Experimental Evidence Concerning the Nature of the Two Charge-Transfer Bands in Pyridinium Iodides

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Abstract: A variety of data (spectral, kinetic, and polarographic) is presented for a series of pyridinium iodides in order to establish evidence for the nature of the charge-transfer (CT) interactions of these salts. Two CT bands are normally observed in the absorption spectra of pyridinium iodides. The experimental evidence corroborates assignment of these bands to electronic transitions from the highest occupied molecular orbital of iodide ion to two closely located vacant molecular orbitals in the pyridinium ion. Support was not obtained for an alternate explanation involving formation of iodine atoms in the $^2P_{1/2}$ and $^2P_{3/2}$ states upon electronic excitation of the pyridinium iodide. It is further affirmed that the CT contribution to the ground state of the pyridinium iodide ion pair is quite small. The ground-state stabilization of the CT complex is thus primarily electrostatic.

It has long been known that pyridinium iodides possess electronic absorption bands which may be ascribed to charge transfer (CT) from the iodide ion to the pyridinium ion.[1] In relatively nonpolar solvents, two such CT bands are observed for a variety of 2-, 3-, and 4-substituted pyridinium iodides, as well as for the unsubstituted salt itself. The positions of these bands are quite sensitive to the solvent; the energy of the first (long wavelength) CT transition in 4-carbomethoxy-1-ethylpyridinium iodide is the basis of *Z* values, an empirical measure of solvent polarity.[2] The transition energy (E_t) is dependent on both the nature and position of the ring carbon substituent. It is also sensitive to the nature of the N substituent, as illustrated in a comparison of ethyl and benzyl derivatives.[3]

Many studies utilizing pyridinium ion have been performed. Examples include investigations of micelle formation,[4] ion-pair reactions,[5] inter- and intramolecular CT interactions of neutral organic donors,[6] and the relation between the biochemical importance of the 3-carbamidopyridinium group and its electron-acceptor properties.[7]

However, relatively little attention has been devoted to the second CT band often observed at lower wavelengths in the spectra of pyridinium iodides. The existence of two CT bands was initially ascribed to the $^2P_{1/2}$ and $^2P_{3/2}$ states of the iodine atom.[8] Upon transfer of an electron to the ring, the resulting iodine atom may be left in its ground state or its first excited state. This explanation was based on the observation that ΔE_t for 1-methylpyridinium iodide was almost equal to the energy difference between the $^2P_{1/2}$ and $^2P_{3/2}$ states of the iodine atom (Table I). It was noted, however, that ΔE_t was greatly influenced by the ring position of electron-withdrawing substituents. Recently, it has been suggested that the two CT bands are caused by the presence of two closely located vacant molecular orbitals in the pyridinium ion.[6] This alternate explanation is based on the observation of two CT bands in the spectrum of 3-cyano-1-methylpyridinium ion with *N*,*N*-dimethylaniline as donor.

Table I. ΔE_t (kcal mol^{-1}) for Iodide Spectral Transitions[a]

Iodide	Solvent	E_{t1}	E_{t2}	ΔE_t
Potassium	H_2O	126.6	147.6	21.0
Sodium	H_2O	126.4	147.8	21.4
Sodium	$(CH_3)_2CO$	112.1	132.3	20.2
1-Methyl-pyridinium	Pure $CHCl_3$	97.1	75.3	21.8

Difference between the $^2P_{1/2}$ and $^2P_{3/2}$ states of iodine atom = 21.74

[a] Reference 8.

We report here spectral, kinetic, and polarographic data for a series of pyridinium iodide salts in order to further elucidate the nature of the CT interaction.

Results

In Table II are given the observed CT band energies for a variety of 1-methyl(and ethyl)-2-, 3-, and 4-substituted pyridinium iodides in methylene chloride. Representative spectra for the 2-, 3-, and 4-cyano derivatives are shown in Figure 1. A definitive second CT band was not observed for the 2-, 3-, and 4-benzoyl compounds and the oxime ether derivatives. The wavelength region in which the second band was expected to be present, by comparison with the other compounds, was obscured for all except the 3-benzoyl derivative. For this 3-substituted compound the short-wavelength CT band either is very weak or has an energy in excess of 17 kcal mol^{-1} higher than the first CT band.

The second-order rate constants (k_p) for the anion-exchange reaction between the pyridinium iodide salts and methyl tosylate in methylene chloride are given in Table III. The pyridinium salts are completely associated in methylene chloride within the experimental limits of detection and the reacting species is thus the ion pair, as shown in eq 1.[5] There appears to be some

$$Py^+,I^- + TsOCH_3 \longrightarrow Py^+ + OTs^- + CH_3I \qquad (1)$$

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[1] E. M. Kosower and J. A. Skorcz, *J. Amer. Chem. Soc.*, **82**, 2195 (1960), and references therein.

[2] E. M. Kosower, *ibid.*, **80**, 3253 (1958).

[3] E. M. Kosower, D. Hofmann, and K. Wallenfels, *ibid.*, **84**, 2755 (1962).

[4] A. Ray and P. Mukerjee, *J. Phys. Chem.*, **70**, 2138 (1966); P. Mukerjee and A. Ray, *ibid.*, **70**, 2144, 2150 (1966).

