mixing of states.
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(49) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(50) Vapor-phase studies involve higher temperatures and lower concentrations than solution studies, which for weak complexes makes the separation of K and ϵ more difficult. Therefore, in several cases where separation has been reported, the results have not been confirmed.[38,51] Verification would be desirable, preferably by a nonspectroscopic method which gives K directly.[51,52]
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