Pyridinium Complexes. III. Charge–Transfer Bands of Polyalkylpyridinium Iodides

2 AUTHORS, INCLUDING:

Edward Malcolm Kosower
Tel Aviv University
300 PUBLICATIONS **9,136** CITATIONS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WISCONSIN]

Pyridinium Complexes. III. Charge-Transfer Bands of Polyalkylpyridinium Iodides

BY EDWARD M. KOSOWER AND JOSEPH A. SKORCZ[1]

RECEIVED AUGUST 10, 1959

A study of the first (long wave length) charge-transfer band of twenty different alkylpyridinium iodides under carefully standardized conditions has established that (1) increasing the number of methyl groups raises the transition energy, (2) changing a methyl group from the 3- to the 2- to the 4-position increases the transition energy, (3) varying the nature of the alkyl group from methyl to t-butyl on the 4-position has virtually no effect upon the transition energy and (4) the solvent sensitivity of 1-methylpyridinium iodide is appreciably greater than that of 1-ethyl-4-carbomethoxypyridinium iodide, as might have been expected on the basis of a previously proposed model. The maxima observed varied from 3738 Å. for 1-methylpyridinium iodide to 3253 Å. for 1,2,3,4,5,6-hexamethylpyridinium iodide. Surprisingly, replacement of the 1-methyl by hydrogen moved the charge-transfer band to 3463 Å. Two points favor the interpretation of the effect of alkyl groups as being due to the bond dipole generated by the combination of an sp^3 bonding orbital with an sp^2 orbital: (1) the effect of the 3-methyl group can be accounted for on the basis of electrostatic stabilization of the ground state and (2) a change in the nature of the alkyl group on the 4-position does not elicit electron-supply dependent on the number of α-hydrogens, as would have been expected for hyperconjugation.

Results

The special light absorption of alkylpyridinium iodides[2] first discovered by Hantzsch[3] is now well established as a transition involving charge-transfer from the iodide ion to the alkylpyridinium ion on the basis of solvent effects,[4] Δ TE values,[5] conductivity measurements[6] and a few substituent effects.[7] In order to define the substituent effects on these absorption bands in a more precise manner, a series of different alkylpyridinium iodides was investigated carefully. It was hoped that the relationships found would also cast some light upon the means by which alkyl groups supply electronic charge to electron-deficient systems. By rigid control of the many variables which affect the environment-sensitive pyridinium iodide transition, it was possible to obtain data applicable to both of these purposes.[8]

Results

Alkylpyridinium iodide charge-transfer band positions are sensitive to solvent, salt concentration and temperature. A non-polar solvent was chosen so as to provide completely associated pyridinium iodide ion-pairs (complex),[6,9] thus simplifying the comparison of absorption intensities. Chloroform containing 0.90% ethanol was used in this study because it possessed the requisite solvent power and had a solvent polarity (dependent upon ethanol content[5]) controllable within certain limits. Ethylene chloride[6] was not a sufficiently good solvent for some of the salts. Salt concentrations (i.e., alkylpyridinium iodide molarity) were held within very narrow limits, $0.91 \pm 0.01 \times 10^{-4}$ M being selected as the concentration which gave adequately high optical

densities in the spectroscopic measurements. It was assumed that the activities of the pyridinium iodide ion-pair complexes were all a constant fraction of the concentrations, but it was not possible to extrapolate the data to zero concentration because of experimental difficulties in working with extremely low concentrations of iodide salts. Although temperature certainly affects the position of charge-transfer bands,[4] it was considered more expedient to allow convenient ambient temperatures to control operating conditions ($\pm 1°$ for almost every measurement) rather than to sacrifice speed in obtaining the maxima. Oxidation could be detected in the rapid procedure by small changes in consecutive curves.

The most serious difficulty in measurement of pyridinium iodide charge-transfer maxima is the ever present possibility that the spectrum may include some absorption by triiodide ion, which possesses two intense maxima in chloroform at 3625 Å. (ϵ 21,600) and 2950 Å. (ϵ 35,000). The long wave length band is about eighteen times as intense as the first charge-transfer maximum of many alkylpyridinium iodides. Fortunately, the ratio of the intensities of the two maxima of triiodide ion differs considerably from that for 1-methylpyridinium iodide, and it was therefore possible to control the experimental techniques used. No analytical method of the accuracy needed to correct for triiodide ion was available; it was necessary to measure the spectra under conditions where triiodide was not formed.

Wet pyridinium iodides seem far more sensitive to light and oxygen than the dry salts. To prevent oxidation in the pyridinium iodides, all salts were stored and weighed in a good dry box under a dry nitrogen atmosphere. All solutions were prepared in the same dry box and all cells for spectroscopic measurements were filled with the same protection. Dim light was used as an additional precaution. Reproducibility of maxima and absorption intensities served as the prime criteria of valid spectroscopic data. The intensity ratio of the two bands of 1-methylpyridinium iodide served as a check on the procedure and indicated that, in general, the triiodide concentration did not exceed 2×10^{-8} M.

The alkylpyridinium iodides used were rigorously purified. All of the maxima listed in the

(1) Based in part on a portion of a thesis submitted by Joseph A. Skorcz in partial fulfillment of the requirements for the M.S. degree, June, 1959.

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

(3) A. Hantzsch, Ber., **44**, 1783 (1911).

(4) E. M. Kosower, THIS JOURNAL, **80**, 3253 (1958).

(5) E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Patton, ibid., **82**, 2188 (1960).

(6) E. M. Kosower and W. M. Schwarz, Jr., unpublished results.

(7) E. M. Kosower and J. A. Skorcz, Paper presented at Fourth Meeting of European Molecular Spectroscopy Group at Bologna, Italy, September 7–12, 1959.

(8) This study was supported by funds granted by the Air Force Office of Scientific Research through contract AF 49(638)-282 and by the National Institute of Allergy and Infectious Diseases under grant E-1608.

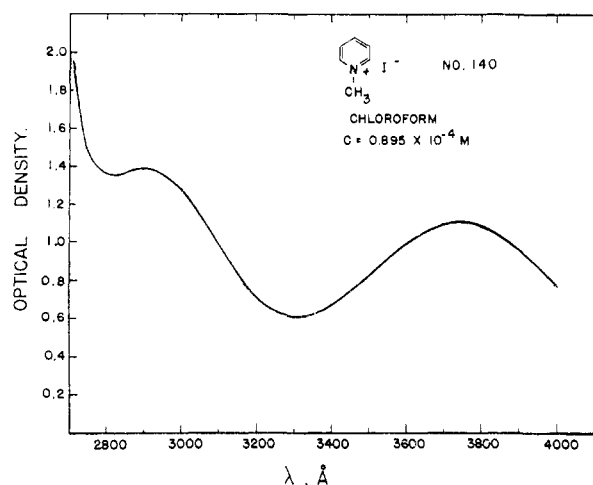(9) E. M. Kosower and J. C. Burbach, THIS JOURNAL, **78**, 5838 (1956).

Fig. 1.—The spectrum of 1-methylpyridinium iodide in "standard" chloroform.

various tables represent the average of the best *five* of *six separate* determinations of absorption curves; *each* determination included three to five measurements of the absorption curve in the region of the maximum. A complete description of the technique is included in the Experimental section.

