[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS]

Infrared Spectra of Pyridine Coördinated Iodine(I) Salts[1]

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RECEIVED JULY 31, 1958

The infrared absorption spectra of nine pyridine coördinated positive iodine salts containing both organic and inorganic anions and of pyridinium iodide have been determined. These compounds have remarkably similar spectra characterized by bands related to those of pyridine in the same region. The observed shifts in some of the pyridine infrared absorption bands can be correlated with those observed for solutions of iodine in pyridine. The results are discussed in the light of previously reported ultraviolet and conductivity studies, and it is suggested that the iodine–pyridine complex has greater polar character than has been previously assumed. The nature of the changes in the infrared spectrum of pyridine which result from coördination with iodine suggests that the 990 cm.$^{-1}$ band of pyridine should be assigned to a hydrogen deformation mode rather than a ring vibration. The preparation of two new compounds, (IPy)CN and (IPy)F, is described. The fluoride is of special interest because of the non-existence of free IF.

Introduction

The nature of solutions of iodine and of iodine halides in pyridine has been the subject of numerous investigations[2] during recent years. The major effort has been devoted to studies of ultraviolet spectra and, to a lesser extent, to the conductivity of such solutions. As regards the nature of pure iodine in pyridine, it is now generally agreed that iodine forms a stable molecular complex with pyridine and that the following equilibria are involved in such solutions

$$\mathrm{Py} + \mathrm{I_2} \rightleftharpoons \underset{\text{"outer complex"}}{\mathrm{Py{\cdot}I_2}} \rightleftharpoons \underset{\text{"inner complex"}}{(\mathrm{PyI})^+\mathrm{I}^-} \rightleftharpoons (\mathrm{PyI})^+ + \mathrm{I}^-$$

On the basis of ultraviolet studies, Reid and Mulliken[2d] concluded that the outer complex, $\mathrm{Py{\cdot}I_2}$, represents the predominant species. The work of Kortum and Wilski[2a] has definitely corroborated previous suggestions that definite concentrations of the ions $(\mathrm{IPy})^+$ and I^- exist in pyridine–iodine solutions. Recent spectrophotometric evidence[2f] has shown that an analogous situation exists in the case of the molecular complexes formed between iodine monochloride and iodine monobromide with pyridine. The stability of these complexes was found to parallel the electronegativity of the anion, the chloride being the most stable in the series $\mathrm{PyICl} > \mathrm{PyIBr} > \mathrm{PyI_2}$. It was also shown that when dissolved in acetonitrile, the pyridine coördinated iodine cation is formed from each complex.

Recent studies by Ham, Rees, Walsh[3] and Mulliken, Glusker and Thompson[4,5] have revealed that the infrared spectrum of pyridine is markedly altered by the addition of iodine. Not only were characteristic pyridine absorption bands shifted or changed in intensity, but new ones were formed. The spectral changes were explained on the basis of the formation of a highly polarized "inner complex," or of the actual ions, $(\mathrm{IPy})^+$ and I^-.

The purpose of the present investigation was to determine whether salts of the type (IPy)X and $(\mathrm{IPy_2})\mathrm{X}$ possess infrared absorption bands which correspond to the new bands reported in the infrared spectrum of iodine–pyridine solutions. Inasmuch as these salts contain the $(\mathrm{IPy})^+$ radical and can be prepared as well characterized solids,[6,7] their infrared absorption may enable one to study the effect of the pyridine–iodine coördination on the infrared absorption of pyridine.

Experimental

Pyridine.—Reagent grade pyridine was dried over sodium hydroxide and barium oxide for several weeks. The final product was distilled from fresh barium oxide and the fraction having a constant b.p. of 114.5° at 750 mm. was collected.

Carbon Tetrachloride and Carbon Disulfide.—Spectroscopic grade reagents were used without further purification. The solvents were stored over calcium chloride and filtered before use.

Preparation of Positive Iodine Salts.—Monopyridineiodine(I) benzoate and acetate, and dipyridineiodine(I) perchlorate and nitrate were prepared according to methods previously described.[6,7] The identification of the compounds was established by iodine analysis[7] and by melting point. The molecular complexes formed by iodine monochloride and iodine monobromide with pyridine were prepared according to the method of Popov and Rygg[2f] and were also checked by iodine analysis and melting point. All the salts were stored in a desiccator over barium oxide.

