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Molecular Compounds and Their Spectra. IV. The Pyridine–Iodine System[1]

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The visible and ultraviolet absorption spectra of dilute solutions of iodine plus pyridine in heptane have been studied, and the existence of an equilibrium with a 1:1 molecular complex $Py{\cdot}I_2$ ("outer complex") was demonstrated [$K = 290$ at 16.7°, where K means $(Py{\cdot}I_2)/(Py)(I_2)$]. The corresponding changes in heat content, entropy, and free energy (at 17°) in formation of the complex were determined to be −7.8 kcal./mole, −15.5 cal./deg. mole, and −3.3 kcal./mole, respectively. The location and intensities of the I_2 band (λ_{max} 4220 Å., ϵ_{max} 1320) and of the charge-transfer band (λ_{max} 2350, ϵ_{max} 50,000) of $Py{\cdot}I_2$ were determined. The λ 4220 band shifts gradually, and increases in intensity, on adding more pyridine to the aforementioned heptane solutions, until for pure pyridine solutions it has reached about λ 3890, with ϵ_{max} 2120, provided the solutions are not too dilute in iodine. These changes can most probably be attributed to a somewhat increased polarity and stability of the $Py{\cdot}I_2$ "outer complex" in the polar solvent pyridine than in the non-polar solvent heptane. There is no evidence of the presence of the "inner complex" $(PyI)^{+}I^{-}$ in more than small concentrations, but conductivity studies by Kortüm and Wilski indicate that appreciable small concentrations of its ions $(PyI)^{+}$ and I^{-} are present in pure pyridine solutions of iodine. Additional studies in *very dilute* solutions of iodine in pyridine show further interesting spectroscopic changes, which are discussed, but we feel that further experimental study will be needed using extreme precautions toward exclusion of side-reactions, moisture or impurities.

Introduction and Survey

Recent studies have confirmed older ideas that in its violet solutions, iodine exists essentially free, but that in its brown solutions it forms 1:1 molecular complexes with the solvent.[3] The strong visible absorption of I_2 vapor with maximum at λ 5,200 is essentially unchanged in "violet" solvents, but in solutions where it forms complexes this peak is shifted toward shorter wave lengths; this accounts for the altered color. In addition, a new very intense peak characteristic of the complex, first noted by Benesi and Hildebrand for aromatic solvents, appears at shorter wave lengths, usually in the ultraviolet. The interpretation of this new peak as a *charge-transfer* spectrum has proved important for a clearer understanding of the electronic structure of these complexes.[3]

There is evidence[4-7] that iodine forms especially stable complexes with pyridine and related compounds. Waentig[4] reported golden crystals, which he attributed to $Py{\cdot}I_2$, crystallizing from a saturated solution of iodine in pyridine. From heats of solution Hartley and Skinner[3] estimated the heat of formation of $Py{\cdot}I_2$ in solution to be about 7.95 kcal./mole, much larger than for other types of iodine complexes. Similarly, the enhancement of the dipole moment in the formation of $Py{\cdot}I_2$ is exceptionally large.[6] Further, the change in the infrared spectrum of Py when it goes into $Py{\cdot}I_2$ is much greater[5] than the corresponding effect in the case of complex-forming solvents of other types.

Audrieth and Birr[8] reported that solutions of iodine in pyridine show high electrical conductivities, which slowly increase with time to asymptotic

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[3] See R. S. Mulliken, (a) THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952); (b) *J. Phys. Chem.*, **56**, 801 (1952), for quantum-theoretical interpretation of molecular complexes and their spectra, and a comprehensive review. These are I, II and III of the present series.

[4] (a) P. Waentig, *Z. physik. Chem.*, **68**, 513 (1909); Chatelet, *Ann. chim.*, [11] **2**, 12 (1934); H. Carlsohn, *Z. angew. Chem.*, **45**, 580 (1932); **46**, 747 (1933).

[5] K. Hartley and H. A. Skinner, *Trans. Faraday Soc.*, **26**, 621 (1950).

[6] Y. K. Syrkin and K. M. Anisimowa, *Doklady Akad. Nauk. SSSR*, **59**, 1457 (1948); G. Kortüm, *J. chim. phys.*, **49**, C127 (1952); G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

[7] D. L. Glusker, H. W. Thompson and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1407 (1953), and references given there; also further unpublished results of Mr. Glusker. Also W. Luck, *Z. Elektrochem.*, **59**, 870 (1952), especially table IV.