All of the maxima are measured under standard conditions, which we shall define as $0.91 \times 10^{-4} M$ alkylpyridinium iodide in chloroform containing 0.90% ethanol at $26 \pm 1°$. Changes in concentration or solvent are specifically noted. Although real ambiguity exists only for 1-methylpyridinium iodide for which two bands are observed under standard conditions, it should be stated explicitly that all maxima belong to the first charge-transfer band (*i.e.*, the longest wave length band).

The first maximum for 1-methylpyridinium iodide is found at 3738 Å., as seen in the absorption spectrum shown in Fig. 1. Replacement of a pyridinium ring hydrogen by another methyl group shifts the maximum but the extent of the change depends markedly upon the *position* of the additional methyl group. At the 3-position, the methyl group moves the maximum to 3700 Å., while a 2-methyl group shifts the band to 3640 Å. and a 4-methyl group to 3590 Å. These data are summarized in Table I.

TABLE I
DIMETHYLPYRIDINIUM IODIDES

Substituent	λ_{max}, Å.	Error, Å.	ϵ_{max}	E_T, kcal./mole
1-Me	3738	±5	1200	76.5
1,2-Me$_2$	3640	±5	860	78.5
1,3-Me$_2$	3700	±5	1310	77.3
1,4-Me$_2$	3590	±5	1230	79.6

Additional methyl groups cause further increases in transition energies, *i.e.*, shifts of the maximum to shorter wave lengths. The positions for the 1,2,5-trimethyl-, 1,3,5-trimethyl- and 1,2,4,6-tetramethylpyridinium iodides are those predicted on the naive basis that the effects of methyl groups as measured with the band positions for the dimethyl pyridinium iodides are additive. Three other polymethylpyridinium iodides possess absorption bands
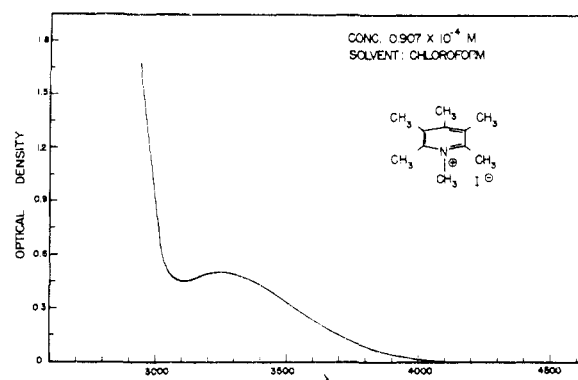
which deviate somewhat from the locations expected, but only hexamethylpyridinium iodide has a maximum at a wave length much shorter than calculated as mentioned above. The data for the polymethylpyridinium iodides are listed in Table II and the curve for hexamethylpyridinium iodide is shown in Fig. 2.

TABLE II
POLYMETHYLPYRIDINIUM IODIDES

Substituent	λ_{max}, Å.	Error, Å.	ϵ_{max}	E_T kcal./mole
1,2,3-Me$_3$	3569	± 5	820	80.1
1,2,4-Me$_3$	3530	± 5	940	81.0
1,2,5-Me$_3$	3607	± 5	1030	79.3
1,2,6-Me$_3$	3580	±10	440	79.9
1,3,5-Me$_3$	3660	± 5	1370	78.1
1,2,4,6-Me$_4$	3418	±10	480	83.7
1,2,3,4,5,6-Me$_6$	3253	±10	560	87.9

A change in the alkyl group on the 4-position of the pyridinium ring causes only a negligible variation in band position or in absorption intensity, as shown by the values listed in Table III.

TABLE III
1-METHYL-4-ALKYLPYRIDINIUM IODIDES

Substituent	λ_{max}, Å.	Error, Å.	ϵ_{max}	E_T, kcal./mole
4-Me	3590	±5	1230	79.6
4-Et[a]	3586	±5	1200	79.7
4-n-Pr	3599	±5	1210	79.4
4-i-Pr	3594	±5	1210	79.5
4-t-Bu	3590	±5	1170	79.6

[a] 1-Methyl-4-ethylpyridinium iodide could not be obtained as a *completely colorless salt, but only as pale yellow crystals, in spite of many repeated crystallizations and charcoal treatments. The close agreement of the maximum absorption intensity with the ϵ values found for other compounds listed in Table III suggests that the yellow color is *not* due to triiodide (which would have increased the ϵ considerably) but to a trace of dihydropyridine formed by loss of a proton from the α-position of the ethyl group. The postulated impurity is

$$CH_2CH=\text{\<}N-CH_3$$
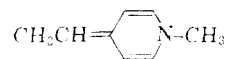
It is also true that the solution for 1-methyl-4-ethylpyridinium iodide was measured at a temperature 2° lower than most of the other solutions; it is easily possible that the maximum listed should be increased 4–6 Å.

A surprising result is noted when the effect of alkyl group variation on the 1-position, *i.e.*, a group
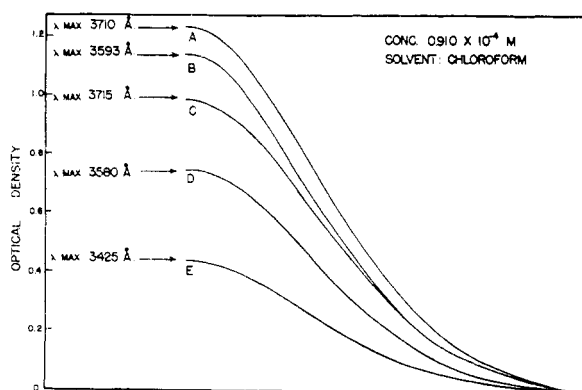

Fig. 2.—The spectrum of 1,2,3,4,5,6-hexamethylpyridinium iodide in "standard" chloroform.

Fig. 3.—Half-curves for the charge-transfer bands of the various iodides: (A) 1,3-dimethylpyridinium iodide; (B) 1-methyl-4-n-propyl-, 1-methyl-4-i-propyl- and 1-methyl-4-t-butylpyridinium; (C) 1-i-propylpyridinium; (D) 1,2,3-trimethylpyridinium; (E) 1,2,4,6-tetramethylpyridinium.

directly attached to the nitrogen, is examined. Pyridinium hydriodide has a charge-transfer maximum at a wave length considerably *shorter* than that of 1-methylpyridinium iodide, although the opposite shift might have been expected from the general effect of methyl groups in moving the pyridinium iodide charge-transfer maxima to shorter wave lengths. Other variations in the alkyl group have only a small effect, as can be noted in Table IV.

TABLE IV

1-ALKYLPYRIDINIUM IODIDES

Substituent	λ_{max}, Å.	Error, Å.	ϵ_{max}	E_T, kcal./mole
1-H	3463	±10	390	82.5
1-Me	3738	± 5	1200	76.5
1-Et	3727	± 5	1140	76.7
1-i-Pr	3710	± 5	1040	77.1

The three 1-methyl-x-t-butylpyridinium iodides also were examined. Unlike the pair of iodides with a methyl and t-butyl group in the 4-position (Table III), change from a 2-methyl to a 2-t-butyl-pyridinium iodide had a considerable effect on both the position and intensity of the charge-transfer maximum (Table V).