Pyridinium Iodide.—Equimolar quantities of pure pyridine and concentrated (47%) C.P. hydriodic acid were evaporated over a steam-bath. The crystals which formed were slightly contaminated with iodine and were recrystallized several times from absolute ethanol in the presence of decolorizing charcoal. The colorless crystals melted at 192–195°.

Monopyridineiodine(I) Cyanide.—In 200 ml. of dry chloroform was suspended 13.4 g. (0.1 mole) of dry, powdered silver cyanide[8] to which was added 15.8 g. (0.2 mole) of pyridine. Addition of the pyridine caused some reduction of the silver salt which was indicated by the blackening of the surface. Powdered iodine was added in small portions, with continual stirring,[9] and silver iodide formed rapidly. Addition of iodine was continued until 23 g. (0.18 mole), corresponding to 90% of the stoichiometric maximum possible according to the following reaction, had been added.

$$\mathrm{AgCN} + \mathrm{I_2} + \mathrm{Py} \longrightarrow \mathrm{AgI} + (\mathrm{IPy})\mathrm{CN}$$

The entire theoretical quantity was not used because previous experience indicated that a cleaner, purer product is obtained if the reaction is stopped before the entire amount

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[1] Presented before the Division of Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

[2] (a) G. Kortum and H. Wilski, *Z. physik. Chem.*, **202**, 35 (1953); (b) R. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **73**, 88 (1951); (c) J. Kleinberg, E. Colton, J. Sattizahn and C. A. VanderWerf, *ibid.*, **75**, 447 (1953); (d) C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954); (e) A. Popov and R. T. Pflaum, *ibid.*, **79**, 570 (1957); (f) A. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957). The foregoing is by no means intended to represent an exhaustive bibliography, but the interested reader will find most of the other pertinent studies cited as footnotes in these references.

[3] N. S. Ham, A. Rees and A. Walsh, *Nature*, **169**, 110 (1952).

[4] D. L. Glusker, H. W. Thompson and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1407 (1953).

[5] D. L. Glusker and H. W. Thompson, *J. Chem. Soc.*, 471 (1955).

[6] H. Carlsohn, "Uber eine neue Klasse von Verbindungen des positiv Einwertigen Jods," Verlag von S. Hirzel, Leipzig, 1932.

[7] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **71**, 575 (1949).

[8] The reaction was also attempted using mercuric cyanide, but the red complex, dipyridinemercury(II) iodide, is quite soluble in chloroform and makes isolation and separation of the product difficult.

[9] Precautions should be taken to exclude atmospheric moisture throughout the course of this preparation.