[8] L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933).

values. According to them the molar conductivity based on I_2 is so high in dilute solutions that it cannot be explained by simple dissociation into I^+ (or PyI^+) and I^-. They suggested instead the formation of a ternary electrolyte

$$Py{\cdot}I_2 \rightleftharpoons Py^{++} + 2I^-$$

However, recent work of Kortüm and Wilski,[9] using very great precautions to keep moisture excluded, indicates that iodine in freshly prepared solutions in pure pyridine at concentrations in the neighborhood of 10^{-4} molar gives only a small conductivity, though larger than for most iodine complexes.[10] They find, however, that this increases with time, and attributes the effect to a slow iodination in the ring; the effect is strongly catalyzed by platinum sponge.

Kleinberg, VanderWerf and associates[11] have made a spectrophotometric investigation of solutions of iodine in pyridine (also in quinoline). They too conclude that a very slow iodination in the ring occurs; this should liberate I^- ions, which may form I_3^- ions with I_2.

Mulliken[12] in 1952 suggested that when I_2 is dissolved in pyridine the following should be considered as the primary reactions

$$Py + I_2 \underset{\text{fast}}{\rightleftharpoons} Py{\cdot}I_2 \text{ ``outer complex''} \qquad (1)$$

$$Py{\cdot}I_2 \rightleftharpoons (PyI)^+I^- \text{ ``inner complex''} \qquad (2)$$

$$(PyI)^+I^- \underset{\text{fast}}{\rightleftharpoons} PyI^+ + I^- \qquad (3)$$

The "outer complex" $Py{\cdot}I_2$ in (1) would be a molecular complex of the usual type. The "inner complex" in (2) would be an essentially ionic structure (N-iodopyridinium iodide). It was suggested that, in iodine solutions in pyridine, the pyridine has a double role, acting as an electron donor toward I_2 in reaction (1), and as a polar medium in assisting reactions (2) and (3).

The present research was undertaken in the hope of studying these two roles of pyridine separately by a spectrophotometric investigation, first, of equilibrium (1) at varying low concentrations of Py and I_2 in a non-polar solvent medium; second, of the combined equilibria (1), (2) and (3) in a polar medium (perhaps pyridine itself, or preferably a different polar solvent). These two phases of the present work are reported in sections I and II below.

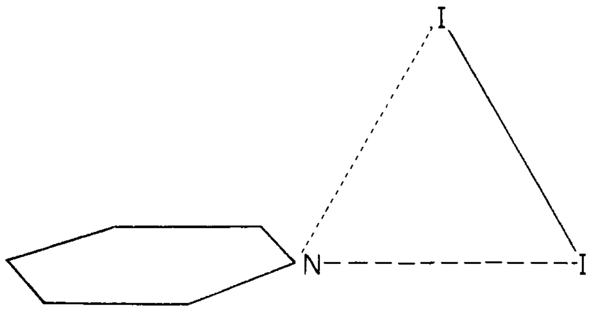

Fig. 1.

In section I equilibrium (1) was successfully studied in heptane solution. The visible iodine band of the outer complex $Py{\cdot}I_2$ was located at the exceptionally strongly shifted position of λ 4,220 (for free iodine it is at λ 5,200), and the expected charge-transfer band at λ 2,350. The equilibrium constant for (1), and the heat of formation of $Py{\cdot}I_2$, were determined. This work confirms other indications[4,7] that $Py{\cdot}I_2$ is an exceptionally tightly bound outer complex. Taking into consideration the observed dipole moments[4] of Py (2.28 *D*) and of $Py{\cdot}I_2$ (4.5 *D*), and assuming a geometrical structure[13] somewhat as shown in Fig. 1, one can estimate that the outer complex $Py{\cdot}I_2$ may easily have as much as perhaps 25% dative character. That is, in the type of formulation given by Mulliken[3]

$$\psi(Py{\cdot}I_2) \approx \underset{\text{no-bond}}{a\psi_0(Py,I_2)} + \underset{\text{dative}}{b\psi_1(Py^+{-}I_2^-)} \qquad (4)$$

with $a^2 \approx 0.75$, $b^2 \approx 0.25$. In eq. 4, because of the asymmetry (Fig. 1) and unusual strength of the complex, the dative function ψ_1 may be already approximately of the structure $\overset{+\;\;I^-}{C_5H_5N - I}$ with the N^+ bonded to one I atom nearly in the Py plane (N-iodopyridinium ion) leaving the other I atom as an I^- above the plane.[14] An outer complex with an exceptionally large amount of dative character may well account for the fact[7] that complex formation causes greater changes in the infrared spectrum in the case of Py than for any other known cases (except the related picolines).