TABLE V

1-METHYL-x-t-BUTYLPYRIDINIUM IODIDES

Substituent	λ_{max}, Å.	Error, Å.	ϵ_{max}	E_T, kcal./mole
2-t-Bu	3694	±5	1240	77.4
3-t-Bu	3678	±5	1150	77.7
4-t-Bu	3590	±5	1170	79.6

A simple demonstration that the electronic transitions observed in each case are all very similar in character in spite of the considerable variation in position and intensity is provided by Fig. 3, in which half-curves for seven of the alkylpyridinium iodides are plotted so that their maxima coincide. All of the curves are quite characteristic for charge-transfer absorption bands of pyridinium iodides and, except for the variation in intensity, are similar in shape and breadth.[10]

(10) Figure 3 is a plot of optical density against wave length but the comparison is still valid for optical density against wave number.
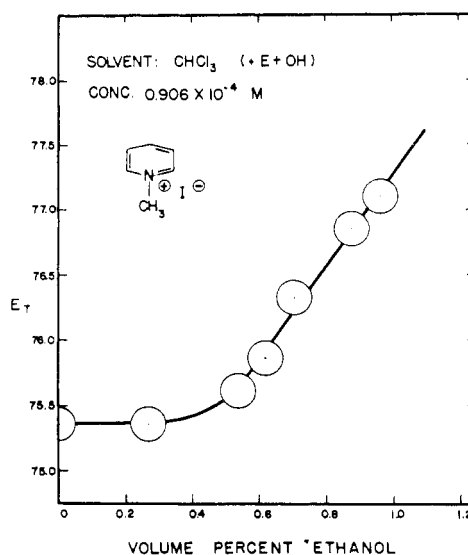

Fig. 4.—Plot of transition energies (charge-transfer band) of 1-methylpyridinium iodide against volume % ethanol in chloroform.

One of the most characteristic properties of the charge-transfer bands of pyridinium iodides is their extreme sensitivity to solvent, and, in fact, the nature of the variation observed on solvent change may be used to identify the maximum as a charge-transfer transition.[11] Variation of ethanol content in chloroform solvent causes a change in the position of the maximum, although, as Fig. 4 makes clear, the shift is not linear over the whole range of ethanol concentrations. The curve shown is a plot of transition energies against ethanol content, based on data reported in an accompanying paper.[5] More extensive increases in the polarity of the solvent cause correspondingly greater changes in the position of the maximum; these data are given in Table VI. Previous studies of 1-ethyl-4-cyanopyridinium iodide[4] led to a plot of charge-transfer transition energies (corresponding to the maxima) E_T against Z, a standard of solvent polarity based on the position of the maxima for 1-ethyl-4-carbomethoxypyridinium iodide,[4] with a slope of 0.97. In contrast, the slope of the plot of E_T for 1-methylpyridinium iodide against Z is 1.12. The linear correlation with Z permits the estimation of the maximum for the charge-transfer band of 1-methylpyridinium iodide in water as 2561 Å., or 111.6 kcal./mole (E_T). As pointed out elsewhere, the 1-methylpyridinium ion is thus shown to be a much more effective electron acceptor than water (λ_{max} 2259 Å.) for the electron excited by light away from the iodide ion.[5]

Two points for pyridinium iodide also are shown in Fig. 5. The large shift in the position of the absorption band observed for pyridinium iodide under standard conditions to much shorter wave lengths in acetonitrile provides evidence that the transition is like that of 1-methylpyridinium iodide, or, in other words, that the long wave length absorption band is a charge-transfer transition (Table VI).

(11) E. M. Kosower, "The Enzymes," Vol. III, Academic Press, Inc., New York, N. Y., 1960, Chapter 13.
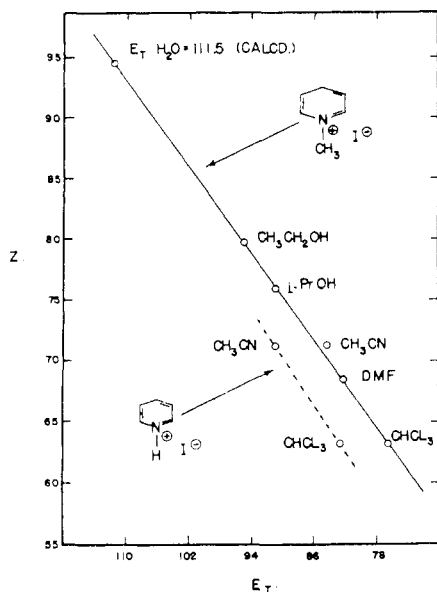
Fig. 5.—Plot of transition energies (charge-transfer band) of 1-methylpyridinium iodide against Z: $E_T = 1.1205\ Z + 5.6190$ (acetonitrile neglected). The dashed line joins two points for pyridinium iodide.

Discussion

The transformation for the charge-transfer excited by light may be expressed as in equations 1 and 2. Since the contribution of charge-transferred form to the ground state is relatively small,[6,12] the results can be considered by an evaluation of the effect of alkyl groups on the pyridinium ion (I) in the ground state and on the pyridinyl radical (II) in the excited state.

$$MPy^+ I^- \xrightarrow{h\nu} MPy \cdot I \cdot \qquad (1)$$
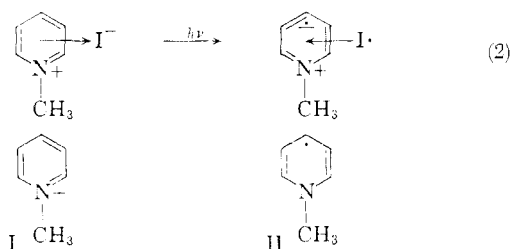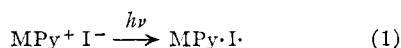
Stabilization of carbonium ion species by electron-supplying groups is far more effective than stabilization of free-radical species by the same groups. Thus, chloromethyl ether is only *ca.* 10^3 more reactive than methyl chloride toward sodium vapor at 275°,[13] while it is about 10^{11} faster in the carbonium ion forming reaction of hydrolysis.[14] Thus regardless of the precise mechanism by which the methyl group supplied electronic charge, it can be predicted that substitution of a methyl group into the pyridinium ring would raise the transition energy. The argument implies that the

(12) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(13) J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., 1956, p. 395.

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334.

TABLE VI

SOLVENT VARIATION: 1-METHYLPYRIDINIUM AND PYRIDINIUM IODIDES

Solvent (Z)[4]	λ_{max}, Å.	$\epsilon_{apparent}$	E_T, kcal./mole
1-Methylpyridinium iodide			
CHCl₃ (63.2)	3738	1200	76.5
DMF[a] (68.5)	3480	17	82.2
CH₃CN (71.3)	3391	31	84.3
i-PrOH (75.9)[b]	3145	394	90.9
EtOH (79.7)[b]	3015	142	94.8
Pyridinium iodide			
CHCl₃ (63.2)	3464	390	82.5
CH₃CN (71.3)	3150	48	90.8

[a] Dimethylformamide. [b] Remeasured for the solvent used for the determination.

methyl group would decrease the electron affinity of the ground state pyridinium ring, that is, *stabilize* the ground state, without making a corresponding change in the energy of the excited state ring, II.