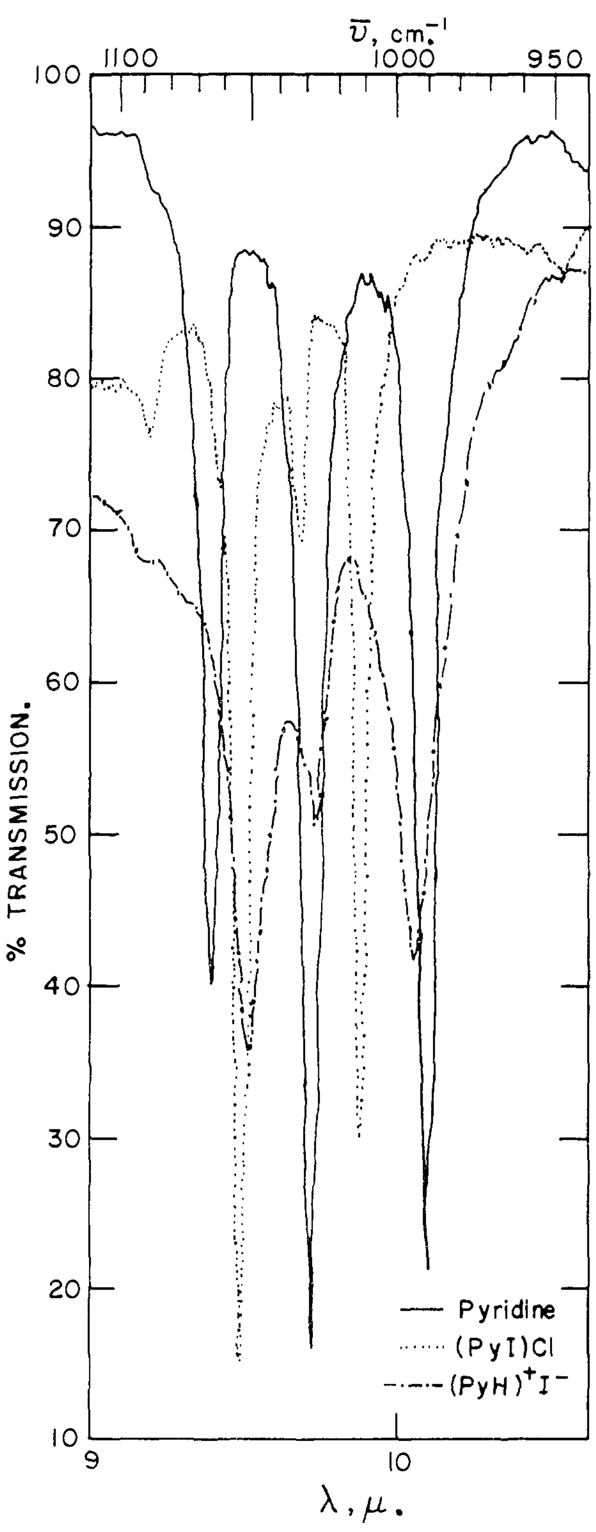

Fig. 1.—Infrared spectra of pyridine, monopyridineiodine(I) chloride and pyridinium iodide in 1000 cm.$^{-1}$ region.

of iodine is added. The pale amber filtrate was then separated from the silver iodide and excess silver cyanide by filtration through a sintered glass filter, care being used to exclude atmospheric moisture. The filtrate was evaporated continually at a pressure of about 1 mm. of mercury at Dry Ice temperature.[10] After 3 days a crop of orange needles was formed. These orange crystals, corresponding to the formula PyICN, decomposed, even in a dry atmosphere, after standing for a few hours at room temperature. They remained stable for a period of ten days stored *in vacuo* at Dry Ice temperature. Heating in a glass tube caused slow decomposition, beginning at 34° which became very rapid and complete at 50–53°. However, the product should be identified by analysis rather than melting point. Iodine was determined by titrating the free iodine liberated when the (IPy)$^+$ ion oxidizes iodide.[7] *Anal.* Calcd. for $C_6H_5N_2I$: I, 54.7. Found: I, 54.0.

Monopyridineiodine(I) Fluoride.—This preparation was analogous to that described in the preceding paragraph except for the following. Silver(I) fluoride (0.1 mole) was used instead of the cyanide, the volume of chloroform was 140 ml., and only a 20% excess of pyridine (0.12 mole) was used. The addition of iodine was stopped after only 19.8 g. (*ca.* 80% of the theoretical maximum) had been consumed. Further addition caused no further precipitation of silver iodide and the solution was colored by unreacted, free iodine. Following removal of the precipitated silver iodide and excess silver fluoride, the filtrate was evaporated to 100 ml.[11] at reduced pressure from a Dry Ice bath. The filtrate was then diluted with 150 ml. of petroleum ether which caused a heavy brown layer to separate. After storage for 48 hr. in a Dry Ice chest the latter yielded a deposit of pale yellow crystals. These were removed from the mother liquor in a moisture-free atmosphere and washed with sodium dried ethyl ether. Analysis for iodine corresponded to the compound (IPy)F. The crystals decomposed over the range of 80–97°, with rapid, complete decomposition occurring at 95–97°. *Anal.* Calcd. for C_5H_5NIF: I, 56.4. Found: I, 57.2.

Solutions.—All solutions of the salts were prepared by dissolving weighed amounts of the solid in appropriate volumes of solvent.