When the work reported in section II was undertaken, it was with the thought,[12] suggested by the conductivity studies of Audrieth and Birr,[8] that in pure Py, acting as a polar medium, (a) equilibrium for reaction (2) lies almost completely to the right; but (b) the reaction proceeds only very slowly, over a high potential barrier; and that as fast as $(PyI)^+I^-$ is formed, reaction 3 proceeds largely to the right. However, the recent work of Kortüm and Wilski[7] indicates that ions PyI^+ and I^- are formed at once in I_2 solutions in Py, in definite relatively small equilibrium concentrations, and that a later slow increase in ionic concentration is due to slow side-reactions. Taken in connection with our spectrophotometric results in sections I and IIA and the discussion presented in IIA, the work of Kortüm and Wilski indicates that in the absence of side-reactions most of the iodine would remain as $Py{\cdot}I_2$, but that a small portion of it has at once undergone reaction (2) followed by (3), or else perhaps the direct ionization

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(9) G. Kortüm and H. Wilski, *Z. physik. Chem.*, **202**, 35 (1953). See also Kortüm, ref. 6.

(10) They find an ionic dissociation constant $(PyI^+)(I^-)/(Py{\cdot}I_2)$ of about 4.6×10^{-8}, which corresponds to about 2% ionization at 10^{-4} molar iodine. This may be compared with 1.2×10^{-11} for $(H_2OI)^+(I^-)/(H_2O{\cdot}I_2)$ as determined by R. P. Bell and E. Gelles [*J. Chem. Soc.*, 2734 (1951)] and smaller values (see ref. 9) for the benzene and dioxane complexes. However, it seems not impossible that some of the alcohols may have larger values [*cf.* L. I. Katzin, *J. Chem. Phys.*, **21**, 490 (1953)].

(11) (a) R. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **73**, 88 (1951); (b) J. Kleinberg, E. Colton, J. Sattizahn and C. A. VanderWerf, *ibid.*, **75**, 447 (1953).

(12) Reference 3a, p. 818; ref. 3b, pp. 812, 819.

(13) This is based on general considerations previously advanced by Mulliken (ref. 3).

(14) The Py would then be acting as an *n* donor in the terminology of ref. 3b. However, to a slight extent, it probably acts simultaneously as a π-donor (like benzene in its iodine complex; *cf.* footnote 42 on page 818 of ref. 3a. ψ_1 in eq. 4 would then involve a mixture of mainly *n* with a little π-donor action by the Py

$$Py{\cdot}I_2 \rightleftarrows PyI^+ + I^- \qquad (5)$$

Further discussion will be given in section IIA.

Experimental

C.P. pyridine was refluxed with chromium trioxide for several hours to remove traces of picolines, dried by NaOH, and distilled from magnesium perchlorate. C.P. iodine was sublimed and kept in a desiccator. Solvents were purified by the methods described by Potts.[15] Absorption measurements were made in a Beckman spectrophotometer, using 10-, 1-, 0.0296- and 0.0109-cm. cell thicknesses. Apart from the use of cells with fairly well fitting lids, no precautions were taken to avoid moisture uptake during a run. No lids at all were possible in experiments using spacers to decrease cell thickness.

I. The Py·I$_2$ Complex in a Non-polar Solvent

The equilibrium (1) was studied in very dilute solutions (<0.1% Py + I_2) in heptane (>99.9% by weight). As pyridine in increasing but small amounts is added to a (violet) dilute solution of iodine in heptane, the solution goes through a reddish color to golden brown. The uncomplexed I_2 peak at 5,200 Å. diminishes and is replaced by a new and somewhat higher but otherwise very similar peak at 4,220 Å. (*cf.* Fig. 2). The peaks are well enough separated for a fairly accurate determination of the equilibrium constant K

$$K = \frac{(Py{\cdot}I_2)}{(Py)(I_2)}\ \text{liters/mole}$$

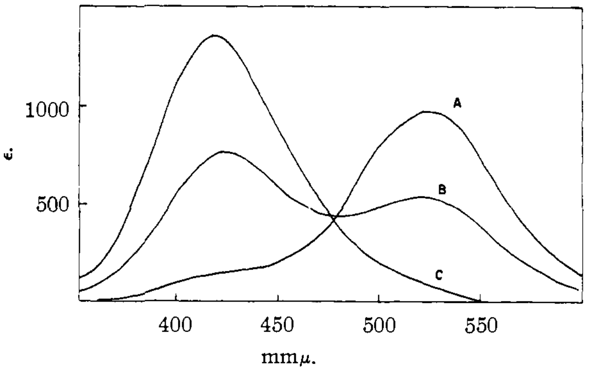

Fig. 2.—Plot of extinction coefficient ($\epsilon = (1/lc) \log_{10} (I_0/I)$, where l = cell thickness, and c = formal molarity based on total iodine added) against wave length for 0.0005 M iodine solutions in heptane, with increasing amounts of pyridine. Room temperature, cell thickness = 1.00 cm.; A, pyridine 0.0005 M; B, pyridine 0.005 M; C, pyridine 0.25 M.