Methyl substitution does, in fact, always lead to an increase in transition energy (*i.e.*, a decrease in λ_{max} for the charge-transfer band). The changes, however, are not the same for the three positions of the pyridinium ring; the data in Table I show that the change in transition energy for monomethyl substitution is, ΔE_T, at 2-, 2.0, at 3-, 0.8 and at 4-, 3.1 kcal./mole, which represent the change from the transition energy for 1-methylpyridinium iodide.

Until recently the effects of alkyl groups have been commonly interpreted in terms of inductive effect or hyperconjugation.[15,16] However, armed with new and accurate information on bond distances,[17] Petro,[18] Fischer-Hjalmars,[19] Costain and Stoicheff,[20] Bernstein[21] and, especially, Dewar,[22] have reinterpreted the effects usually attributed to hyperconjugation in terms of the hybridization of the orbitals composing the bonds under discussion. Mulliken,[23] in acknowledging the validity of some of the criticism of hyperconjugation, has warned against the unconsidered use of "whole-number combinations" in forming hybrid orbitals. Clement[24] has concluded from a comparison of *p*-methylbenzyl chloride and *p-t*-butylbenzyl chloride that differential solvation could account for the Baker–Nathan effect ("hyperconjugative order")[23] observed in hydrolysis rates.

(15) R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 45 (1941).

(16) J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952.

(17) G. Herzberg, *Nature*, **175**, 79 (1955).

(18) A. J. Petro, THIS JOURNAL, **80**, 4230 (1958).

(19) I. Fischer-Hjalmars, private communication.

(20) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

(21) H. J. Bernstein, *J. Phys. Chem.*, **63**, 565 (1959).

(22) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(23) R. S. Mulliken, *ibid.*, **6**, 68 (1959), has pointed out that the latest calculations of bond order in conjugated molecules (and estimates for hyperconjugated molecules) suggest that a *combination* of bond hybridization and conjugation can satisfactorily account for the bond distances. On p. 78, Mulliken states that the fundamental premise of Baker and Nathan [the predominant role of α-hydrogen] is not necessarily correct and has thus made this *lapin agile* a difficult one to catch.

(24) R. A. Clement and J. N. Naghizadeh, THIS JOURNAL, **81**, 3154 (1959).

With the assumption that polarization of the σ-bond framework can be ignored and utilizing the bond moments estimated by Petro[18] for C_{sp^2}–C_{sp^2}, H_{1s}–C_{sp^3} and H_{1s}–C_{sp^2} bonds, the gain in interaction energy upon substitution of a methyl group for a hydrogen on the pyridinium ring can be calculated from $E = q_1 q_2 / Dr$. The results, expressed as increased stabilization energy in kcal./mole, are for 2-, 1.2, for 3-, 0.8 and for 4-, 0.8.[25] To a first approximation, these stabilization energies should be reflected directly as increased transition energies in the corresponding pyridinium iodides. Even allowing for the nature of the approximations involved, the agreement between the value calculated for electrostatic stabilization of the ground state by a 3-methyl (0.8 kcal./mole) and the observed increase in the transition energy (0.8 kcal./mole) is excellent and suggests that this factor is sufficient to explain the effect of the 3-methyl group.[27]

In contrast, it seems certain that the model used for the 3-methyl group does not account for the effects obtained with 2- and 4-methyl groups. The discrepancy for the latter position is particularly striking. The simplest manner of rationalizing the increases is to consider the contributions of Ia, Ib and Ic to the structure of I. Longuet-Higgins and Coulson[28] have calculated the π-electron densities at the 2-, 3- and 4-positions in pyridine as 0.849, 0.947 and 0.822, respectively. More recently, Barnes[29] has revised these figures to 0.943, 0.991 and 0.950. The increased positive charge at the 2- and 4-positions would increase the interaction with the methyl substituent.

Three plausible explanations may be advanced for the difference between ΔE_T for the 2- and 4-positions. A greater contribution of Ic to the structure of the hybrid might lead to greater "effectiveness" for the 4-methyl.[30] Second, the

Ia   Ib   Ic

exclusion of solvent by the 2-alkyl group from the region near the ion-pair dipole would lead to a decreased transition energy. The alkyl group can be regarded as a region of hydrocarbon solvent

$(Z$ 60.1$)$ replacing chloroform $(Z$ 63.2$)$.[4,31] The third possibility is that steric strain in the pyridinium iodide complex generated by interaction of the 2-alkyl group and the iodide ion reduces the transition energy. We have pointed out elsewhere[5] that a more precise description of the excited state than previously given[4] suggests that the aforementioned strain would be considerably lessened upon excitation, because electron transfer leads to a reduction in the size of the iodide ion (2.15 Å. → ca. 1.33 Å.) without, probably, a corresponding increase in the size of the pyridinium ring. From models, steric strain does not seem very important for the 2-methyl group but of consequence for the 2-t-butyl group. Steric strain alone or a combination of steric strain with "local solvent effect" could explain the appreciable reduction in transition energy for 1-methyl-2-t-butylpyridinium iodide (1.1 kcal./mole, 54 Å., cf. Table V).

A series of 1-methyl-4-alkylpyridinium iodides (Table III) exhibits very little change in charge-transfer band position. It seems simpler to explain the identity of the maxima for 4-methyl and 4-t-butyl with the proposal that the electrical effects of saturated alkyl groups are the same and largely dependent upon the nature of the bond by which they are attached to a given molecule.[27] Deviations from equality of effect would be explained in other terms, such as steric hindrance to solvation.[24,32] Alternatively, the methyl group would be required to stabilize the excited state of the pyridinium ion (pyridinium ion plus an electron) more effectively than the t-butyl group to exactly the same extent as the ground state.

The maximum absorption intensities of the pyridinium iodide charge-transfer band can be compared with one another since the band shapes are similar (Fig. 3) and calculation of the oscillator strengths, a number proportional to the integrated absorption intensity, demonstrates that ϵ_{max} is approximately parallel to f_0, the oscillator strength.

As compared with 1-methylpyridinium iodide, substitution at the 4-position has little effect upon ϵ_{max}, while 3-substitution increases ϵ_{max} by a small amount. (The highest absorption intensity at the maximum was found for 1,3,5-trimethylpyridinium iodide.) In general, substituents at the 2-position reduce ϵ_{max} by a large factor but the 2-t-butyl group is a noteworthy exception. Polymethylpyridinium iodides conform reasonably well to the general behavior outlined here.

The position of the charge-transfer band for 1-methylpyridinium iodide is about 12% more sensitive to solvent than the band for the salt used to measure solvent Z-values,[4] that is, 1-ethyl-4-carbomethoxypyridinium iodide. According to the

(25) The parameters used are: ring C–C (C–N) distance, 1.38 Å.,[26] ring C–H distance, ~1.07 Å.,[26] ring C-methyl C, 1.50 Å.,[21] dielectric constant, $D = 2.0$. The bond dipoles were considered as point charges centered on the atoms of the bond and the interaction energies were obtained separately for hydrogen and methyl. The difference is the "gain" referred to in the text and can be regarded as an electrostatic stabilization.

(26) A. Almenningen, O. Bastiansen and L. Hansen, *Acta Chem. Scand.*, **9**, 1306 (1955).

