rapidly, with evolution of large amounts of HF, and finally set to red gels.

Acknowledgment.—The authors are pleased to acknowledge their indebtedness to Dr. E. R. Blout for suggesting this work, to Drs. M. S. Simon, S. G. Cohen and H. C. Haas for many helpful discussions, and to Miss Adelaide Sutton for infrared spectroscopy.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LEHIGH UNIVERSITY]

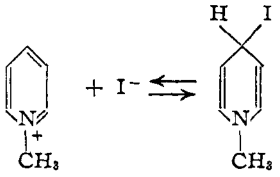
Additions to Pyridinium Rings. II. Charge-Transfer Complexes as Intermediates

BY EDWARD M. KOSOWER AND PAUL E. KLINEDINST, JR.[1]

RECEIVED NOVEMBER 29, 1955

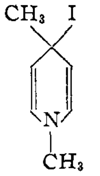
Investigation of the spectra of aqueous solutions of substituted 1-methylpyridinium iodides provides evidence that the new species, previously shown to be present in solutions of 1-methylpyridinium iodide itself, is a *charge-transfer complex*. Other cases where a charge-transfer complex may be present and where complex formation is essentially due to the "transfer" of an electron to a π-electron system containing a unit positive charge are discussed.

A study of the spectra of aqueous solutions of 1-methylpyridinium iodide[2] revealed that a new species was present to an extent dependent upon the square of the concentration of the quaternary salt. It was suggested that this new species might be the product of addition of the iodide ion to the pyridinium ring.[2,3] In an effort to substantiate this proposal, substituted 1-methylpyridinium iodides were investigated. The prediction was made that replacement of a hydrogen by a methyl group would prevent addition at that particular position, so that the concentration of the new species would be reduced or made to disappear altogether. If we examine the formula for a possible product of addition, I, on the right-hand side of equation 1, we see that I is a reactive secondary iodide and that dissociation to the 1-methylpyridinium and iodide ions represents its solvolysis. It would be expected that replacement of the hydrogen at the 4-position by a methyl group would yield the far more reactive tertiary iodide, II.[5] Thus, the equilibrium position for dissociation and association of II should lie much farther over on the side of the separated ions. Since the amount of new species present in any solution is not too large in any case,[2] serious displacement of the equilibrium toward the dissociated ions should preclude the observation of addition at the methyl-substituted position.



(1)

(I)



II

A second argument in support of the proposition that methyl groups will prevent addition is based upon the report of König[6] that, although 1-cyanopyridinium bromide and 1-cyano-2-methylpyridinium bromide reacted with amines to give glutacondialdimine derivatives, a reaction which no doubt proceeds through preliminary addition, 2,4,6-trimethylpyridine (*sym*-collidine), cyanogen bromide and aniline in ether did not react.[7]

Experimental

The quaternary salts were prepared by refluxing reagent grade substituted pyridines with the appropriate halide in absolute ethanol.

1,2-Dimethylpyridinium iodide was obtained as white crystals by the addition of acetone to an aqueous solution of the crude product, m.p. 229–231°[10] (reported 224°[11,12]).

1,4-Dimethylpyridinium iodide was crystallized by the slow addition of ether to a solution prepared by diluting a very concentrated aqueous solution with a large volume of acetone. It was recrystallized by dissolving in a large volume of boiling acetone, cooling and adding ether; white plates or needles, m.p. 153.3–154.3° (reported 157–158°[13]).

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[1] A portion of this paper is drawn from a thesis submitted by P. E. K. in partial fulfillment of the requirements for the degree of Bachelor of Science, June, 1955.

[2] E. M. Kosower, THIS JOURNAL, **77**, 3883 (1955).

[3] In a paper previously overlooked, Hantzsch and Burawoy[4] have written formulas corresponding to 2-addition and 4-addition, probably to "modernize" the earlier formulations of Hantzsch. No new experimental evidence was presented. They also stated that triiodide ion could not be responsible for the yellow color of chloroform solutions of 1-methylpyridinium iodide because the yellow color disappears upon dilution with alcohol. This statement must be considered insufficient in the absence of spectral data and the objection[2] to the "new absorption maxima" in chloroform solution must stand.