From the K values at 2° (649), 16.7° (290), and 41° (101)—*cf.* Fig. 3—a graph was made (Fig. 4) from which in the usual way the heat of dissociation of Py·I$_2$ was calculated to be 7.8 ± 0.2 kcal./mole. It is of some interest that this result agrees closely with the value 7.95 kcal./mole estimated from the heat of solution of I_2 in pure Py by Hartley and Skinner.[3] From the available data the free energy and entropy changes for reaction 1 were also computed, the results, in conventional units, at 17°, being $\Delta F = -3.3$, $\Delta H = -7.8$, $\Delta S = -15.5$.

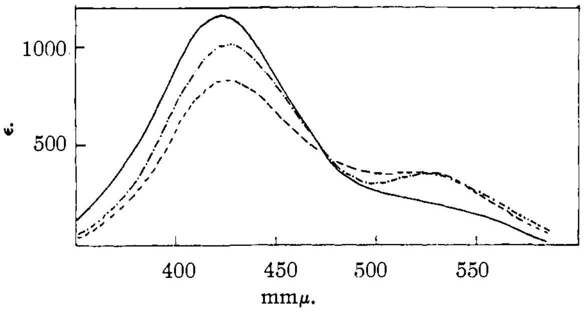

Fig. 3.—Plot of formal extinction coefficient (see Fig. 2) against wave length of I_2 + Py in heptane for a series of temperatures; cell thickness = 1.00 cm.

- - - - - 2° Py = 0.005 M I_2 = 0.0005 M
——— 16.7° Py = 0.025 M I_2 = 0.000625 M
- - - - - 41° Py = 0.025 M I_2 = 0.000625 M

The equilibrium shifts strongly toward Py·I$_2$ as the temperature is lowered, but the pyridine concentration has been lowered in the 2° experiment so that both peaks are measurable.

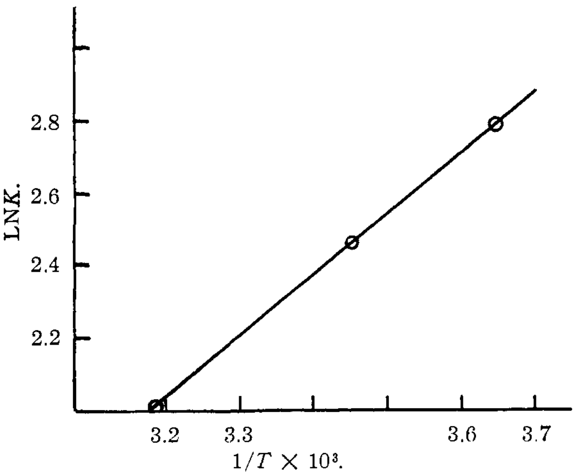

Fig. 4.—Plot of $K = (Py{\cdot}I_2)/(Py)(I_2)$ (liters/mole) against $1/T$ for the equilibrium between iodine and pyridine in heptane.

McConnell, Ham and Platt[16] have predicted that the charge-transfer peak of Py·I$_2$ should occur at 38,000 kayser (2,635 Å.), on the basis of an electron impact value of 9.8 volts[17] for the ionization potential of pyridine. Use of the same ionization potential in an equation given by Hastings, Franklin, Schiller and Matsen,[18] which fits a great number of iodine complexes closely, gives a similar prediction (38,300 kayser or 2,610 Å.). A search of this region using Py·I$_2$ in heptane at concentrations of 0.01 M in Py and 0.0005 M in I_2, with thin cells to avoid excessive pyridine absorption, showed such a band with peak at 42,600 kayser (2,350 Å.). The extinction coefficient is sufficiently large (ϵ = 50,000) that no difficulty was experienced in locating this band in spite of the considerable pyridine absorption in this region.

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[15] W. J. Potts, *J. Chem. Phys.*, **20**, 809 (1952).

[16] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[17] Hustrulid, Kusch and Tate, *Phys. Rev.*, **54**, 1037 (1938). Stevenson and Schissler in unpublished work have recently obtained 9.85 volts (private communication from D. P. Stevenson).

[18] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953). The form of their equation is based on Mulliken's theoretical discussion in ref. 3a.

The charge-transfer band is shown in Fig. 5, in which the pyridine absorption was automatically cancelled out by using as a blank part of the heptane + pyridine solution which had been used to dissolve iodine. No correction for free I_2 was needed, in view of its very low concentration and small absorption near λ 2,350.

