Intermolecular Complex Formation between Iodine or Iodine Cyanide and Organic Molecules: Vibrational Spectra.

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The interaction between iodine or iodine cyanide on the one hand and a variety of organic molecules on the other, has been examined by measuring the infra-red vibrational spectra. The effect of dissolved iodine on the spectra of hydrocarbons, ketones, ethers, esters, ring ethers, pyridine, and picolines was first measured. Further details were usually obtained by dissolving both components in "inert" solvents (carbon disulphide and carbon tetrachloride). The results suggest that complex formation with the ketones and ethers occurs through the carbonyl group or ether-oxygen atoms. With pyridine and the picolines there is a more profound change which suggests a cleavage of the iodine molecule and formation of ions. Experiments with iodine cyanide gave similar results. By contrast with iodine, which has no infra-red absorption, iodine cyanide has three absorption bands, and the effect of complex formation upon these gives additional information. Preliminary studies have been made on the equilibrium constant for the iodine–dioxan complex formation and its variation with temperature.

THE differences in colour between solutions of iodine in different organic solvents have not yet been conclusively explained. That they arise from variations in the degree of molecular association of iodine as the solvent is changed is improbable, for although definite indications of association have been found, the same variation of apparent molecular weight with concentration occurs with such solvents as *cyclo*hexane and dioxan in which the difference of colour of iodine is marked (Kortüm and Friedheim, *Z. Naturforsch.*, 1947, **22**, 20). The suggestion that colloidal phenomena are responsible is also not substantiated by experimental results.

Of the two remaining theories, the first supposes that a cage of solvent molecules around the iodine molecule exerts a perturbing effect on its electronic energy levels, leading to spectral changes as the solvent is altered (Bayliss and Rees, *J. Chem. Phys.*, 1940, **8**, 377; Bayliss, *ibid.*, 1950, **18**, 292). The other assumes the formation of some type of intermolecular complex between solute and solvent (Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703; Mulliken, *ibid.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801). While it seems to us unjustifiable at present to regard the cage theory as having no experimental support, most of the results can be explained more satisfactorily by the second hypothesis.

In some cases, for example with pyridine or dioxan and iodine, crystalline compounds have been isolated (Rheinboldt and Boy, *J. pr. Chem.*, 1931, **129**, 273; Chatelet, *Compt.*

rend., 1933, **196**, 1421, 1907); Fairbrother (*J.*, 1936, 847; 1948, 1051) first found direct evidence for the polarisation of iodine in non-polar solvents from measurements of dipole moment, and other workers have studied the electrical conductivity of such solutions (Audrieth and Birr, *J. Amer. Chem. Soc.*, 1933, **55**, 668; Kortüm and Wilski, *Z. physikal. Chem.*, 1953, **202**, 235). Hartley and Skinner (*Trans. Faraday Soc.*, 1950, **46**, 621) also found a marked parallelism between the heats of solution of iodine in organic solvents and the colour of the solutions. The visible and ultra-violet absorption spectra have also been measured, and are in accordance with the idea of complex formation (Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1948, **70**, 2832; 1949, **71**, 2703; 1950, **72**, 2273). Mulliken (*loc. cit.*) has surveyed the experimental results and has tried to systematise the various phenomena in terms of a theory of " outer " and " inner " complex formation, and the occurrence of " charge-transfer " complexes. In this formulation iodine is an " acceptor " and the organic molecule is a " donor."

It seemed likely that the infra-red absorption spectra might provide direct evidence for the nature of the intermolecular interaction, since the vibrational frequencies of the solvent will be affected, and the absence of vibrational absorption by iodine makes the circumstances favourable for this study. Mulliken has suggested, on quantum-mechanical grounds, the mode of interaction to be expected between iodine and certain solvent molecules, and this can be examined by observing which molecular vibration frequencies are most affected and which nuclei are therefore involved in the interaction.

Experiments were begun in this laboratory several years ago by Wood (Diss., Oxford, 1950) and have now been repeated in greater detail and extended to include iodine cyanide as solute. In the latter case, there is a particular additional advantage in that we can also examine the effect of any complex formation on the vibration frequencies of the solute, and as shown below this provides important information. A preliminary account of our work was published earlier (Glusker, Thompson, and Mulliken, *J. Chem. Phys.*, 1953, **21**, 1407) and similar measurements with hydrocarbons and with pyridine have been described by other workers (Pimentel, Jura, and Grotz, *ibid.*, 1951, **19**, 513; Ham, Rees, and Walsh, *Nature*, 1952, **169**, 110; *J. Chem. Phys.*, 1952, **20**, 1336).