[4] A. Hantzsch and A. Burawoy, *Ber.*, **65**, 1059 (1932).

[5] A quantitative evaluation of the rate effect to be expected for α-methyl substitution on solvolyses which involve ionization of the leaving group is given by S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

[6] W. König, *J. prakt. Chem.*, **69**, 105 (1904).

[7] Since no particular difficulty is associated with the conversion of 2,4,6-trimethylpyridine to the 1-methyl quaternary iodide, the lack of reaction should not be attributed to failure to form a 1-cyanopyridinium salt. H. C. Brown[8] has found that pyridine reacts with methyl iodide in nitrobenzene at 60° almost 17 times faster than 2,6-dimethylpyridine (2,6-lutidine), but 2,4,6-trimethylpyridine should be more reactive than the 2,6-derivative because a 4-methyl group doubles the rate over that for the unsubstituted case.[9]

[8] H. C. Brown and D. Gintis, footnote 37 in H. C. Brown, *et al.*, THIS JOURNAL, **75**, 1 (1953).

[9] H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

[10] All melting points were taken with a Hershberg apparatus using Anschütz thermometers.

[11] P. Murill, THIS JOURNAL, **21**, 828 (1899).

[12] H. O. Jones, *J. Chem. Soc.*, **83**, 1415 (1903).

[13] E. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, THIS JOURNAL, **74**, 5979 (1952).

1,2,6-Trimethylpyridinium iodide was purified in the same manner as the 1,2-dimethylpyridinium salt to give white crystals, m.p. 239–240° (reported 233°,[14] 238°,[15] 235–240°[16]).

1,2,4,6-Tetramethylpyridinium iodide was first crystallized by the addition of ether to a solution in ethanol, followed by two recrystallizations from methanol, to give hard white crystals, m.p. 213.2–214.3° (reported 205°[17]).

1-Methylpyridinium perchlorate was prepared by treating the iodide with a slight excess of silver perchlorate in aqueous solution. The crude salt was isolated by removal of the water under reduced pressure and purified by exposure to light (thus converting the slight excess of silver ion to metallic silver) and recrystallization from dry acetone until the ultraviolet spectrum of a concentrated aqueous solution indicated that essentially no iodide was present.[2] Low temperature crystallization from water gave hygroscopic needles, but the small prisms obtained from acetone are only slightly hygroscopic and can be handled without particular difficulty; m.p. 135.9–137.0° (reported as hygroscopic crystals, m.p. 130°[18]).

The perchlorate is extremely soluble in water and does not separate at room temperature from solutions of any concentration. The ultraviolet spectrum of very dilute solutions of the perchlorate is identical with that of iodide solutions of similar concentration, with λ_{max} 2595 Å., log ϵ 3.67 for the perchlorate and λ_{max} 2590 Å., log ϵ 3.68 for the iodide. Concentrated solutions differ greatly. The perchlorate, at a concentration of 1.62 molar, shows no absorption at wave lengths greater than 2880 Å., and a plot of optical densities against concentration at 2840 Å. for four different concentrations gives a perfectly straight line with the intercept at the origin. The iodide, of course, does not obey Beer's law[2] and might be estimated to have an optical density of *ca.* 6700 at 2840 Å. for a 1.6 molar solution.

3-Carbamyl-1-benzylpyridinium chloride was recrystallized from aqueous acetone; flat plates, m.p. 236.5–237.5° (reported 236°[19]).

3-Carbamyl-1-methylpyridinium iodide was also recrystallized from aqueous acetone; light yellow crystals, m.p. 207–209° (reported 204°[20]).