(27) The further increase (0.4 kcal.) in transition energy observed for a 3-t-butyl group may be due to slightly greater interaction of the same kind, although calculation in the manner described for 4-t-butyl predicts an increase smaller than the experimental error in the measurement.

(28) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

(29) R. A. Barnes, THIS JOURNAL, **81**, 1935 (1959).

(30) Preliminary examination of an ion with both 2- and 4-methyl groups by n.m.r. gives results not in accord with this suggestion. J. W. Patton, unpublished results.

(31) Since the standard solvent contained ethanol and the latter was probably segregated in part from the bulk solvent (see Fig. 4), the exclusion effect might well be more serious than indicated by a comparison of Z-values.

(32) Cf., for example, B. M. Wepster, *Rec. trav. chim.*, **75**, 1473 (1956), in which the decrease in basicity between 2-methylpyridine and 2-t-butylpyridine (no change for the same two groups in the 4-position) is explained as steric hindrance to solvation in the 2-t-butyl-pyridinium ion. This point of view seems more satisfactory than that of Brown[33] which depends upon hyperconjugation, inductive effect and the difference between o-quinoid and p-quinoid resonance forms.

(33) H. C. Brown and X. R. Mihm, THIS JOURNAL, **77**, 1723 (1955).

model previously discussed for the transition,[4] the dipole of the ground state ion pair "flips" into the ring, removing electrostatic interaction between the pyridinium iodide ion-pair dipole and the cybotactic region[4] solvent molecules and, in fact, producing an unstable state, with solvent molecules organized for a dipole which is no longer there.[4] The 4-carbomethoxy group causes the ion-pair dipole to deviate somewhat from a perpendicular orientation to the pyridinium ring and reduces thereby the energy requirements for the "flip." It is reasonable that the unsubstituted salt has a greater solvent sensitivity than the carbomethoxy derivative; even the size of the increase in sensitivity is in accord with this interpretation (cf. ref. 4, footnote 19, p. 3259).

The change in the position of the maximum for 1-methylpyridinium iodide when the ethanol content of the chloroform is varied (Fig. 4) suggests an interesting competition between ion-pairs and chloroform molecules for ethanol. At the concentration levels used (ca. 0.91×10^{-4} M) and for other reasons, it is less likely that the curve found reflects initial dissociation of quadrupoles such as found by Stern[34] for tetrabutylammonium bromide in benzene plus methanol.

It was anticipated that replacement of the 1-methyl group by hydrogen would lead to a further displacement of the charge-transfer maximum in pyridinium iodide to longer wave lengths.[35] The maximum for pyridinium iodide in chloroform proved to be at 3464 Å., 274 Å. *shorter* than for 1-methylpyridinium iodide. The shift observed in the maximum on change to acetonitrile as solvent is so great (314 Å.) as to leave little doubt that a charge transfer transition of a type similar to that found for alkylpyridinium iodides was not involved (Table VI). Further study of the charge-transfer spectra of pyridinium iodides is required.

Extensive studies have been made of the spectra of complexes of methylated benzenes and iodine,[36] iodine monochloride[37] and tetracyanoethylene.[38] It is of some interest to compare the effectiveness of methyl groups in promoting electron transfer (equation 3) from aromatic rings to electron acceptors with their role in *preventing* electron transfer *to the pyridinium ring* in the alkylpyridinium iodides.[39] As in the case of the pyridinium iodides, the arrangement of methyl groups around the ring affects the position of the charge-transfer band, and the change in transition energy for a particular
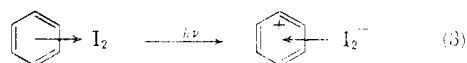
combination depends upon the nature of the acceptor.[40] Rather than estimate a "corrected" position for hydrogen in pyridinium iodide (cf. previous paragraph), a comparison between the aromatic ring with one methyl and that with six methyl groups can be made. The transition energy differences are listed in Table VII; they represent the change in transition energy, for example, on changing the donor from toluene to hexamethylbenzene in an aromatic hydrocarbon–iodine complex.

TABLE VII

EFFECT OF METHYL GROUPS ON TRANSITION ENERGIES

Donor:acceptor	Δ, kcal./mole
Iodide–1-methylpyridinium	+11.4
	+15.5[a]
Toluene–iodine	−18.3
Toluene–iodine monochloride	−13.5
Toluene–tetracyanoethylene	−17.9

[a] Based on effect of 4-methyl group, i.e., 5×3.1 on the assumption that the maximum effect is found only at this position (see text).

If the figure of 15.5 kcal./mole is considered, it can be seen that "maximum electron donation" by methyl groups is roughly of the same magnitude in acceptors as in donors.

Conclusions.—Measurement of the position of a charge-transfer band for a substituted pyridinium iodide offers a new and potentially valuable method of evaluating substituent effects. While electrical effects alone appear to determine the results for 3- and 4-substituents, a steric factor modifies the results for a 2-substituent. Scattered data for 4-substituted pyridinium iodides, reported in another paper,[7] demonstrate that the pyridinium iodide charge-transfer transition is extremely sensitive to the nature of the substituent, with a ρ of 13.4 resulting from a plot of transition energies against the Hammett σ-constant.

Experimental

Materials. 1. Alkylpyridines.—Most of the alkylpyridines used were commercially available. All were carefully redistilled and their refractive indices checked against the literature values. The 4-*t*-butylpyridine was prepared by the method of Brown and Murphey.[41] Samples of 2-*t*-butylpyridine and 3-*t*-butylpyridine were kindly provided by Professor Brown. Pentamethylpyridine was synthesized according to the procedure of Karrer and Mainoni.[42] The physical properties of the pyridines are listed in Table VIII.

2. Alkylpyridinium Iodides.—The purified pyridine was treated with excess alkyl iodide in ethanol under reflux for several hours and under nitrogen, if sensitivity to oxygen required such protection. Not surprisingly, 2-*t*-butylpyridine was less reactive and 100 hr. reflux was used with success but these conditions failed with pentamethylpyridine. Hexamethylpyridinium iodide was obtained by heating the reactants in a sealed tube as reported by Karrer.[42] Pyridinium iodide was isolated easily by evaporation of a mixture of pyridine and concentrated hydriodic acid.

(34) E. A. Richardson and K. H. Stern, American Chemical Society Abstracts, 135, 50 R (1959), Boston, Mass.

(35) Hantzsch[3] reported on both 1-methylpyridinium iodide and pyridinium iodide many years ago. However, there are considerable difficulties attached to obtaining good spectra from pyridinium iodides. The results with 1-methylpyridinium iodide indicate the possible presence of some triiodide; the result for pyridinium iodide, though, does in fact show the same direction of shift for the maximum as found in the present work. In addition, the method used by Hantzsch (variation in cell length, photography) was not suitable for accurate spectra (cf. W. R. Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1939, p. 189).

(36) R. M. Keefer and L. J. Andrews, THIS JOURNAL, 74, 5400 (1952).

(37) R.M. Keefer and L. J. Andrews, ibid., 72, 5170 (1950).

(38) R. E. Merrifield and W. D. Phillips, ibid., 80, 2778 (1958).

(39) Contribution of the charge-transferred form to the ground state is small, as shown by the small dipole moments of most complexes of this type, S. P. McGlynn, Chem. Revs., 58, 113 (1958).