Solids.—Solids were examined as potassium chloride pressed plates. About 1.2–1.4 mg. of the salt was powdered intimately with 0.4 g. of specially prepared and purified potassium chloride. The ground sample was pressed in a Beckman polished stainless steel die for a minimum of 5 minutes at 20,000-lbs. pressure.

Infrared Measurements.—The spectra were obtained using a Beckman IR-4 with standard sodium chloride optics as a double beam instrument. It was found necessary to place a pellet of pressed potassium chloride as a blank in the reference beam. The measurements were made in a temperature controlled room at about 25°.

Results and Discussion

The infrared absorption spectra of a positive iodine salt, of pyridine and of pyridinium chloride in the 950–1100 cm.$^{-1}$ region are shown in Fig. 1. The location, relative intensity and width of the absorption bands typical of pyridineiodine(I) salt can be compared with those of pyridine and pyridinium ion in this region. It should be noted that the pyridine band at 990 cm.$^{-1}$ was observed as a well defined singlet at 989 cm.$^{-1}$, using the highest resolution obtainable with this instrument. Glusker and Thompson[5] also reported this band as a singlet at 990 cm.$^{-1}$, but Ham, *et al.*,[3] observed it as a doublet at 990 and 996 cm.$^{-1}$. The discrepancy has little bearing on the results of this investigation, but it merits mention as a possible impurity in this pyridine.

The data for all the compounds investigated are listed in Table I along with those previously reported for iodine and iodine cyanide solutions in pyridine. There is a remarkable similarity in the infrared absorption of these compounds as compared with that of either iodine or iodine cyanide in pyridine. This similarity involves not only the location of their own characteristic absorptions,

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(10) Attempts to evaporate the solvent at room temperature, or even at ice–salt temperatures, led to decomposition.

(11) Attempts to evaporate the filtrate to dryness at low pressure, even at Dry Ice temperature, caused heavy evolution of gaseous iodine, indicating decomposition of the product.

TABLE I

INFRARED ABSORPTION OF PYRIDINE AND PYRIDINE COÖRDINATED IODINE(I) SALTS

	Compound	Physical state	Location of band (cm.$^{-1}$)									
1	Pyridine	Liquid, 10% in CS_2	1070			1027		989	750	710		675
2	Iodine[a]	Satd. soln. in Py		1060	1031		1005		755		692	
3	ICN[a]	Satd. in CS_2 + 15% Py		1065	1030		1002		747		705–692	
4	(IPy) acetate	10% in $CHCl_3$		1065	1035		1011					
5	Same as 4	Solid		1065	1035		1012	Obscured by acetate			693	
6	(IPy) benzoate	10% in $CHCl_3$		1065	1035	1026[b]	1012					
7	Same as 6	Solid		1065	1035	1025[b]	1012			750	703	
8	Same as 6	10% in Py		1065	1033		1012					
9	(Ipy)CN	10% in $CHCl_3$		1060	1034		1005	Obscured by solvent				
10	Same as 9	10% in CS_2		1065		1028	1001			748	703	
11	(IPy)F	Solid		1056	1032	1027	1014	Very broad			688	
12	(IPy)Cl	Solid		1054	1033		1012		751		693	
13	(IPy)Br	Solid		1057	1031		1011		750		688	
14	$(IPy_2)ClO_4$	Solid		[c]	[c]		1014		753		692	
15	$(IPy)NO_3$	Satd. in $CHCl_3$[d]		1060	1031		1012			750–690		
16	$(IPy_2)NO_3$	*Solid*		*1057*	*1035*		*1013*		*752*		*692*	
17	$(PyH)^+I^-$	Solid		1051	1030			995	748			675

[a] From data of Glusker and Thompson.[5] [b] Probably aromatic ring vibrational frequency. [c] Examination obscured by intense ClO_4^- absorption in this region. [d] Only slightly soluble.

but also their relationship to the disappearance and change in intensity of the pyridine bands.