Reaction of 3-Carbamyl-1-benzylpyridinium Ion with Iodide Ion.—When concentrated aqueous 3-carbamyl-1-benzylpyridinium chloride solution was mixed with a roughly equimolar amount of potassium iodide, also in concentrated aqueous solution, an immediate cloudy yellow suspension was obtained, from which a yellow oily liquid soon separated. After standing for a short time, bright yellow crystals formed and grew in the lower oily layer, and this layer eventually solidified completely. Additional yellow crystals appeared in the still somewhat cloudy upper layer. When the upper layer was clear, crystallization was complete. The yellow crystals were filtered off and dried by pressing between sheets of filter paper. Within a short time, however, the bright yellow color of the crystals noticeably lightened, and white spots could be seen. At the end of periods varying between 1 and 30 minutes, the solid product is completely white. The white product was best purified by recrystallization from methanol, ensuring separation by the addition of a small amount of ether after the methanol solution cooled to room temperature. Occasionally, some yellow crystals separated along with the white form, but these were transformed into the white material on allowing the solid to stand in contact with the solvent for a short time. The white crystals were sensibly harder than the yellow crystals, and they also differed in their rate of solution in chloroform, the yellow form giving an immediate yellow coloration to the solvent, the white form doing so only after a few moments. The white crystals were identified as 3-carbamyl-1-benzylpyridinium iodide by analysis and ultraviolet spectrum, m.p. (white crystals) 170.3–171.5°.

Anal. Calcd. for $C_{13}H_{13}N_2OI$: C, 45.88; H, 3.85; I, 37.29. Found[21]: C, 45.90; H, 4.00; I, 36.95.

Spectra of 3-carbamyl-1-benzylpyridinium: chloride, λ_{max} 2650 Å., log ϵ 3.61; iodide, λ_{max} 2650 Å., log ϵ 3.66.

Although numerous attempts were made to prepare a sample of the yellow crystals for a study of their infrared spectrum, no sample was successfully preserved for the requisite length of time. A few qualitative observations were possible, though. The white crystals could be reconverted into the yellow ones by dissolving in a small amount of hot water and cooling the solution rapidly in ice. The solution became cloudy yellow, and the sequence of observations described above could be repeated. Yellow crystals also separated from a solution of the white material in glacial acetic acid–acetone (prepared by dissolving in hot acetic acid and *then* adding acetone) and formed from the oil which separated on the addition of a large amount of ether to a methanolic solution. The colors of the solutions of the white crystals follow the pattern for other pyridinium iodides previously described by Hantzsch, *i.e.*, the lower the dielectric constant of the solvent and the hotter the solution, the more yellow the color.[22]

3-Carbamyl-1-methylpyridinium Ion and Iodide Ion.—Equal weights of the pyridinium iodide and potassium iodide were dissolved separately in small volumes of hot water, the solutions mixed and the faintly yellow clear solution cooled rapidly in ice. Fine, light yellow needles precipitated and these were filtered off and pressed dry with filter paper. These crystals were indistinguishable from the starting material, 3-carbamyl-1-methylpyridinium iodide, in solubility and melting point, except that the precipitated needles were much softer and changed into hard crystals (like starting material) on standing overnight.

Spectral Studies.—Aqueous solutions containing small amounts of sodium thiosulfate to control triiodide formation[2] were prepared. Ultraviolet transmissions (or, in the case of the tetramethylpyridinium salt, optical densities) were measured with a Warren Spectracord,[23] and the data were treated in the manner previously described. Representative plots of optical density, *D*, divided by the concentration, *C*, *versus* concentration, *C*, are given in Fig. 1.

The concentrations used may be tabulated as follows: **1,4-dimethylpyridinium iodide**, 14 concentrations from 0.00641 to 0.801 *M* at sodium thiosulfate concentration, 5.053×10^{-3} *M*; **1,2-dimethylpyridinium iodide**, 14 concentrations from 0.00544 to 0.648 *M* at sodium thiosulfate concentration, 5.048×10^{-3} *M*; **1,2,6-trimethylpyridinium iodide**, 15 concentrations from 0.00471 to 0.982 *M* at sodium thiosulfate concentration, 5.048×10^{-3}*M*; **1,2,4,6-tetramethylpyridinium iodide**, 24 concentrations from 0.00867 to 0.867 *M* at sodium thiosulfate concentration, 5.005×10^{-3} *M*.