EXPERIMENTAL

Iodine was resublimed and stored before use in a desiccator over phosphoric oxide. Iodine cyanide was prepared by adding iodine slowly to concentrated aqueous potassium cyanide, and the mixture kept for some hours in a refrigerator. The precipitate was filtered off, washed with ice-water, recrystallised from water, and resublimed.

Considerable care was taken to eliminate traces of water from the organic compounds and solvents used. The following substances were dried with anhydrous calcium sulphate and refractionated in an all-glass apparatus closed by a drying tube containing phosphoric oxide: acetone (b. p. 56·4—56·5°), *n*-hexyl methyl ketone (b. p. 173·5—174°), acetophenone (b. p. 200·0—200·2°), diethyl ketone (b. p. 101·1—101·3°), ethyl acetate (b. p. 76·8—77·0°). *cyclo*Hexanone was separated from traces of *cyclo*hexanol by formation of its bisulphite addition compound, the latter being decomposed by aqueous sodium carbonate and the *cyclo*hexanone refractionated (b. p. 153·8—154°) and stored over anhydrous calcium sulphate. The following compounds were recrystallised from light petroleum-alcohol and dried in a vacuum-desiccator: benzophenone (m. p. 48—49°), benzil (m. p. 94·5—95·0°), dimethyl-4-pyrone (m. p. 132·5—133°), dibenzylideneacetone (m. p. 107—108°). " AnalaR " ether was redistilled (b. p. 34·4—34·6°) and stored over sodium. " AnalaR " dioxan was dried (KOH), refluxed over sodium, and finally distilled (b. p. 101·1—101·3°). Mesitylene was refluxed with sodium for 24 hr., fractionated (b. p. 166·6—167°), and stored over anhydrous calcium sulphate. " AnalaR " pyridine was dried for a week over potassium hydroxide, and distilled from and stored over barium oxide (b. p. 114·8—115°). Samples of α-, β-, and γ-picoline of high purity were obtained from the Chemical Research Laboratory, Teddington.

Carbon disulphide, acetonitrile, and carbon tetrachloride were purified in the standard way (Weissberger and Proskauer, " Organic Solvents," Oxford, 1935).

All the measurements were made with a Perkin–Elmer 12C spectrometer, prisms of lithium fluoride, rock-salt, and KRS 5 (thallium bromoiodide) being used. For most of the work the absorption cell was made from a pair of rock-salt plates separated by an amalgam washer about 0·1 mm. thick. The filling holes could be sealed by Polythene plugs. For measurements at the very long wave-lengths, a cell made from thin Polythene sheets was used.

The formation of complexes was studied in two ways. First, the effect of the solute upon the pure solvent was measured, and secondly, the two components were mixed in an " inert " solvent. It was often possible to observe changes in the latter case which were obscured in the former by the intense absorption of one component, and it was also possible by using an " inert " solvent to study more satisfactorily changes of equilibrium as the concentrations and temperature were varied.

Special care was taken throughout to exclude atmospheric water vapour by preparing the solutions in a dry box, and as a test of this procedure some solutions were subsequently allowed to absorb moisture and the spectral effects examined.

Many of the observed spectral shifts were small, and it was therefore necessary to be certain of their reality. In general, the spectrum of a dilute solution of one component (*e.g.*, acetone) in carbon disulphide or carbon tetrachloride was recorded. The solution was then saturated with the second component (iodine or iodine cyanide) and its spectrum was superposed upon the former record. All measurements were made a few minutes after preparation of the solutions, and repeated some hours later.

A water-jacketed cell holder was also built, by means of which the spectra could be measured at temperatures between 15° and 50°, and attempts were made to study the change in equilibrium constants with temperature.

RESULTS AND DISCUSSION

The vibrational spectra of saturated solutions of iodine in carbon disulphide or carbon tetrachloride are indistinguishable from those of the pure liquids. Also, the electronic spectra of these solutions are almost identical with that of iodine vapour (Benesi and Hildebrand, *loc. cit.*). These two solvents have therefore been assumed to behave as " inert " media and have been used as such for studying the complex formation between iodine or iodine cyanide and the " active " solvents.