The 990 cm.$^{-1}$ band of pyridine, which is shifted by 15 cm.$^{-1}$ to 1005 cm.$^{-1}$ upon the addition of iodine, is shifted even further in the case of each of the salts[12] to a frequency of from 22–25 cm.$^{-1}$ higher. This[12] is the most intense of the absorption bands in the 1000 cm.$^{-1}$ region. The data show that the location of the bands is almost unaffected by the solvent[12] (Table I, 4–8), physical state or number of moles of base coördinated (Table I, 14–16). When iodine is added to pyridine, the 1027 cm.$^{-1}$ band of pyridine is shifted to 1031 cm.$^{-1}$ and is largely diminished in intensity. This effect is noted for all the pyridineiodine(I) salts. Although of weak or medium intensity, a sharply defined band is always present at 1030–1035 cm.$^{-1}$ for each positive iodine compound studied. There is a shift of the 1070 cm.$^{-1}$ pyridine band to a lower frequency at 1060 cm.$^{-1}$ upon the addition of iodine, which is noted also for the cationic iodine salts. This band is extremely well defined and its intensity is almost equal to that of the 1010 cm.$^{-1}$ band. The characteristic absorption bands located at the longer wave lengths also parallel those of the iodine–pyridine system. The 675, 710 and 750 cm.$^{-1}$ pyridine bands are observed as two bands; the first, unchanged at about 750 cm.$^{-1}$, and a second, at an intermediate frequency of 688–703 cm.$^{-1}$.

These observations strongly confirm the hypothesis that the iodine–pyridine complex is an extremely stable one. The foremost question at the present time concerns itself with the structural nature of the species formed.

Although complete dissociation into ions (IPy^+ and I^-) has been suggested,[2b] recent conductivity studies[2a] have established that, while such ionization does, in fact, take place, it is only very slight. In a recent critical survey of this problem,[2d] it has been suggested that the predominant species is $Py \cdot I_2$, the outer complex, possessing about 25% ionic character.

Further consideration of the shift in the 989 cm.$^{-1}$ band of pyridine as related to the electronegativity of the anionic portion of the pyridine coördinated iodine(I) salt is significant. It is reasonable to assume that in a series of compounds of the type IX, structures of the type $I^+ X^-$ should become increasingly contributory as the electronegativity of substituent X increases. The ionic structure should be stabilized upon coördination with a base such as pyridine. Evidence of such stabilization is manifest in the very existence of solid positive iodine salts, the transformation of ICl and IBr into solids having much higher melting points and in the stabilization of non-existent, free IF[13] by coördination with pyridine. It is interesting to note that the shift in the 989 cm.$^{-1}$ band of pyridine seems to be directly related to the electronegativity of the anionic substituent. Among the interhalogens themselves we observe this band at a maximum frequency of 1014 cm.$^{-1}$ for the fluoride, then shifting gradually to slightly lower frequencies of 1012 and 1011 cm.$^{-1}$ for the chloride and bromide and finally to 1005 cm.$^{-1}$ for the iodine–pyridine system. The only other salt possessing an absorption band at a frequency as high as the fluoride is the perchlorate, and this would be expected to be highly ionic. The consistency in the intensity and the location of the 1012 cm.$^{-1}$ band throughout the whole series of positive iodine salts suggests that this band must be related to the IPy^+ grouping and that it results directly from the effect of this coördination on the vibration giving rise to the 990 cm.$^{-1}$ band of pyridine. Since the shift, in the case of iodine–pyridine solutions, is only 60% as great as that observed for the positive iodine salts, it is clear that the polarization is not sufficient to bring about formation of a species which is polarized to the extent to which it occurs in the solid IPy^+ salts.

The conclusions to be drawn from these data concerning the nature of the iodine–pyridine complex are in essential agreement with the model sug-

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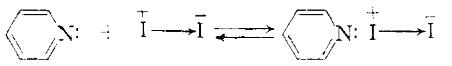
[12] With the exception of (IPy)CN which will be discussed independently.