(40) Change in charge-transfer band for toluene–iodine (3020 Å.) to p-xylene–iodine (3040 Å.) is only 20 Å., whereas for toluene–tetracyanoethylene (4060 Å.) to p-xylene–tetracyanoethylene (4600 Å.), the shift is 540 Å.

(41) H. C. Brown and W. A. Murphey, THIS JOURNAL, 73, 3308 (1951).

(42) P. Karrer and S. Mainoni, Helv. Chim. Acta, 34, 2151 (1954).

TABLE VIII

PHYSICAL PROPERTIES OF ALKYLPYRIDINES

Pyridine	B.p., °C.	Mm.	n^{25}D	Source
Pyridine	114	742	1.5064	a
2-Methyl-	125–126	741	1.4987	b
3-Methyl-	140–142	740	1.5003	c
4-Methyl-	141–142	738	1.5013	c
2,3-Dimethyl-	58–59	20	1.5038	c
2,4-Dimethyl-	153–154	739	1.4977	c
2,5-Dimethyl-	154–156	740	1.4974	d
2,6-Dimethyl-	139–140	741	1.4956	b
3,5-Dimethyl-	166–168	738	1.5033	e
2,4,6-Trimethyl-	57–58	8	1.4998	c
Pentamethyl-	87–89	4	....	Synthesis[42]
4-Ethyl-	165–166	741	1.5000	f
4-n-Propyl-	86–87	33	1.4948	f
4-i-Propyl	74–75	29	1.4944	g
4-t-Butyl	73	18	1.4943	Synthesis[41]

a Merck and Co.; b Crude commercial material; c Matheson–Coleman–Bell; d K and K laboratories; e Reilly Tar and Chemical Corp.; f Eastman Organic Chemicals.

The melting points corresponded in most cases to those found in the literature. Equivalent weights were determined by titration with silver nitrate using 0.1% eosin in alcohol as indicator. The melting points, recrystallization methods and titration results are recorded in Table IX. The criteria of purity were therefore melting point and equivalent weight. All salts were colorless solids with the exception of 1-methyl-4-ethylpyridinium iodide as noted in Table III.

The alkylpyridinium iodides were stable on storage away from light, moisture and oxygen. Phillips[53] has reported that 1-methyl-2-ethylpyridinium iodide darkened rapidly even in the absence of light and was difficult to recrystallize. The same author also reported 1-methyl-2-(2-phenylethyl)-pyridinium iodide to be pale yellow.

An interesting consequence of steric strain was observed in the behavior of 1-methyl-2-t-butylpyridinium iodide. On recrystallization from hot solvents, some reversal of the original quaternization reaction ensued and the product had the odor of 2-t-butylpyridine. A similar odor was noted after the salt had been stored for a long time (ca. 2 years) in a sealed ampoule under nitrogen. Recrystallization from methanol by dissolving the salt at room temperature, cooling, and adding ether gave odorless white crystals. In contrast, hexamethylpyridinium iodide appeared to be stable even in boiling methanol. Most of the salts melted to

TABLE IX

ALKYLPYRIDINIUM IODIDES

Substituents	M.p., °C. Found	M.p., °C. Reported	Recrystallization Solvent	Method[a]	Eq. weight Calcd.	Eq. weight Found
1-H–	199–202 dec.	193–195[44]	EtOH	A	207.0	207.3
1-Me–	116.6–117.2	117[45]	EtOH	A	221.1	221.7
1-Et–	93–94	90.5[45]	EtOH	A	235.1	236.0
1-i-Pr–	119.6–121	114–115[45]	EtOH	A	249.1	249.7
1,2-Me$_2$–	230–231	229–231[52b]	H$_2$O	B	235.1	235.3
1,3-Me$_2$–	99–100	92[46]	i-PrOH	C	235.1	236.8
1,4-Me$_2$–	153–153.8	153–154[52b] 157–158[47]	EtOH	A	235.1	234.9
1,2,3-Me$_3$–	206–206.8	205[48]	EtOH	A	249.1	249.9
1,2,4-Me$_3$–	117–118	118[49]	i-PrOH	A	249.1	249.6
1,2,5-Me$_3$–	184–185		EtOH	A	249.1	248.9
1,2,6-Me$_3$–	236.8–238	238–240[52b]	EtOH	A	249.1	249.6
1,3,5-Me$_3$–	268–270	275[50]	EtOH	A	249.1	249.0
1,2,4,6-Me$_4$–	213–214.2	213.2–214.3[52b]	MeOH	A	263.2	263.1
1,2,3,4,5,6-Me$_6$–	184–185	183[42]	MeOH	C	291.2	292.2
1-Me-4-Et–	109–110	113,[51] 280[52a]	EtOH	C	249.1	250.2
1-Me-4-n-Pr–	80.8–81.4		EtOH–MeOH	C	263.2	262.8
1-Me-4-i-Pr–	117–120 dec.		i-PrOH–MeOH	C	263.2	263.2
1-Me-4-t-Bu–	124–125		EtOH	C	277.1	277.6
1-Me-2-t-Bu–	227–227.5 dec.		MeOH	C	277.1	277.1
1-Me-3-t-Bu–	168.2–169.4		i-PrOH	C	277.1	278.6

a A, dissolved in warm solvent, then cooled. B, forced from aqueous solution with acetone. C, dissolved at room temperature, cooled, ether added.

Recrystallization of the crude salts was carried out in an alcohol, with minimal exposure to light and air. Ether was used in a number of cases to reduce solubility. After filtering the solid and washing with ether, the salts were dried in a vacuum desiccator over calcium chloride. Activated charcoal proved to be useful in eliminating triiodide and other impurities from the solutions of iodide salts. From three to ten recrystallizations were carried out to achieve constancy of melting point. The sensitivity of many of the 1-methyl-4-alkylpyridinium iodides to moisture and air was so great that these salts were recrystallized in a dry box under nitrogen atmosphere. The crude salt was dissolved in methanol or methanol–isopropyl alcohol mixture in a brown bottle at room temperature. The bottle was cooled in Dry Ice and ether added dropwise until crystals had formed. A rubber sheet pierced by a slit was placed over the mouth of the bottle and supernatant solvent removed by a syringe with a long needle. (All solvent containers were, of course, covered except during transfer operations.) The salt was washed several times with ether using the syringe, then dried with a gentle stream of dry nitrogen.[43]

yellow liquids. Pyridinium hydriodide and 1-methyl-4-i-propylpyridinium iodide decomposed on melting, and 1-methyl-2-t-butylpyridinium iodide melted, then vanished

(43) Suggestion of Dr. Richard Heck, Research Department, Hercules Powder Co., Wilmington, Delaware.

(44) R. A. Zingaro and W. E. Tolberg, THIS JOURNAL, 81, 1353 (1959).

(45) A. B. Prescott, ibid., 18, 91 (1896).

(46) E. A. Coulson and J. Jones, J. Soc. Chem. Ind., 65, 169 (1946).

(47) E. A. Bergmann, J. E. Crane, Jr., and R. M. Fuoss, THIS JOURNAL, 74, 5979 (1952).

(48) A. Mustafa and M. K. Hilmy, J. Chem. Soc., 1698 (1947).

(49) T. Takahashi and K. Sotake, J. Pharm. Soc. Japan, 74, 135 (1954).