The measurements reported by different workers for mesitylene–iodine are confusing. Pimentel, Jura, and Grotz (*loc. cit.*) first suggested that a number of new bands appear upon addition of iodine to mesitylene, but Ham, Rees, and Walsh (*loc. cit.*) could find no changes at all. Wood's measurements in this laboratory indicated that one new band appeared in the spectrum of mesitylene, near 1300 cm.$^{-1}$, and this has been confirmed by our later work which also revealed a noticeable change in intensity of a band near 880 cm.$^{-1}$. We have since been informed by Prof. Pimentel that his earlier results were unreliable because of impurities in the mesitylene used, and the failure of Ham, Rees, and Walsh to observe the band near 1300 cm.$^{-1}$ may have been due to its being very weak. The most plausible interpretation of our results with mesitylene is that the mutual interaction of the two molecules causes a breakdown of certain selection rules, enabling the vibration frequency near 1300 cm.$^{-1}$, which is active in the Raman effect, to appear in infra-red absorption. The alteration in the intensities of other bands such as that near 880 cm.$^{-1}$ could be explained similarly.

No spectral changes have been found on addition of iodine to benzene, toluene, xylenes, or dimethylnaphthalenes (Wood, *loc. cit.*). Similarly, no changes could be found in the spectrum of acetonitrile after addition of iodine, nor when the two components were mixed in an " inert " solvent. In view of the brown colour of the solution of iodine in acetonitrile, this result was surprising, and in the light of the other results given below a complex might have been expected, formed through the ·C⋮N group. It would appear that, if this occurs, the effect is not large enough to be noticed because of the high force constant of the ·C⋮N bond.

The effects found with many compounds containing the carbonyl group are more informative. Displacements of the stretching vibration band of this group were noticed when iodine was added to pure liquid ketones, but from measurements in an " inert " solvent the changes can be seen more clearly. Typical results were given in our earlier note (*J. Chem. Phys.*, 1953, **21**, 1407). In general a new band due to the complex appears, lying about 20 cm.$^{-1}$ below that of the ketone itself. The relative intensity of the two bands changes as the concentrations of the two components are altered, as seen from the results in different " inert " media in which the solubilities are different. Apart from this effect in the carbonyl group band, the only spectral change found was the appearance in some cases of a weak band between 1200 and 1300 cm.$^{-1}$. It must therefore be concluded that the complex formation occurs essentially through the carbonyl link.

Now, since the only significant change in the spectra of these ketones after addition of iodine appears to involve the carbonyl group, it is unlikely that the change can be due to any chemical interaction which will lead to a new chemical species and to larger spectral changes. However, some measurements were carried out to discover whether the spectra of the solutions of iodine in the ketones changed over a long period. It was found that with ketones which have a methylene group adjacent to the carbonyl group, a slow irreversible reaction can occur, which is moreover accelerated by the presence of small amounts of water. With acetone, the new spectrum showed many similarities to that of iodoacetone, for which the frequency of the carbonyl group stretching vibration lies somewhat higher (*ca.* 1725 cm.$^{-1}$) than that of acetone itself. This rise in frequency is to be contrasted with the fall previously noticed in the initial complex formation. There is a similar slow reaction with dibenzylideneacetone, and with *cyclo*hexanone the chemical process proceeds too rapidly for the characteristics of the initial complex to be seen.

With benzophenone, where there are no reactive methylene groups, the spectrum of the mixture with iodine remains constant with time, and shows the pair of bands due to the carbonyl groups of the free molecule and the complex. With benzil, a new band near 1656 cm.$^{-1}$ appears after addition of iodine, but its intensity relative to the normal carbonyl group band near 1678 cm.$^{-1}$ is much lower than in the case of benzophenone. This point is discussed below.

Complex formation was also studied by using molecules containing an ether-type oxygen atom. Ham, Rees, and Walsh found no spectral changes with ethers, but using dilute solutions of ether in " inert " solvents saturated with iodine, we have found a new band near 1098 cm.$^{-1}$ linked with that of ether itself at 1119 cm.$^{-1}$. Exactly the same pair of bands at 1098, 1119 cm.$^{-1}$ are found for the dioxan–iodine system, where there is another new band at 830 cm.$^{-1}$ linked with the ring-ether band at 874 cm.$^{-1}$. Addition of iodine to tetrahydrofuran also produces new bands near 1052 and 842 cm.$^{-1}$. In all these cases the spectra of the mixed solutions remain constant with time.

TABLE 1.