Absorption spectra for very dilute solutions of these pyridinium salts were also measured. The pertinent data are recorded in Table I.

TABLE I

ABSORPTION DATA FOR PYRIDINIUM IONS

Pyridinium ion	λ_{max} Å.	log ϵ
1-Methyl—	2527 (s)[a]	3.63
	2588	3.68
	2653 (s)[a]	3.54
1,2-Dimethyl—	2654	3.74
1,4-Dimethyl—	2553	3.56
	2630 (s)[a]	3.44
1,2,6-Trimethyl—	2728	3.89
1,2,4,6-Tetramethyl—	2690	3.88
	2745 (s)[a]	3.86
3-Carbamyl-1-methyl—	2650	3.60
3-Carbamyl-1-benzyl—	2650	3.64

[a] Shoulder.

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(14) Crippa and Verdi, *Ann. Chim. Applicata*, **26**, 418 (1936).

(15) Conloon and Jones, *J. Soc. Chem. Ind.*, **65**, 169 (1946).

(16) R. Lukes and M. Jurecek, *Chem. Zentr.*, **115**, **I**, 426 (1944).

(17) M. Q. Doja and K. B. Prasad, *J. Indian Chem. Soc.*, **25**, 514 (1948).

(18) W. Ismailski, *J. Russ. Phys.-Chem. Soc.*, **52**, 348; *Beilsteins Handbuch Organischen Chem.*, **XX E 2**, 131.

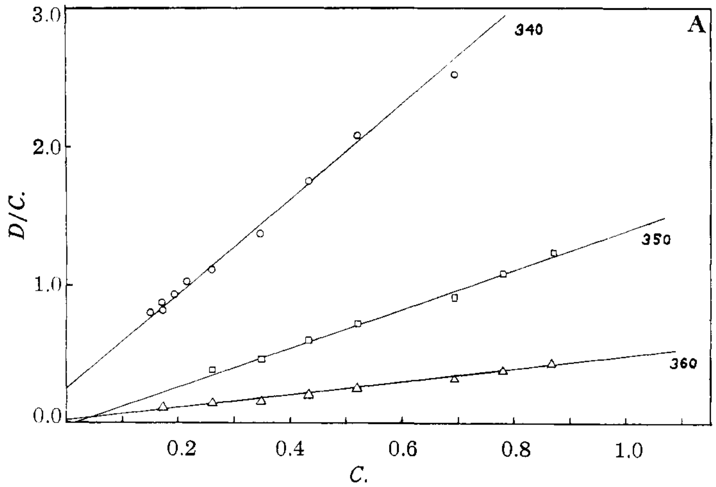
(19) P. Karrer and F. J. Stare, *Helv. Chim. Acta*, **20**, 418 (1937).

(20) P. Karrer, G. Schwarzenbach, F. Benz and U. Solmssen, *ibid.* **19**, 811 (1936).

(21) Carbon–hydrogen analysis by Dr. V. Fish, Chemistry Department, Lehigh University.

(22) A. Hantzsch, *Ber.*, **52**, 1544 (1919).

(23) The Spectracord is an automatized Beckman spectrophotometer.