(50) M. P. Oparina, J. Russ. Phys. Chem. Soc., 61, 2001 (1929).

(51) T. Takahashi and J. Shibasaki, J. Pharm. Soc. Japan, 72, 1137 (1952).

(52) (a) T. Takahashi, K. Sotake and S. Yasui, ibid., 74, 577 (1954); (b) E. M. Kosower and P. E. Klinedinst, Jr., THIS JOURNAL, 78, 3493 (1956).

(53) A. P. Phillips, J. Org. Chem., 13, 622 (1948).

as the salt was transformed into 2-*t*-butylpyridine and methyl iodide, both of which boil below the melting point.

The ultraviolet spectra of the twenty pyridinium iodides used in our study also were measured in dilute aqueous solution. The data were in good agreement with those previously measured. The perchlorate salts would have been more suitable for dilute aqueous solution ultraviolet spectra but it was not possible to include them in this study. Perchlorate ion is transparent to light in the region of an intense pyridinium absorption (*ca.* 2200 Å.).[54] Alkyl substitution shifts 2600 Å. pyridinium absorption to longer wave lengths and raises the absorption intensity. Groups in the 4-position are considerably less effective than on either the 2- or 3-positions in changing the wave length maximum and, in addition, have little effect upon intensity. Groups in the 2-position are very effective in raising the absorption intensity. Hexamethylpyridinium ion has the longest wave length maximum, while 1,2,6-trimethylpyridinium ion has the highest absorption intensity at the maximum. Table X summarizes the data.

3. Solvents.—Dimethylformamide, acetonitrile and isopropyl alcohol were Spectro grade solvents purchased from Matheson, Coleman and Bell. Ethanol (absolute) was dried by distillation from 4A Molecular Sieve (Linde Products).

Pure chloroform was prepared by the procedure outlined by Fieser[55] by successive treatments of analytical reagent grade solvent with sulfuric acid, water and calcium chloride, followed by distillation under nitrogen. The distillate was collected directly in volumetric flasks containing dry ethanol measured with a micropipet.[56] After the flasks had been filled to the mark, the solvents were examined with a Baird Infrared Spectrophotometer, Model B, and a Perkin-Elmer Infracord (Model 137) in 1.0 mm. cells. Curves obtained with the Baird at slow speed were read at 2.71 μ and a calibration line prepared by plotting the optical density for alcohol absorption against the volume % ethanol. A good straight line was obtained (equation 4)

$$\Delta D_{2.71} \mu = 0.7298V + 0.0115 \qquad (4)$$

where V = volume % ethanol. A similar line was constructed from data obtained with the Infracord, setting ΔD equal to zero for pure chloroform. The slope of the line differed somewhat from that found with the Baird and the two lowest points were not on the line. The chief difficulty is the inferior resolution of the Infracord. Since it was impractical to use any machine but the Infracord to standardize the chloroform solutions during the times when solvents were prepared for use in ultraviolet measurements, the ethanol percentages are valid to only about ±6%, *i.e.*, ±0.05% for the standard chloroform.

The variation in the position of the charge-transfer band for 1-methylpyridinium iodide with a change in the ethanol content of the chloroform was of considerable intrinsic interest. It was found necessary to standardize even freshly opened bottles of analytical reagent chloroform. Sufficient variation in ethanol content occurred so that *each* bottle had to be analyzed and corrected. The chloroform used initially had an ethanol content of 0.90% and this percentage was fixed as "standard." Samples found to contain less ethanol were converted easily to suitable solvent by the addition of ethanol with a micropipet after calculating the amount needed from the infrared spectrum and the Infracord calibration line. Samples with excess ethanol contents were suction filtered through alumina in the dry box under nitrogen, then reanalyzed by infrared. It was then necessary to add ethanol to produce standard solvent. Both magnesium sulfate and sodium sulfate were ineffective in reducing the ethanol content of chloroform. Calcium chloride reduced the alcohol content but also added an impurity to the solvent (perhaps traces of calcium chloride) which changed the spectrum of 1-methylpyridinium iodide.

Spectra.—The chief difficulty anticipated was the change in absorption curves produced by the presence of small amounts of triiodide. Although satisfactory curves (corroborated by later work as described below) could be obtained for many salts on cool days of relatively low humid-

(54) W. M. Schubert and J. Robins, THIS JOURNAL, **80**, 559 (1958).

(55) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., Boston, Mass., 1955.

(56) Small amounts of ethanol added to chloroform give the volumes expected from simple addition.

TABLE X

ULTRAVIOLET MAXIMA OF ALKYLPYRIDINIUM IONS

Substituents	λ_{max},[a] Å.	(ϵ_{max})
1-H-	2615(s),[b] 2558, 2509	3070, 4230, 4200
1-Me-	2652(s), 2587, 2533(s)	3120, 4370, 3840
1-Et-	2649(s), 2587, 2530	3400, 4710, 4140
1-*i*-Pr-	2646(s), 2583, 2529	3140, 4370, 3850
1,2-Me₂-	2649	6150
1,3-Me₂-	2657	4690
1,4-Me₂-	2624, 2598(s), 2548	3270, 3340, 4350
	2497, 2473(s)	3990, 4050
1,2,3-Me₃-	2707	4930
1,2,4-Me₃-	2667, 2623(s)	4970, 4870
1,2,5-Me₃-	2723	4560
1,2,6-Me₃-	2725	8120
1,3,5-Me₃-	2710	5250
1,2,4,6-Me₄-	2732, 2688	7130, 7360
1,2,3,4,5,6-Me₆-	2852, 2817	7300, 7180
1-Me-4-Et-	2606, 2552	3310, 4330
1-Me-4-*n*-Pr-	2611, 2552	3290, 4380
1-Me-4-*i*-Pr-	2609, 2547	3320, 4340
1-Me-4-*t*-Bu-	2615, 2549	3190, 4170
1-Me-2-*t*-Bu-	2677	7210
1-Me-3-*t*-Bu-	2650	4730

[a] The aqueous spectra were run in 2-cm. cells at a concentration of 1.25×10^{-4} M in water redistilled from potassium permanganate. Error of ±5 Å. [b] Shoulder.

ity,[57] no independent checks of purity were available for the solutions used, other than reproducibility of results obtained upon similar solutions. In addition, it was necessary to use rather low concentrations in order to ensure rapid solution. To avoid doubts all solutions for ultraviolet work (except those in water as solvent) were prepared in a *good* dry box[58] equipped with utilities and seven-ply rubber iris ports. A dry nitrogen atmosphere was maintained in the box under slight positive pressure. During manipulations within the box, the hands of the operator were protected by long latex gloves.

Samples were weighed in the weighing chamber of a Cahn Electrobalance, model M 10, fixed at a convenient height within the box, with the control portion of the balance outside, on top of the box, within easy reach. Not only does this balance allow routine, accurate and rapid weighing of samples in the 1 mg. range, but it is hard to conceive another technique whereby sample weights could be duplicated in a dry box with the desired accuracy.

Spectra were measured on a Cary Recording Spectrophotometer Model 11 at a speed of 5 Å./sec. from 4000 Å. down to the wave length where optical density exceeded 2.1 (a point dependent upon the absorption band of the pyridinium ring, *cf.* Table X). The peaks were rerun three to five times at one or both of the lowest speeds 1 and 2 Å./sec.