Acceptor = iodine. Donor = Dimethyl-4-pyrone.
N = new band (cm.$^{-1}$). I = change of band intensity.

15% Donor in CS_2 sat. with I_2		15% Donor in CCl_4 sat. with I_2		Probably associated with band at	15% Donor in CS_2 sat. with I_2		15% Donor in CCl_4 sat. with I_2		Probably associated with band at
N	I	N	I		N	I	N	I	
—	2957	—	—	—	1329	—	1329	—	1325
—	2922	—	—	—	—	1193	—	1193	—
—	2850	—	—	—	1161	—	1161	—	1155
—	2800	—	—	—	1032	—	1032	—	1029
—	2782	—	—	—	—	952	—	953	—
1658	—	1658	—	1674	940	930	939	930	930
1580	—	1584	1635	1635 ?	897	—	898	—	891
1400	—	1401	—	1390	—	867	—	867	—
—	1367	—	1370	—	845	—	—	—	867 ?

With ethyl acetate, the carbonyl group frequency appears to be affected by iodine in the same way as with the ketones, but the bands connected with the ether-type part of the molecule ($\cdot C \cdot O \cdot C_2H_5$) are not influenced like those in the ethers themselves. With dimethyl-4-pyrone, on the other hand, changes occur across the entire spectrum (Table 1, Fig. 1), suggesting that interactions may occur through both the carbonyl group and the ring-ether oxygen atom. The spectrum of the mixture is constant with time.

The specific spectral shifts found above with all the ketones and ethers point to a mechanism of complex formation by electron donor and acceptor between the organic molecule and iodine. This would correspond to the formation of an "outer complex" in the sense discussed by Mulliken. He further suggested that in these structures formed from an iodine molecule and a carbonyl group, the iodine atoms should lie in the plane of the group (I), with their internuclear axis perpendicular to the C=O bond. Benzil has two adjacent carbonyl groups and a structure which will hinder the approach of an iodine molecule if the orientation just mentioned has to be achieved, whereas if the axis of the iodine molecule were to lie perpendicular to the plane of the group (I) no such hindrance would arise. It is therefore worth noting that with benzil the intensity of the new band due to the complex is abnormally low, and this may indicate greater difficulty of its formation.

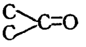

(I)

TABLE 2.

Acceptor = iodine. N = New band. I = Intensity change.
d = donor. Band positions in cm.$^{-1}$.

(i) Saturated solution of iodine in 100% donor.
(ii) 15% Donor in CS_2 saturated with iodine.
(iii) 15% Donor in CCl_4 saturated with iodine.
(iv) Probably associated with band at the position given.

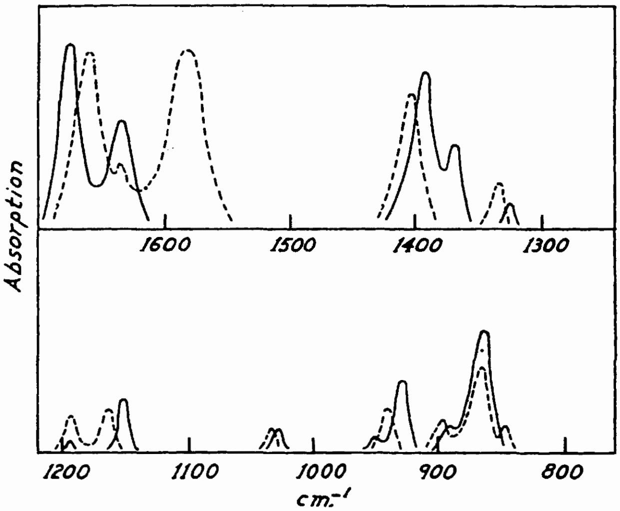
(Some changes in the bands near 3 μ were also measured with the picolines, but since these were only examined with a rock-salt prism, where accuracy is less than that with lithium fluoride, the results are not included in the table.)