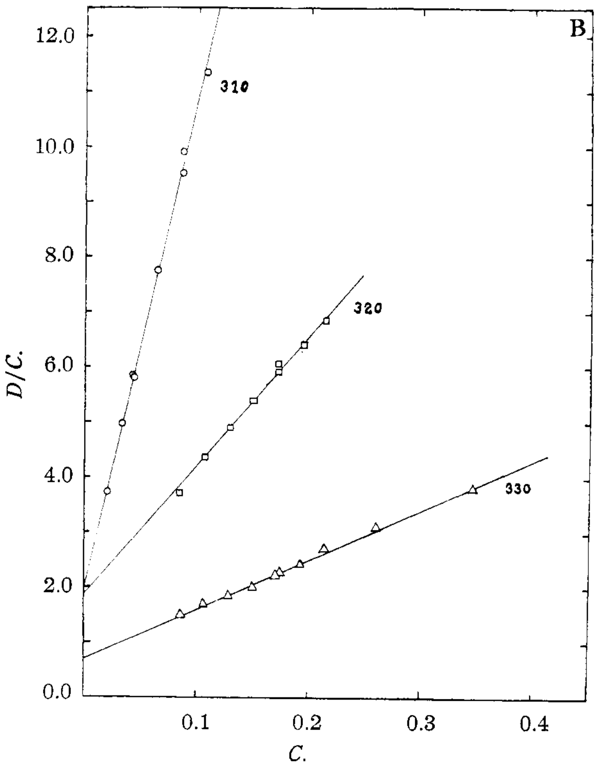


Fig. 1.—(A and B) *D/C versus C* plots for 1,2,4,6-tetramethylpyridinium iodide in aqueous solution. Wave lengths are given in mμ.

Results

It has been shown[2] that one may write an equation, (2), for the behavior of the optical density,

$$D/C = \epsilon + K_x\epsilon_{IIx}C_x + K\epsilon_{III}C \qquad (2)$$

D, with respect to the concentration, *C*, of a salt (for example, 1-methylpyridinium iodide) involved in an equilibrium like that illustrated in equation 1. When C_x is kept constant, a plot of *D/C* against *C* should give a straight line with a slope equal to $K\epsilon_{III}$. (ϵ_{III} is the absorption coefficient for the new species.) Such a line, with the slope, $K\epsilon_{III}$ significantly greater than zero, constitutes evidence that a new species is present in the solution.

It has been found that a new species *is* present in the aqueous solutions of 1,2-dimethylpyridinium iodide, 1,4-dimethylpyridinium iodide, 1,2,6-trimethylpyridinium iodide and 1,2,4,6-tetramethylpyridinium iodide. Sample plots of *D/C versus C* are given in Fig. 1. The values of $K\epsilon_{III}$ derived from these plots are listed in Table II. "Absorption" curves for the various new species, $K\epsilon_{III}$ *versus* λ, are shown in Fig. 2.

It must be emphasized, however, that the foregoing considerations are *quantitatively* valid only when *K* is quite small. In point of fact, the calculation of *K* by the use of an iteration procedure[24,25] leads to values larger than are permissible. Such calculations also revealed that *K* is a function of the concentration range used, and we have confirmed that this variation is caused by the change in the ionic strength of the solution, by varying μ with lithium perchlorate.[26] At present, only the qualitative interpretation of our spectral results is undertaken; a forthcoming article will deal with the sensitivity