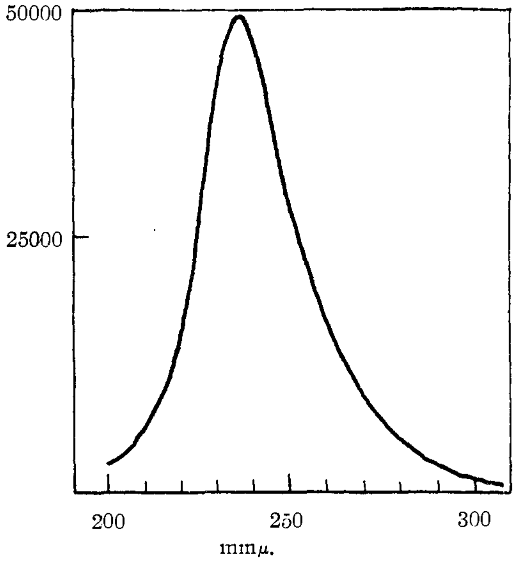

Fig. 5.—The Py·I_2 charge-transfer spectrum at room temperature. The absorption of pyridine which lies in this region was cancelled out exactly by dividing a 0.05 *M* pyridine solution in heptane into two parts, adding iodine (0.0005 *M*) to one half, and using the other half as a blank; cell thickness = 0.0296 cm. Free I_2 is negligible in its effect.

The fact that the observed charge-transfer band is at somewhat shorter wave lengths than predicted may perhaps be connected with the exceptionally high stability of the Py·I_2 complex. The validity of the predictions mentioned above is dependent on an approximate constancy of certain parameters in the equations used. Although this constancy is apparently surprisingly well fulfilled for most iodine complexes,[18] it has no obvious theoretical basis. On the other hand, a value of 10.3 volts for the ionization potential would give a prediction corresponding to the observed position of the charge-transfer band.

Perhaps the observed 9.8 volts is the first π-ionization potential, but the relevant potential, which should correspond not to a π but to a non-bonding (*i.e.*, "onium" or *n*) ionization potential essentially of the N atom,[14] is higher. However, the absorption spectrum of pyridine suggests that the π and *n* ionization potentials are actually almost equal. This statement is based on the fact that, taking the means of the frequencies of transitions to corresponding singlet and triplet states,[19] the frequencies of the first "*n*–π" and "π–π" transitions are nearly equal. But even if the two ionization potentials are equal one should bear in mind that it has never been proved that, in the so-called *n*–π transitions in the aza-substituted aromatics, the transition is really from a true localized non-bonding (*n*) orbital of the N atom. It would be safer to call such transitions σ–π transitions, where the σ orbital may be only partly localized on the N atom. The appropriate localized N atom true *n* ionization potential required in predicting the location of the charge-transfer band would then correspond to a weighted mean of several σ-ionization potentials and might be appreciably greater than the minimum σ ionization potential.

II. The System Pyridine Plus Iodine in Polar Solvents

A. The Transition to Pure Pyridine as Solvent.—When, in a dilute solution of iodine plus pyridine in heptane, the pyridine concentration is gradually increased, the λ 4,220 Py·I_2 iodine band begins to shift toward shorter wave lengths, and its extinction coefficient increases. The relations between position and ε of the band maximum, and pyridine concentration, are shown in Fig. 6, for a fixed concentration (0.0005 molar) of iodine. (At these concentrations, practically all the iodine should be complexed.) The position of the band approaches a limiting value of 3,890 Å., and ϵ_{max} a limiting value of 2,120 in pure pyridine.[20] These changes, as distinct from some of the phenomena to be described in Part C of this section, are reversible: dilution of the solution with heptane results in a return of the position of the band to λ 4,220 with corresponding diminution in intensity.

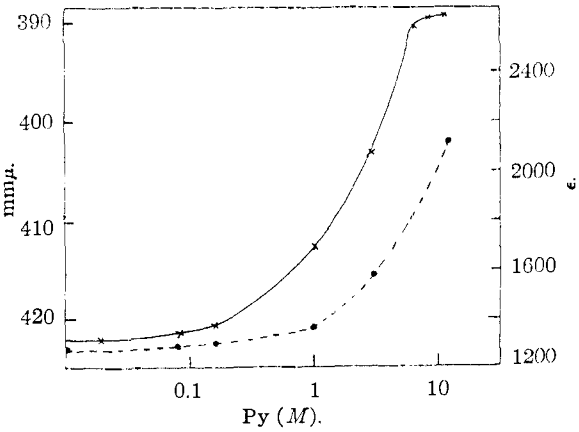

Fig. 6.—Variation in position (×——×) and extinction coefficient (●- - -●) of the Py·I_2 absorption band with increasing pyridine concentration. I_2 = 0.0005 *M*; solvent, heptane; room temperature.

Attempts were made also to see what happens to the "charge-transfer" band at 2,350 Å. as the pyridine concentration is increased. Unfortunately, even using special thin cells (0.001-cm.) constructed by putting a rolled lead spacer between quartz plates the experiments could be carried out only up to 1.5 *M* Py (see Fig. 7). At this Py concentration, with 0.06 *M* iodine, the position of the charge-transfer band appears to be shifted to about 2,450 Å. No appreciable change in the ratio of the pyridine

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(19) *Cf. e.g.*, J. H. Rush and H. Sponer, *J. Chem. Phys.*, **20**, 1847 (1952), Table VII.