(i)		(ii)		(iii)			(i)		(ii)		(iii)		
N	I	N	I	N	I	(iv)	N	I	N	I	N	I	(iv)
d = Pyridine.													
3065	3076	—	—	—	—	3076	1060	—	1064	—	—	—	1067
3028	—	—	—	—	—	3024	—	—	—	1027	—	—	—
—	2998	—	—	—	—	—	1005	—	1004	—	—	—	—
—	—	—	—	1628	—	1616	—	—	993	990	—	—	990
1453	—	—	—	1446	—	1441	—	—	973	—	—	—	—
—	1351	—	1350	—	1350	—	—	—	938	—	—	—	—
1241	1239	—	—	—	—	—	*ca.* 755	—	745	—	—	—	742
1207	—	1208	—	—	—	1215	—	—	705—	—	—	—	711—
—	—	1150	—	—	—	1144			692				692
d = α-Picoline.													
—	—	—	—	—	1452	—	—	—	—	1035	—	—	—
—	—	—	—	1423	1432	1432	—	1021	—	—	—	—	—
—	—	1379	—	1378	—	1375	1010	—	1008	—	—	—	—
—	1237	1237	—	—	—	1232	986	—	983	—	—	—	999
—	—	1207	—	—	—	1232	801	—	801	—	—	—	798
—	—	1150—	—	—	—	1146	—	—	757—	—	—	—	753—
		1155							743				740
1109	—	1107	1100	—	—	1100	714	—	714	—	—	—	724
—	—	1054	—	—	—	1045							
d = β-Picoline.													
2490	2450	2490	—	—	—	2450	1099	—	1098	1103	—	—	1103
1591	—	—	—	—	—	1572	1050	—	1049—	—	—	—	1041
—	—	1258	1240	—	—	1225 ?			1058				
—	1228	—	1225	—	—	—	—	—	—	1028	—	—	—
1187	—	1187	1190	—	—	1190	—	—	913	—	—	—	923
—	1168	1161	—	—	—	1168	816	—	786—	—	—	—	780
1122	1126	—	1125	—	—	1125			803—814				
							700	—	694	705	—	—	705
d = γ-Picoline.													
2480	—	2380—	—	—	—	2440	1011	—	1008	993	—	—	993
		2470					—	—	968	—	—	—	965
—	—	1608	1598	1608	1598	1598	870	872	—	—	—	—	872
1243	1210—	1240	1210—	—	—	1210—	—	—	805	793—	—	—	793—
	1218		1218			1218				799			799
—	1168	—	—	—	—	—	709	—	705—	715—	—	—	715—
1064	1069	1067	1069	—	—	1069			710	719			719
1025	—	—	1037	—	—	1037 ?							

The spectra of solutions of iodine in pyridine and the picolines show very marked changes from those of the pure solvents. The positions of the bands for pyridine, α-picoline, and β-picoline are given in Table 2, and the manifold changes of intensity are shown in Fig. 2.

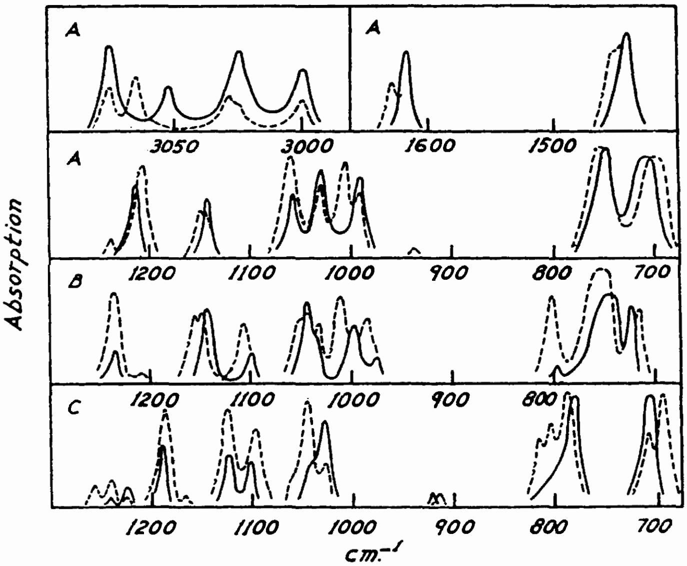
The spectra of the mixtures were unchanged after long storage, and although elaborate precautions were taken here to exclude traces of water, it was found that the addition of a little water to a pyridine–iodine solution did not affect the results.

FIG. 1. *Dimethyl-γ-pyrone and iodine in carbon disulphide or carbon tetrachloride.*



———— without iodine.
– – – – – after addition of iodine.

FIG. 2. *Pyridine and picolines with iodine in carbon disulphide or carbon tetrachloride.*



A. Pyridine ———— without iodine, – – – – – after addition of iodine.
B. α-Picoline ———— without iodine, – – – – – after addition of iodine.
C. β-Picoline ———— without iodine, – – – – – after addition of iodine.