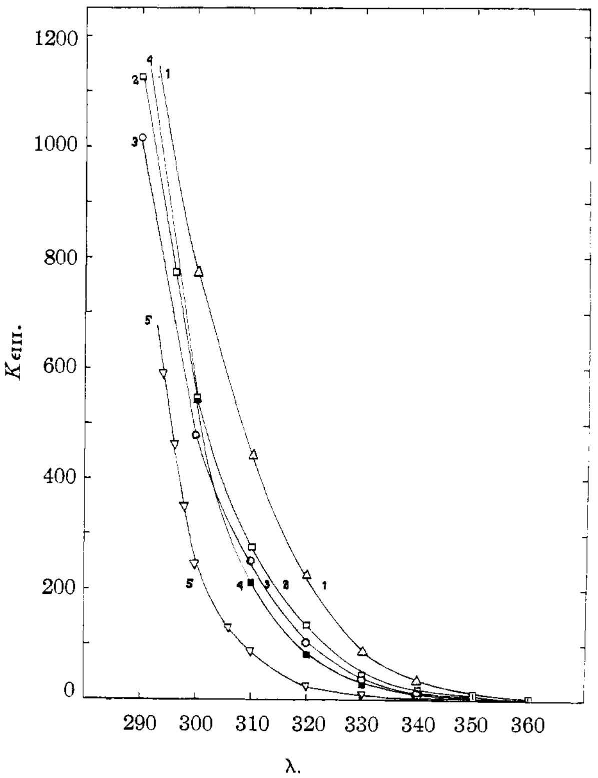


Fig. 2.—$K\epsilon_{III}$ *versus* λ curves: 1, 1-methylpyridinium iodide; 2, 1,2-dimethylpyridinium iodide; 3, 1,4-dimethylpyridinium iodide; 4, 1,2,6-trimethylpyridinium iodide; 5, 1,2,4,6-tetramethylpyridinium iodide.

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[24] The treatment of R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952), was suggested to us in a private communication by Dr. Sidney D. Ross, who has used it in a series of studies on "molecular compounds" (ref. 25).

[25] S. D. Ross, *et al.*, *ibid.*, **76**, 69 (1954), and subsequent papers.

[26] E. M. Kosower and J. C. Burbach, unpublished results.

TABLE II

$K\epsilon_{III}$ VALUES

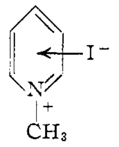
Wave length, Å.	1-MP$^+$I^{-a}	1,4-DMP$^+$I$^-$	1,2-DMP$^+$I$^-$	1,2,6-TMP$^+$I$^-$	1,2,4,6-TeMP$^+$I$^-$
3600	5.7	1.81	2.55	1.29	0.42
3500	10	5.16	6.48	3.27	1.42
3400	35	13.9	19.5	9.45	3.48
3300	85	38.4	45.7	28.9	9.00
3200	225	104	136	82.6	24.0
3100	440	250	275	211	87.5

[a] 1-Methylpyridinium iodide. The values are taken from ref. 2. The other initials are, in order, 1,4-dimethyl-, 1,2-dimethyl-, 1,2,6-trimethyl- and 1,2,4,6-tetramethylpyridinum iodides.

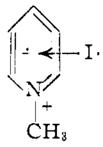
of K to the degree of methylation of the 1-methylpyridinium ion.[27]

Discussion

If the argument that addition does not occur at a methyl-substituted position is accepted, the spectral results demonstrate clearly that the formation of new species in aqueous solutions of 1-methylpyridinium iodides is not due to the addition of iodide ion to the pyridinium ring. The only reasonable hypothesis for the nature of the new species is that it is a *charge-transfer complex*[28,29] with principal contributing forms which may be depicted as III and IV. The charge-transfer complex is a logical intermediate in nucleophilic addition, although not an obligate one. It can be shown, however, that consideration of the ability of a nucleophile to form charge-transfer complexes allows a prediction of the position of addition.[30]



III



IV

While electron transfer involving ground states A^+B^- and excited states $A^\circ B^\circ$ has long been postulated to explain certain absorption phenomena in inorganic systems, *e.g.*, $Ag^+Br^- \rightarrow Ag^\circ Br^\circ$, the charge-transfer complexes formed from 1-methylpyridinium ions and iodide ions appear to be the first reported with fairly quantitative support among organic systems. (Mulliken[29] has tabulated and discussed all conceivable types of charge-transfer complexes.) The novel feature present in the 1-methylpyridinium case, as well as in a couple of apparently analogous examples, is that the electron which is "transferred" must enter an upper molecular orbital of the π-electron system, in spite of the full positive charge carried by one or several atoms of the system. Neutralization of the positive charge is achieved when addition occurs,[2] which suggests that solvation forces stabilizing the ions are not quite overcome in the case of the iodide ion and simple methyl-substituted pyridinium ions in aqueous solution. The charge cannot be neutralized in molecules related to azabicyclooöctene (VII) without disrupting the ring, and interaction of such cations with anions is limited to charge-transfer complex formation. The products of complex formation and addition correspond formally to Mulliken's "outer" and "inner" complexes, respectively.[29]