(20) Kleinberg and collaborators (ref. 11b), for iodine at 2 × 10^{-4} molar in pyridine, find λ_{max} = 383–380 mμ and ϵ_{max} = 2600–2700. The moderate difference between their results and ours at 5 × 10^{-4} molar can be understood in terms of our findings at high dilution, as reported in section IIC and Fig. 8.

molar absorption to that of the charge-transfer band could be detected.

In connection with the interpretation of the foregoing observations, some unpublished infrared work of Glusker[7] on solutions containing Py and I_2 is highly relevant. He finds no appreciable difference between the modified Py infrared bands in CS_2 solutions very dilute in Py and in those much more concentrated, up to I_2 solutions in pure Py. This strongly indicates that these modified bands are due to essentially the same $Py \cdot I_2$ entity whether the solvent is an inert one (CS_2) or pure Py. The gradual shift of the λ 4,220 $Py \cdot I_2$ band in heptane to λ 3,890 in Py solvent may now probably be attributed to a gradual clustering of polar Py molecules around the strongly polar $Py \cdot I_2$ molecules, causing these to become more polar [increased b in eq. 4] and more stable; but the infrared evidence indicates that these changes cannot be very large.[21]

It was suggested earlier[12] that the "inner complex" of structure $(PyI)^+I^-$ may be so much stabilized by the polar solvent pyridine as to be present in predominant amount in that solvent. But according to the preceding paragraph, it appears that $Py \cdot I_2$ remains predominant even in pure Py, and this suggests that $(PyI)^+I^-$ if present is only in small amounts. The definite presence[9] of the *ions* of $(PyI)^+I^-$ in small concentrations does, however, presumably indicate that a correspondingly small amount of the inner complex itself is present in accordance with eq. 3.[22]

B. **Pyridine Plus Iodine in Other Polar Solvents.**—In order to differentiate between specific effects due to excess pyridine and effects due to increasing polarity of the solvent as pyridine is added to heptane solutions of iodine, attempts were made to study the pyridine–iodine complexes in other polar solvents.

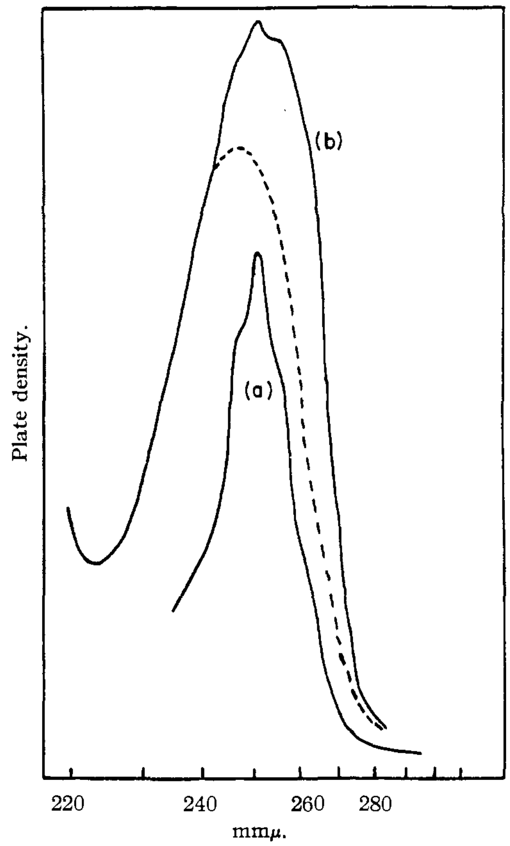

Fig. 7.—Densitometer trace showing (a) 1.5 M pyridine, (b) 1.5 M pyridine + 0.06 M iodine showing charge-transfer peak shifted to about 2,450 Å. and superposed on the pyridine absorption. The dotted curve gives the estimated shape of the charge-transfer band.

Experiments in which pyridine was added to iodine dissolved in methanol were inconclusive because the very strong $MeOH \cdot I_2$ charge-transfer band showed that most of the iodine was complexed with methanol rather than with pyridine. This was true up to concentrations of 4–5% of pyridine, beyond which it was impracticable to go.

When $Py \cdot I_2$ solutions in Py were diluted with water, precipitation of golden-yellow "$Py \cdot I_2$" crystals resulted.[23] Examination of the resulting solutions after filtration showed no trace of the characteristic $Py \cdot I_2$ bands, but only I_3^- bands and visible and charge-transfer bands attributable to small amounts of complexes of I_2 with the solvent.[24] Apparently the solid $Py \cdot I_2$, or perhaps[23] $(PyI)^+I^-$, phase is but little soluble in these solvents.