With γ-picoline, addition of iodine caused a similar set of changes, listed in Table 2, but a rapid reaction soon set in and the whole mixture solidified. Efforts were made to establish the products of this reaction by solvent extraction, by analysis, and from spectra, but no definite conclusions were reached. There are, however, indications that salts of the type [γ-Pic—I]$^+$ I$^-$ are present, complicated by ionic solvation with the picoline molecule.

The spectral changes involved in the addition of iodine to pyridine and its homologues are so strikingly greater than those found previously with the ketones and ethers as to suggest some essentially different feature in the formation of the complexes. Whereas with the ketones the only significant change of frequency appears to concern the carbonyl group, many vibrations of the pyridine ring seem to be affected. This may imply that an essentially new structure of markedly different electronic configuration, such as the [Py–I]$^+$ ion, has been produced. In the lists of heats of solution quoted by Hartley and Skinner (*loc. cit.*), pyridine occupied an extreme place. Also, measurements using radioactive iodine have suggested that exchange with iodine in a pyridine–iodine complex is complete immediately after mixing (Kleinberg and Sattizahn, *J. Amer. Chem. Soc.*, 1951, **73**, 1865).

In order to examine this further, the spectrum of the pyridine–iodine complex in carbon disulphide was measured over a wide range of concentrations of the two components. The concentration of pyridine was varied between 0·005 and 3·0M, and that of iodine between 0·0005 and 0·5M. If there is a transition point between the " outer " and " inner " complex, as suggested by Mulliken, it might be observed in this way. The visible absorption band of iodine in pyridine–heptane solutions shifts appreciably as the concentration of pyridine changes from 0·01 to 10·0M, and there are signs that the onset of the shift occurs at about 0·1M (Reid and Mulliken, personal communication). If this is true, and if the shift is linked with the transition from " outer " to " inner " complex, we might expect to find corresponding changes in the vibrational spectrum. In fact, our results failed to reveal any spectral alterations which could be interpreted in this way.

Having regard to the results of Fairbrother (*loc. cit.*) which showed that there is a polarisation of iodine in many non-polar solvents and even in some hydrocarbons, we might regard the formation of a charge-transfer complex as applicable to all the above cases, with pyridine and picolines in an extreme class in which ionisation is complete. Further information was sought by using iodine cyanide as the " acceptor " molecule, for we can follow here not only the vibrational spectrum of the " donor," but also that of the " acceptor," and complete cleavage of the iodine cyanide molecule into ions should be directly observable.

The infra-red spectrum of iodine cyanide dissolved in carbon tetrachloride or carbon disulphide gives as fundamental vibration frequencies $\nu_1 = 462$ cm.$^{-1}$, $\nu_3 = 2167$ cm.$^{-1}$, $\nu_2 = 315$ cm.$^{-1}$, corresponding to the values 470, 2158, and 321 cm.$^{-1}$ obtained from the Raman spectrum in methanol (West and Farnsworth, *J. Chem. Phys.*, 1933, **1**, 402). Addition of benzophenone to a saturated solution of iodine cyanide in carbon tetrachloride causes the band at 2167 cm.$^{-1}$ (ν_3), largely controlled by the C≡N link, to shift to 2162 cm.$^{-1}$, and when benzophenone is added to a saturated solution of iodine cyanide in carbon disulphide the band at 462 cm.$^{-1}$ (ν_1), largely controlled by the C–I link, shifts to 458 cm.$^{-1}$. It was impossible to study the effect on the bending vibration ν_2 because of overlapping absorption by benzophenone.

Similarly in carbon disulphide, the addition of dioxan to iodine cyanide shifts the band at 462 cm.$^{-1}$ to 456 cm.$^{-1}$, and that at 315 cm.$^{-1}$ to 326 cm.$^{-1}$.

All these small shifts indicate the formation of a weak complex which affects the vibration of the whole iodine cyanide molecule.