The solvent was examined periodically in a 1 cm. cell against air as reference. The wave length at which the optical density became 1.0 varied between 2420 and 2480 Å. in an irregular fashion at a speed of 5 Å./sec. using chloroform stored in a brown bottle. Since the point taken is on a sharply rising curve, the reproducibility is considered satisfactory and agrees with the usual "cutoff" point quoted for chloroform, 2450 Å. (*i.e.*, the wave length at which the solvent has an optical density of one against air). Solvent stored in a polyethylene "squeeze" bottle (to facilitate rapid but accurate filling of volumetric flasks) showed little change in cutoff point after 17 hr. Absorbance at 2700 Å. of solvent stored in a glass bottle fluctuated between 0.017 and 0.040 while the solvent kept in the polyethylene container increased from 0.023 to 0.045 in 17 hr. In practice, a single

(57) The exceedingly salubrious winter climate of Wisconsin offers many days of the proper quality.

(58) Constructed by Krueger Fabricating Company, Madison, Wisconsin, from stainless steel, using all welded seams and an effective method of applying uniform pressure to the front glass plate. It was necessary to seal the edges of the glass plate and the pipe joints on the gas recirculation system.

batch of standard chloroform was never in contact with the polyethylene for more than 2 hr. The solvent thus proved to be satisfactory and constant with respect to ultraviolet absorption over the time periods of interest in this work. The technique used in preparing a cell for spectroscopic examination can be described as follows: The Electrobalance was calibrated and set for a given sample weight. A sample of salt was obtained from a brown bottle stored in the dry box and quickly placed on the aluminum pan of the balance. The weighed sample was transferred to a 50 ml. volumetric flask through a funnel, and the pan and funnel were thoroughly rinsed with chloroform solvent from a polyethylene squeeze bottle (see previous paragraph). The flask was stoppered and shaken for approximately 30 sec. The colorless solution was used to rinse a 10 cm. cell several times, then used to fill the cell (ca. 33 ml.). The cell was removed through one of the rubber irises, placed in a box for protection from the light and rushed to the spectrophotometer, in which a solvent–solvent baseline already had been run. All spectra were started within two minutes of mixing; curves and reruns over maxima required another 30 minutes. All solutions were prepared and run at night with the small bulb in the weighing chamber of the Electrobalance as the only source of light. The weights of sample were chosen to give optical density between 0.5 and 1.5 at the maximum. The temperature of the area in which the solutions were prepared varied between 25 and 27° while that of the room in which the spectra were measured was usually about 24°. Although it would have been desirable to control the temperature more closely than this difference of two or three degrees, speed was considered of greater importance than a small difference in temperature.

Each pyridinium iodide was measured at least six times, that is to say, six separate solutions were made for each salt. The best five of the six averages of the maxima (read from slow reruns) were again averaged to give the numbers reported in this work. It will be noted that the errors stated in the tables of the text are larger than those directly derived from the data by obtaining the average deviation from the average. In these cases, the somewhat lower reliability of results from relatively flat absorption curves at optical densities below 0.5 caused us to assign larger error limits. Three sample sets of data are shown in Table XI.

Previous work[4] had shown that a large change in salt concentration could cause a considerable change of the maximum of an alkylpyridinium iodide in chloroform solution. To establish that the absorption intensities observed reflected intrinsic properties of the pyridinium iodide complex and not dissociation, absorption intensities were measured over a three to fourfold range for three salts, 1-methylpyridinium iodide, 1,2,6-trimethylpyridinium iodide (low ϵ_{max}) (given in Table XII) and 1,3,5-trimethylpyridinium iodide (high ϵ_{max}). The lowest concentrations in particular had the same absorption intensity as the one used in the determination of the maximum except in the case of the lowest concentration of 1-methylpyridinium iodide where an increase in the intensity ratio of the first and second charge-transfer bands led to the conclusion that ca. 10^{-7} molar triiodide ion was present. The absence of such indication in virtually every other case where the change could be directly observed as in 1-methylpyridinium iodide suggested that our precautions and routine kept the triiodide concentration down to less than 2×10^{-8} M. The difficulty in ensuring that the contents of iodide solutions are free from triiodide ion when the iodide concentration is 10^{-4} M or lower has been discussed by Reid and Mulliken.[59]

Oscillator Strengths.—Curves were measured from the point at which light absorption was the same as that of the blank to the maximum. The curves were replotted as absorption intensity against wave number. The absorption curve was cut out and weighed and the integrated absorption intensity determined by direct comparison with a rectangular section of the same graph paper, followed by multiplication by two. The latter, of course, assumes that the curve is symmetrical about the maximum. Oscillator strengths were obtained from the equation

$$f_0 = 4.32 \times 10^{-9} \int \epsilon_\nu d\nu \qquad (5)$$

(59) C. Reid and R. S. Mulliken, THIS JOURNAL, 76, 3869 (1954).

TABLE XI

CHARGE-TRANSFER MAXIMA OF ALKYLPYRIDINIUM IODIDES

Chart no.	Temp., °C.	Concentration Mg./50 ml.	$M \times 10^{-4}$	λ_{max}, Å.	D_{max}	ϵ_{max}	E_T, kcal./mole
		1-Methylpyridinium iodide					
138	25	1.000	0.905	3736	1.085	1200	76.5
				2895	1.372	1510	98.8
139	26	1.024	.926	3738	1.111	1200	76.5
				2895	1.422	1530	98.8
140	26	0.989	.895	3743	1.100	1230	76.4
				2905	1.380	1540	98.4
141	25	1.000	.905	3738	1.086	1200	76.5
				2892	1.413	1560	98.9
142	25	1.000	.905	3735	1.090	1200	76.6
				2880	1.447	1600	99.3
		Hexamethylpyridinium iodide					
327	25	1.320	0.907	3255	0.500	550	87.8
328	25	1.328	.912	3253	.500	550	87.9
329	25	1.320	.907	3252	.502	550	87.9
330	25	1.320	.907	3252	.517	570	87.9
331	25	1.330	.914	3253	.525	570	87.9
		1-Methyl-2-t-butylpyridinium iodide					
347	27	1.262	0.911	3694	1.120	1230	77.4
348	27	1.262	.911	3695	1.150	1260	77.4
349	27	1.262	.911	3695	1.123	1230	77.4
350	27	1.262	.911	3692	1.137	1250	77.4
351	27	1.262	.911	3694	1.127	1240	77.4

TABLE XII

CONCENTRATION VARIATION: 1,2,6-TRIMETHYLPYRIDINIUM IODIDE

Concn., $M \times 10^{-4}$	λ_{max}, Å.	Error, Å.	ϵ_{max}	E_T, kcal./mole
1.148	3590	±10	430	79.6
0.905	3580	±10	420	79.9
.685	3590	±10	400	79.6
.465	3600	±10	400	79.4

The f_0 values obtained were: potassium iodide in water, 0.228; 1,2,4,6-tetramethylpyridinium iodide in chloroform, 0.012; 1-methylpyridinium iodide in pure chloroform, 0.026, possibly significantly higher than the f_0 value in "standard" chloroform, 0.024.

MADISON 6, WISCONSIN