C. **Very Dilute Solutions of Iodine in Pure Pyridine.**—In pure pyridine at concentrations below about 0.001 molar in iodine, the position and particularly the intensity of the λ 3,890 band become increasingly concentration-dependent (*cf.* Fig. 8), a fact which was not observed by Kleinberg and

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[21] Or perhaps the observed continuously shifting peak is the result of a *superposition* in changing proportions of two distinct bands; if so, these may most probably be attributed to unsolvated and fully solvated $Py \cdot I_2$ molecules. The limiting positions λ 4220 and λ 3890 are so close together (unlike those of the $Py \cdot I_2$ and free I_2 iodine peaks in Fig. 1) that the superposition of two such bands would give a single peak. Another conceivable explanation of the λ 3890 peak, namely, that it might correspond to a superposition of the λ 4220 $Py \cdot I_2$ peak and the λ 3600 I_3^- peak can almost certainly be ruled out because these peaks are too far apart. [A very small, probably negligible, amount of the very strongly absorbing ion I_3^- should be present in equilibrium in accordance with eqs. 6 and 7 of section IIC. In addition, the possible presence of a trace of water or other impurities should give rise to additional I_3^-, but probably not enough to affect the observed absorption appreciably except for the very low I_2 concentrations discussed in section IIC.]

[22] The present work does not throw doubts on the concept of an "inner complex" as discussed in reference 1b, but indicates that the inner complex of $Py \cdot I_2$ is *not so low in energy* as was at first surmised. (Consideration of the system $I_2 + H_2O$ similarly indicates that there, too, the inner complex $(H_2OI)^+I^-$ in water solution is a structure of higher energy than the outer complex $H_2O \cdot I_2$.) It is conceivable, however, that the solvated inner complex or ion-pair $(PyI)^+I^-$, while separated by a considerable activation barrier from the lower-energy outer complex, may be somewhat unstable with respect to the interposition of a Py molecule between the $(PyI)^+$ and I^- ions, so that instead of the equilibria (2) and (3) one has something like

$$Py \cdot I_2 + Py \rightleftarrows (PyI)^+(Py)I^- \qquad (2')$$

$$(PyI)^+(Py)I^- \rightleftarrows PyI^+ + I^- + Py \qquad (3')$$

all participants in (2′) and (3′) being of course solvated. If more than one Py is interposed between $(PyI)^+$ and I^-, the Py may be regarded simply as a dielectric medium separating the ions.

[23] An X-ray study of these crystals would be of interest. It seems possible that they may be built from $(PyI)^+$ and I^- ions (*cf.* ref. 3b, section VI, and the discussion of $NH_4^+ + Cl^-$ crystals on p. 811 of section VIII), although their insolubility in water seems to indicate the contrary.

[24] L. I. Katzin [*J. Chem. Phys.*, **21**, 490 (1953)] has studied the spectra of solutions of iodine in water and the alcohols and has demonstrated the presence of I_3^-, probably due largely, however, to the presence or formation of I^- from impurities.

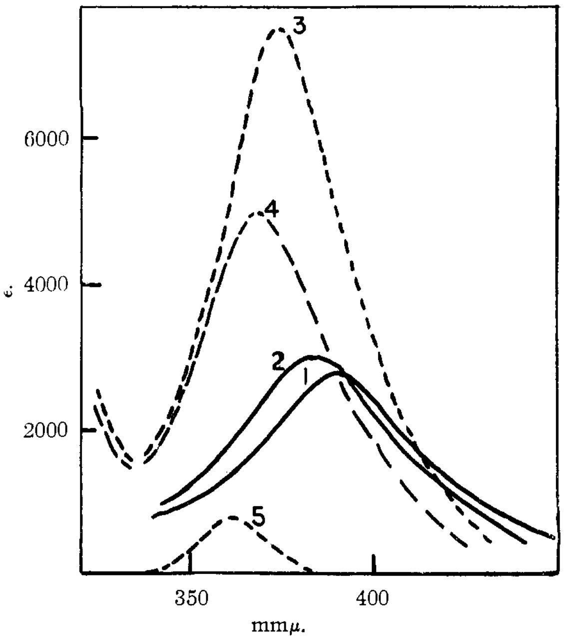

Fig. 8.—Increasing dilution (1–5) of I_2 solution in pure Py. Solid curves 1 and 2 are essentially due to $Py \cdot I_2$. Curve 3 shows the I_3^- curve nearing its maximum value. In curves 4 and 5 the I_3^- intensity falls again presumably because of dissociation into I^- ions. All ε values are based on formal I_2 concentration: 1, 0.025 *M;* 2, 0.0005 *M;* 3, 0.00005 *M;* 4, 0.0000125 *M;* 5, 0.00000612 *M;* 6, 0.00000306 *M.*

his associates[11b,20] because their cell thickness could be changed only by a factor of two, whereas it was varied by a factor of >1,000 in the experiments here described.