Perchlorate Ion.—1-Methylpyridinium perchlorate obeys Beer's law in aqueous solution perfectly up to very high concentrations, and perchlorate ion, therefore, does not form a charge-transfer complex with the 1-methylpyridinium ion. The perchlorate ion is generally considered to be a poor complex-former, although Sykes[31] has recently reported complex formation between perchlorate ion and ferric ion. The lack of complex formation with the perchlorate salt allows one to dispense with the preparation of a desired binary salt, *e.g.*, 1-methylpyridinium thiocyanate, at least in preliminary studies. Thus, it can be shown that thiocyanate ion forms a complex with the 1-methylpyridinium ion, although probably to a lesser extent than iodide ion.

"Bathochromie durch Salzbildung..."—Kröhnke[32,33] has published a number of papers concerned with quaternary pyridinium, quinolinium and isoquinolinium salts, finding that these salts have deeper colors than one would expect on the basis of the corresponding alkali metal salts. The depth of the color was related to the oxidation potential of the anion. He proposed that the deepening of color had its source in ion-deformation and "redox-mesomerism." However, Kröhnke made his comparisons for the colors of the solid salts, and such colors are scarcely objective physical properties. Indeed, since they often depend on what may be completely extraneous factors like crystal size, we cannot accept Kröhnke's conclusions as applying to properties of these cation–anion pairs in solution. As a matter of fact, Kröhnke stated that ". . . a comparative spectral investigation is scarcely possible, because the colors are, above all, observed in the solid state, and the color changes must be subjectively judged. . ."[32c] One cannot even be sure of obtaining the same color salt under all conditions; the work reported in the Experimental for 3-carbamyl-1-benzylpyridinium iodide illustrates this well and also raises the question as to whether the colored salts may not also be addition compounds.

Related Cases.—Strauss[34] has found that poly-(1-dodecyl- or 1-ethyl)-4-vinylpyridinium bromide binds more than the stoichiometric quantity of bromide ion as shown by its electrophoretic behavior in concentrated potassium bromide solutions. It seems possible that part of the binding energy for the excess bromide ion is derived from charge-transfer complex formation of the type described in this paper.

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(27) Large variations in K with ionic strength for "outer complex" formation from two charged species have been observed recently by F. A. Posey and H. Taube, THIS JOURNAL, **78**, 15 (1956).

(28) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(29) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(30) E. M. Kosower, Paper III of this series, THIS JOURNAL, **78**, 3497 (1956).

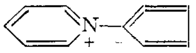
(31) K. W. Sykes in "Kinetics and Mechanism of Inorganic Reactions in Solution," Special Publication No. 1, Chemical Society, London, 1954, p. 64.

(32) (a) F. Kröhnke, *Chem. Ber.*, **83**, 35 (1950); (b) **87**, 1126 (1954); (c) **88**, 851, 863 (1955).

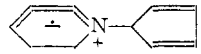
(33) F. Kröhnke and I. Vogt, *ibid.*, **86**, 1132 (1953).

(34) U. P. Strauss, N. L. Gershfeld and H. Spiers, THIS JOURNAL, **76**, 5909 (1954).

Lloyd and Sneezum have recently described the interesting compound pyridinium cyclopentadienylide (V),[35] a molecule which appears to behave as an "internal" charge-transfer complex. Salt-like character is shown by the lack of a melting point (did not melt under 350°) and low solubility in non-polar solvents. Addition of the anion to the pyridinium ring to give a highly trained tricyclic compound, which would be electrically neutral, is rather improbable thermodynamically. Yet, the solutions are intensely colored, varying from colorless in acidic aqueous solution (proton addition to give the colorless 1-alkylpyridinium ion) through yellow in alkaline aqueous solution, orange in alcohol, red in acetone and chloroform, reddish-purple in benzene and ether and bluish-purple in petroleum ether. The variation in color with solvent dielectric constant is precisely what would be predicted for a charge-transfer complex in which the ionic ground state was becoming progressively destabilized through loss of solvation energy with respect to an "uncharged" excited state, VI, thus shifting light absorption to longer and longer wave lengths. A similar, smaller, but apparently analogous shift has been found for 1-methylpyridinium iodide when the solvent is changed from water to ethanol.[26]