[13] The existence of free IF based on studies of the band spectrum of the iodine–fluorine flame has been reported; see R. A. Durie, *Proc. Roy. Soc.* (*London*), **207**, 380 (1951).

gested by Reid and Mulliken.[2d] The marked effect of iodine on the infrared spectrum of pyridine together with the absence of solvent effects[14] on the infrared absorption of the positive iodine salts requires that the complex is, *per se*, highly polarized, the ionic character being perhaps greater than 25%. The simplest and most satisfactory representation of the pyridine–iodine complex and its formation, based on all studies to date, may be given in the following manner. The pyridine polarizes the iodine molecule resulting in structures of the type, $\overset{+}{I}\rightarrow\overset{-}{I}$, and the resultant polarized molecule is then stabilized through coördination with pyridine forming a polar complex approaching the ionic structure $(PyI^+)I^-$. This can be indicated as



the simplest picture being given by $(Py^+I\rightarrow I)$. The distribution of the positive charge throughout the aromatic ring would greatly stabilize such a structure.

The results reported in a recent paper by Person[15] and co-workers are highly relevant. They investigated the shift of the ICl fundamental at 385 cm.$^{-1}$ in various solvents and observed a very large change in pyridine solution. Their results suggest that the ionic structure IPy^+Cl^- may contribute as much as 50% to the structure of the ICl–pyridine complex. They further propose for the pyridine interhalogen complexes a type of bonding approaching that found in hydrogen bonded structures. It is clear that the experimental data presented here leads to conclusions which parallel these almost exactly.

A more quantitative understanding of this problem should result from an X-ray investigation[16] on positive iodine salts.

In contrast with the behavior of the other salts, the cyanide complex (Table I, 9, 10) exhibits an appreciable shift in its infrared absorption in different solvents. In mildly polar chloroform the absorption bands are almost identical with those of iodine in pyridine. In carbon disulfide, each of the three bands is located more closely to those of pure pyridine. In every respect, the pyridine–ICN complex appears to be less polar and less stable than the parent ICN. Its thermal stability and chemical stability are much lower than that of free ICN and its solubility is limited to non-polar solvents (CS_2, CCl_4, $CHCl_3$) in contrast with ICN (soluble in ether and alcohol). It has already been mentioned in the Experimental part that this compound could only be made and kept at very low temperatures. The pyridine coördinated ICN possesses a pair of bands of weak intensity at 2340 and 2460 cm.$^{-1}$. These are probably associated with the C≡N link, although at a somewhat higher frequency than the 2300–2000 cm.$^{-1}$ region where covalent nitrile absoprtion is expected.[17] Cyanogen iodide possesses a 2167 cm.$^{-1}$ band[5] which has been attributed to C≡N.

The compound, (PyI)F, as expected, possesses decidedly polar characteristics. It is insoluble in CCl_4, $CHCl_3$ or CS_2 and readily dissolves in ethanol and acetone, but with subsequent decomposition. On contact with water, gross decomposition occurs instantaneously. Atmospheric moisture also causes rapid decomposition. Both the chemical and physical properties of PyIF and PyICN are being further investigated.

Further consideration of the data leads to some pertinent conclusions concerning the assignments of the pyridine absorption bands in the 1000 cm.$^{-1}$ region. The bands in this region are either ring vibrations or hydrogen deformation. modes.[18] It would be expected that formation of the pyridinium ion $(PyH)^+$ should bring about greater shifts in the ring vibrational frequencies since the formation of this ion causes very strong polarization within the aromatic ring. Reference to Table I and to Fig. 1 shows that formation of the pyridinium ion results in only a very small shift to 995 cm.$^{-1}$ in the 989 cm.$^{-1}$ band of pyridine, but a significant shift, larger than that observed for any of the IPy^+ salts, in the 1070 cm.$^{-1}$ band to 1051 cm.$^{-1}$ The effect on the 1027 cm.$^{-1}$ band is about the same as that observed for the positive iodine salts; shifted slightly to 1030 cm.$^{-1}$ and largely diminished in intensity. It seems reasonable to conclude that since coördination with the much less electropositive iodine leads to a larger shift in the 989 cm.$^{-1}$ band of pyridine, than does the very strong coördination of the ring nitrogen with the small, highly charged proton, the band should be assigned to a hydrogen deformation mode. The very large, polarized iodine atom could approach very closely the field of the adjacent hydrogens and thus affect their normal bending modes.[19]