Strong dilution of more concentrated pyridine solutions (>0.07 molar), or the preparation of more dilute ones from pyridine and solid iodine, results in an *instantaneous* shift in the band maximum, accompanied by an increase in extinction coefficient (*cf.* Fig. 8, curves 1–3). If the dilution is to between 10^{-4} and 10^{-6} molar, the maximum shifts to 3,680 Å. and the apparent extinction coefficient based on I_2 rises to a maximum value of 9,000. The simultaneous appearance of a characteristic band of nearly double the extinction coefficient at 2,875 Å. makes it fairly certain that the maximum at 3,680 Å. is due to I_3^- ions. (The usual absorption spectrum of I_3^- consists of two peaks, one at λ 3,650 and one of nearly double as great peak intensity at λ 2,950.[25]) The observed maximum extinction coefficient suggests that under optimum conditions about four I_2 molecules yield one I_3^- group. This would indicate that about half the iodine remains as $Py \cdot I_2$, but that about half has reacted instantaneously in some way involving the formation of I^- followed by

$$Py \cdot I_2 + I^- \rightleftarrows I_3^- + Py \qquad (6)$$

If dilution is continued below 10^{-5} molar, a new phenomenon is observed. The I_3^- peak near λ 3,650 diminishes rapidly in intensity (*cf.* Fig. 8, curves 4 and 5), and no new band appears in the visible or ultraviolet to take its place. This change occurs just below the concentration range where Audrieth and Birr[8] reported the onset of anomalously high conductivity,[26] and may be attributed to redissociation of I_3^- ions, by a reversal of eq. 6 accompanied by a passage of eq. 5 to the right, as is to be expected at sufficiently high dilutions; the net result would be

$$I_3^- + Py \longrightarrow (PyI)^+ + 2I^- \qquad (7)$$

Conceivably also

$$\left\{\begin{array}{ll} Py + PyI^+ \rightleftarrows 2Py^+ + I^- & (8) \\ Py^+ + Py \longrightarrow Py^+Py & (9) \end{array}\right.$$

In all the reactions (5–9), the ions should of course be solvated. It is of interest that the ion Py^+, containing an odd electron, should be paramagnetic. Such an ion in Py solution should at once acquire extra stability by the formation with Py according to eq. 9 of an interesting ion of biphenyl-like structure with a three-electron bond between the two nitrogen atoms and further stabilized by various kinds of conjugation or resonance; this ion would still be paramagnetic.

Since our results were obtained under conditions of moisture-exclusion less rigorous than those of Kortüm and Wilski, it seems possible that the almost instantaneous I_3^- ion production which we report in the 10^{-4} to 10^{-5} molar concentration range may be moisture-dependent. Or conceivably it may have been due somehow to impurities or to side-reactions which had occurred in spite of all precautions. It is known that in water or the lower alcohols I_3^- ions in erratic amounts are instantaneously formed from dissolved iodine, probably largely as a result of the presence of impurities and/or side-reactions which form I^-.[24]

If we suppose, however, that our solutions were free from side-reactions or other foreign sources of I^-, and that the only important equilibria involved were (1), (5) and (6), it can be shown that the relative concentration of I_3^-, that is, the ratio $(I_3^-)/(Py \cdot I_2)$, should be small and approximately constant in the higher ranges of total iodine concentration, but should slowly *diminish,* not strongly increase as we observed, at high dilutions. Hence it may be that our results at high dilutions were due to impurities or side-reactions which somehow gave rise to I^- in relative concentrations which became large enough to form spectroscopically noticeable amounts of I_3^- near 10^{-4} molar iodine concentration[27]; the observed subsequent redissociation of this I_3^- at higher dilutions according to eq. 7 would be exactly what one should expect. Conceivably (although this seems very unlikely) the rise in I^-, hence in I_3^-, below 10^{-4} molar, might be due to reactions (8)–(9). To obtain a more reliable understanding of what actually happens at high dilution, further investigations will be required.

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(25) (a) A. D. Awtrey and R. E. Connick, This Journal, **73**, 1842 (1951); (b) R. E. Buckles, J. P. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952).

(26) The occurrence of eqs. 7–9 would account for the anomalously high conductivity observed by Audrieth and Birr without assuming the presence of Py^{++} ions as they did. However, since these results of Audrieth and Birr were obtained from aged solutions, after occurrence of what other investigators (ref. 9 and 11) consider to be a slow ring iodination liberating I^- ions, it would seem that their results may not be relevant to what occurs in pure Py without side-reactions.

(27) Our results and conclusions at higher concentrations in pyridine, and our results in heptane solution, are not called in question by this possibility.