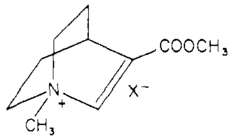


V



VI

It has been shown that the bicyclic quaternary salts, VII (X = Cl^-, Br^-, I^-), do not obey Beer's law in aqueous solution,[36] and a charge-transfer complex is probably present.



VII

The colors of tropylium salts[37] can also be explained on the basis of charge-transfer complex formation. Doering and Knox[38] have reported that 7-methoxy-1,3,5-cycloheptatriene (tropyl methyl ether) is a colorless liquid, and measurement of the spectrum of 7-hydroxy-1,3,5-cycloheptatriene (tropyl alcohol; tropylium ion at high *p*H in water) gave a curve with a clear maximum, λ_{max} 2510 Å., log ϵ 4.00. Tropylium ion possessed an absorption maximum at 2750 Å., log ϵ 3.64. Although Doering and Knox say that ". . . the yellow color of the cation is due to a long tailing . . ." (in the absorption band), this does not explain the colors found for the solid tropylium halides, chloride, pale yellow,[38] white[37]; bromide, yellow[37,38]; iodide, *black*.[37] While the color of solid salts is hardly a reliable index of events on the molecular level, it seems significant that such a range of colors exists between the tropylium ion on the one hand and the covalently bonded and colorless tropyl methyl ether on the other. If the charge-transfer complex is indeed the logical intermediate in nucleophilic additions, then it ought to be present in certain tropylium ion–anion combinations. The series of colors observed for the halides is consistent with this possibility, but a definitive proof must await an investigation of the type carried out in this and the previous paper.[2]

Acknowledgment.—The authors would like to express their appreciation to Mr. John C. Burbach for obtaining some of the spectral data and for other valuable technical assistance.

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[35] D. Lloyd and J. S. Sneezum, *Chemistry and Industry*, 1221 (1955).

[36] C. A. Grob and E. Renk, unpublished results in private communication from Prof. C. A. Grob, Organisch-chemische Anstalt der Universität, Basel, Switzerland.

[37] R. Pettit, paper presented at the XIVth International Congress of Pure and Applied Chemistry, Zürich, Switzerland, July 26, 1955.

[38] W. v. E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954).

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Additions to Pyridinium Rings. III. Chemical and Biochemical Implications of Charge-Transfer Complex Intermediates

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Consideration of the occurrence of charge-transfer complexes formed from 1-methylpyridinium ions and electron donors together with data from the literature suggest the following conclusion regarding addition to pyridinium rings. Donors which form complexes substitute at the 4-position and those which do not, or do so only poorly, substitute at the 2-position. It is also proposed that the previously observed complexes formed from diphosphopyridine nucleotide (DPN) and enzymes, and those from DPNH and enzymes are charge-transfer complexes. A consequence of the importance of donor ability in determining position of addition leads to a revision of the schematic mechanism for the reaction of ethanol and DPN.

A spectral study of aqueous solutions of 1-methylpyridinium iodide showed that a new species was present.[1] Similar studies using substituted 1-methylpyridinium iodides suggested that the new species was a charge-transfer complex[2] and that these complexes may be intermediates in the addition of nucleophiles to the pyridinium ring.

A tabulation of the results of addition to pyridinium rings, made in Table I, reveals that nucleophiles which form charge-transfer complexes easily, or which might be expected to do so (*cf.* the following Discussion), add at the 4-position, while

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[1] E. M. Kosower, THIS JOURNAL, **77**, 3883 (1955).

[2] E. M. Kosower and P. E. Klinedinst, Jr., *ibid.*, **78**, 3493 (1956).