Similar reasoning suggests that the 1070 cm.$^{-1}$ band of pyridine should result from ring vibrations. The shift would be expected to be proportional to the degree of polarization, and the formation of the pyridinium ion leads to a maximum observed shift of 19 cm.$^{-1}$. To give this argument further support it is to be noted that those positive iodine salts which have maximum polar character (those with the most electronegative anions) show a significantly greater shift. Thus, the 1070 cm.$^{-1}$ band is shifted from 13 to 16 cm.$^{-1}$ for the halide complexes (Table I, 11, 12, 13), but only 5 cm.$^{-1}$, to 1065 cm.$^{-1}$, for the much more covalent substit-

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(14) Reid and Mulliken (ref. 2d, p. 3873) attributed considerable importance to the similarity of infrared spectrum of pyridine–iodine in non-polar CS_2 and in pure pyridine. Our results (see Table I, 4,5, 6,7,8) indicate that the changes in the pyridine spectrum are due entirely to pyridine–iodine coördination and are not significantly affected by the physical state or polarity of the solvent.

(15) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958).

(16) Such studies are currently being undertaken by Dr. E. A. Meyers of this department. This should establish the existence (or non-existence) of the IPy^+ ion as a discrete entity. Nitrogen–iodine and interhalogen distances in these complexes may also become available.

(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 223.

(18) Ref. 17, p. 235.

(19) There is a strong similarity in a not quite analogous situation in that the absorption of what we are also calling the hydrogen deformation for benzene at 1040 cm.$^{-1}$ is no longer present in iodobenzene but is changed to three new intense bands at slightly different frequencies.[20] The large, polarized iodine atom is probably exerting appreciable force on the adjacent ring hydrogens in both iodobenzene and in the IPy^+ ion.

(20) Spectra Nos. 579 B and 2891, Samuel P. Sadtler and Son, Inc. Phila. 7, Pa.

uents, acetate and benzoate (Table I, 4–8).

This investigation is being extended to include the salts of iodine(I) coördinated with the picolines, quinoline and other amines, as well as analogous compounds of bromine(I).

COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY POLYTECHNIC INSTITUTE OF BROOKLYN]

Photoreduction of Acridine Dyes[1,2]

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RECEIVED SEPTEMBER 5, 1958

A number of acridine dyes in the presence of allylthiourea are reduced to their leuco forms on irradiation with blue light. Those acridines which have amino substituents in both the 3- and 6-position undergo photoreduction rapidly. Another group of acridines undergoes photoreduction at one tenth the rate of the first and a third group exhibits no reactivity. A correlation exists between phosphorescence of the dyes and their ability to undergo photoreduction. The detailed kinetics of photoreduction of proflavin at its *p*H for maximum rate, namely *p*H 4, coupled with flourescence studies showed that: (a) the reduction proceeds through a long-lived excited state, (b) the transition from the first singlet excited state to the long-lived state is induced by dye molecules in the ground state, (c) the inductive forces of interaction act over distances of 500 Å.

Introduction

An examination of a wide variety of water-soluble dyes shows that dyes of only a few families are susceptible to photoreduction. Kinetic studies of photoreduction of the fluoresceins,[3,4] of the thiazines[5] and of the basic triphenylmethanes in the bound state[6] have shown that the reaction proceeds *via* a long-lived excited state. The acridine dyes are noted for their resistance to reduction in the dark.[7,8] Acriflavin, however, under certain conditions, does undergo photoreduction.[9]

The present paper is concerned with the photoreductive properties of a large number of acridine dyes in order to investigate the generality of the role played by the long lived state and to correlate structure, luminescence and photoreducibility. As will be shown, the kinetics of photoreduction of proflavin reveals a number of unusual features, in particular, energy transfer processes involving action over extremely long distances.

Experimental

A. **Materials.**—The practical grade of 3,6-diaminoacridine, obtained as the sulfuric acid salt (mol. wt. 307, Eastman Organic Chemicals), was purified by treating an aqueous solution with activated charcoal. The solution was then concentrated, chilled overnight, filtered and rinsed with a little ethyl ether. The precipitate was air-dried and then dried overnight in a vacuum oven at 70°.