When pyridine is added to a solution of iodine cyanide in carbon disulphide or carbon tetrachloride, all the bands of iodine cyanide diminish in intensity as the addition proceeds, and finally disappear. There are no signs of fresh bands displaced from those of iodine cyanide, although it is just possible that if these were weak they might be masked by bands of pyridine. This behaviour is in contrast to that observed with a ketone or ether as " donor " molecule, and strengthens the previous hypothesis that in the case of pyridine complexes a definite split has occurred, probably leading to [Py–I]$^+$ and [CN]$^-$ ions. We might expect to detect a vibration band of the [CN]$^-$ ion, but none has been found, probably because of intense absorption by the other species present. The formation of [Py–I]$^+$ rather than [Py–CN]$^+$ ions is supported by Fairbrother's results on the

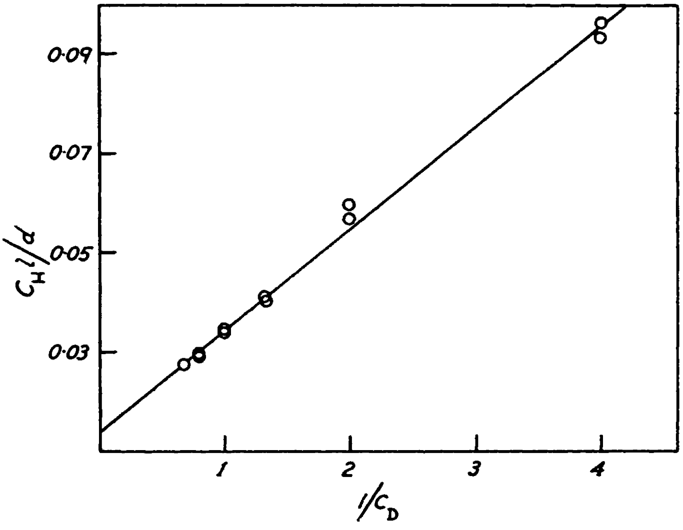
TABLE 3.

Acceptor = iodine cyanide. d = Donor.
N = new band (cm.$^{-1}$), I = change of band intensity.

15% d in CS_2 sat. with ICN		Probably connected with band at (cm.$^{-1}$)	15% d in CS_2 sat. with ICN		Probably connected with band at (cm.$^{-1}$)
N	I		N	I	
	d = Pyridine.			d = Dimethyl-4-pyrone.	
1235	—	1215	1662	—	1674
1210	—	1215	1590	1631	1631
1150	—	1144	1400	—	1390
1065	—	1067	1372	—	1366
1030	—	1027	1329	—	1325
1002	990	990	—	1193	1193
940	—	—	1161	—	1155
747	—	742	1032	—	1029
705—692	—	711—692	956	—	953
			939	—	930
			898	—	891
			863	—	862

polarisation of iodine cyanide in pyridine, and also by the fact that the changes in the spectrum of pyridine caused by addition of iodine cyanide (Table 3) are almost identical with those which occur when iodine is added.

FIG. 3. *Equilibrium between dioxan and iodine in carbon disulphide : plot of $C_H \, l/d$ against* $1/C_D$.



The addition of iodine cyanide to dioxan, benzophenone, or dimethyl-4-pyrone leads to spectral changes exactly similar to those already found with iodine.

Preliminary measurements have been made of the equilibrium constants for the complex formation between iodine or iodine cyanide on the one hand and ketonic or ether compounds on the other. Qualitatively, the band intensities show that the complexes are more easily formed with iodine cyanide than with iodine. The case of iodine–dioxan has been studied by means of the band at 830 cm.$^{-1}$ associated with the complex, which is assumed to be 1 : 1 in composition. Then at 830 cm.$^{-1}$,

$$d = \text{optical density} = \varepsilon \, . \, C_x \, . \, l$$

in which ε is the extinction coefficient, l the path length, C_x the concentration of complex, and d is the optical density. The equilibrium constant $K = C_x/C_1C_2$, in which C_1, C_2 are the concentrations of free dioxan and free iodine, respectively. If C_D, the total concentration of dioxan, is much greater than C_H, the concentration of iodine, then $C_1 = C_D$ and $C_2 = (C_H - C_x)$ and it follows that

$$C_H l/d = 1/K\varepsilon C_D + 1/\varepsilon$$

In Fig. 3 the left-hand side of this equation is plotted against $1/C_D$, and from the slope and intercept we obtain $K \sim 0{\cdot}7$ at 25°. From a series of such determinations at different temperatures, it was possible to calculate a value for the heat of formation of the complex, the result being roughly 5 kcal./mole. These results must be regarded as uncertain owing to errors in determining the intensity of the weak band of the complex. More accurate measurements are now being carried out with a double-beam spectrometer, and particularly on complexes with the carbonyl group near 5·8 μ.

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