The following persons and institutions graciously donated purified samples of acridine dyes, listed in Table I: Dr. Adrien Albert, The Australian National University, Canberra, A. C. T. (compounds 1b, 1d, 1e, 2b, 2c, 3a, 3d, 3f and 3g); Dr. Peter P. H. De Bruyn, the University of Chicago, Illinois (compounds 2a, 2d, 3b and 3e); General Aniline and Film Corp. (compound 1g); Abbott Labs. (compound 2e); and Sterling–Winthrop Research Institute (compound 3c). Compounds 1c and 1f are commercially available (National Aniline) and were used as received.

Allylthiourea (Eastman) was decolorized with charcoal and recrystallized from acetone. Ascorbic acid (Hoffmann–LaRoche Inc.) was U. S. P. grade. All other reagents were C.P. grade. Helium (Airco) was used to flush oxygen from reactant solutions.

B. **Procedures.**—A representative photoreductive solution consisted of proflavin (10^{-6} to 10^{-4} mole/liter), allylthiourea (10^{-2} mole/liter), in water, buffered to *p*H 4.0 (10^{-2} mole/liter sodium dihydrogen phosphate or potassium hydrogen phthalate, brought to the desired *p*H with sodium hydroxide or hydrochloric acid). The solutions were deaerated with helium 15 minutes prior to and then during illumination, in cells of 5 × 5 cm. cross-section and 1 cm. thickness. The period of deaeration proved to be adequate as judged by the fact that the initial rates of photoreduction were unaffected by longer periods.

TABLE I

THE ACRIDINE DYES AND THEIR SPECTRA ABSORPTION MAXIMA[a]

Class I. 1a. 3,6-Diaminoacridine, proflavin[b] (444); 1b. 3,6-diamino-10-methylacridinium chloride, euflavin[b] (452); 1c. 2,7-dimethyl-3,6-diaminoacridine, acridine yellow[b] (442); 1d. 2,7-dimethoxy-3-6-diaminoacridine (445); 1e. 3,6-diamino-4,5-dimethylacridine (452); 1f. 3,6-bis-(dimethylamino)-acridine, acridine orange[b] (494); 1g. 2,7,9-trimethyl-3,6-diaminoacridine (437).

Class II. 2a. Atebrin[b] (445, 425, 340); 2b. 9-(β-hydroxyethylamino)-acridine (433, 410, 390;) 2c. N,N′-bis-(9-acridyl)-ethylenediamine (440,[c] 410); 2d. 10-methylacridinium chloride (410, 358, 340); 2e. 9-(*p*-cyclohexyloxyphenyl)-10-methylacridinium chloride, acrizan R chloride[b] (430, 360)

Class III. 3a. 2-Aminoacridine (460, 370); 3b. 3-aminoacridine (460, 370); 3c. 9-aminoacridine (425, 400, 380); 3d. 2,6-diaminoacridine (490, 368); 3e. 2,7-diaminoacridine (490, 368); 3f. 3,7,9-triaminoacridine (445); 3g. 9,9′-bis-(36,-diamino-10-methylacridinium)-dinitrate, bis-trypaflavin[b] (475).

[a] All spectral maxima (in mμ) and the photoreductive property classification refer to solutions buffered in the range of *p*H 2.5–4. [b] The trivial name of the dye is given. [c] A shoulder and not a peak is present.

For relative rate measurements the sample cell was illuminated with white light from a 500-watt tungsten lamp TDC slide projector (stabilized with a Sola constant-voltage transformer) at a distance of 15 cm., through a Corning No. 3389 near ultraviolet cut-off filter. Interference filters of 100 Å. band width (Photovolt Corp., N. Y. C.) were employed directly in front of an RCA No. 931-A photomultiplier tube. With each dye an appropriate interference filter was chosen which had its maximum transmission at the maximum of the absorption band of the dye. The relative transmittances of the solutions were measured

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[1] This paper represents a part of the dissertation submitted by Frank Millich to the faculty of the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1182 and under Contract No. AF 19(604)-3065.

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