[5] R. A. Mackay and E. J. Poziomek, *J. Amer. Chem. Soc.*, **92**, 2432 (1970).

[6] J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *Tetrahedron*, **25**, 3395 (1969).

[7] G. Cilento and P. Giusti, *J. Amer. Chem. Soc.*, **81**, 3801 (1959).

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

Table II. Charge-Transfer Band Energies for Various Pyridinium Iodides in Methylene Chloride

Substituent	E_{t1}[a]	$1/\lambda_1$	E_{t2}[a]	$1/\lambda_2$	ΔE_t[b]	$\Delta 1/\lambda$
1-CH_3, 2-CN	59.8	20900	81.2	28400	21.6	7500
1-CH_3, 3-CN	65.0	22750	79.0	27600	14.0	4850
1-C_2H_5, 3-CN	66.0	23050	78.8	27550	12.8	4500
1-CH_3, 4-CN	58.2	20350	85.3	29850	27.1	9500
1-C_2H_4, 4-CN	59.3	20750	86.0	30050	26.7	9300
1-CH_3, 2-$COOC_2H_5$	67.8	23700	89.6	31350	21.8	7650
1-CH_3, 3-$COOC_2H_5$	71.3	24950	86.6	30300	15.3	5350
1-CH_3, 4-$COOC_2H_5$	65.2	22800	93.6	32750	28.4	9950
1-CH_3, 2-$COCH_3$	64.7	22600	87.2	30500	22.5	7900
1-CH_3, 3-$COCH_3$	70.6	24700	80.8	28250	10.2	3550
1-CH_3, 4-$COCH_3$	63.8	22300	92.5	32350	28.7	10050
1-CH_3, 2-COC_6H_5	69.5	24300				
1-CH_3, 3-COC_6H_5	70.4	24600				
1-CH_3, 4-COC_6H_5	64.6	22600				
1-CH_3	76.7	26800	98.2	34350	21.5	7550
1-CH_3, 4-$C(CN){=}NO(CH_2)_2CH_3$	62.0	21700				
1-CH_3, 4-$C(H){=}NO(CH_2)_2CH(CH_3)_2$	69.5	24300				
1-CH_3, 4-$C(CN){=}NOCH_2C_6H_5$	61.1	21400				

[a] E_{t1} and E_{t2} are the energies of the first (longer wavelength) and second (shorter wavelength) CT bands in kilocalories per mole. $E_t = 2.859 \times 10^5/\lambda$ Å: E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 296. $1/\lambda_1$ and $1/\lambda_2$ are the corresponding frequencies in reciprocal centimeters (±70). $\Delta E_t = E_{t2} - E_{t1}$ kcal mol^{-1}. $\Delta 1/\lambda = 1/\lambda_2 - 1/\lambda_1$ cm^{-1}. Precision and accuracy for the E_t values listed are in the order of ±0.2 and ±0.4 kcal mol^{-1}, respectively.

Table III. Kinetic and Polarographic Data for Various Pyridinium Iodides at 25°

Substituent	10^2k_p[a]	$-E_{1/2}$[b]
1-CH_3, 2-CN	8.0	0.60 ± 0.01
1-CH_3, 3-CN		0.76 ± 0.01
1-C_2H_5, 3-CN	7.3	
1-CH_3, 4-CN	6.7	0.65 ± 0.01
1-C_2H_5, 4-CN	7.3	0.70 ± 0.02
1-C_2H_5, 4-CN[c]		0.72 ± 0.01
1-CH_3, 2-$COOC_2H_5$	11.8	0.83 ± 0.02
1-CH_3, 3-$COOC_2H_5$	8.5	0.93 ± 0.01
1-CH_3, 4-$COOC_2H_5$	8.2	0.77 ± 0.02
1-CH_3, 2-$COCH_3$	11.7	0.76 ± 0.01
1-CH_3, 3-$COCH_3$	7.7	0.89 ± 0.01
1-CH_3, 4-$COCH_3$	10.3	0.70 ± 0.01
1-CH_3, 2-COC_6H_5	9.3	0.75 ± 0.01
1-CH_3, 3-COC_6H_5	9.0	0.83 ± 0.01
1-CH_3, 4-COC_6H_5	7.8	0.65 ± 0.01
1-CH_3	9.8	1.21 ± 0.01
1-CH_3, 4-$C(CN){=}NO(CH_2)_2CH_3$	7.9	0.58 ± 0.01
1-CH_3, 4-$C(H){=}NO(CH_2)_2CH(CH_3)_2$	10.4	
1-CH_3, 4-$C(CN){=}NOCH_2C_6H_5$	8.3	

[a] Second-order rate constant for eq 1 in liters per mole per minute (±0.3). Solvent is CH_2Cl_2; 0.1 *M* $TsOCH_3$; *ca.* 10^{-3} *M* pyridinium iodide salt. [b] Polarographic half-wave potential in acetonitrile (volts *vs.* sce), 0.1 *M* in $[CH_3(CH_2)_3]_4N^+ClO_4^-$. [c] Perchlorate.

trend, for a given position, toward increasing values of k_p with increasing values of E_{t1}. However, a number of points do not correlate, and in any event the entire range of k_p values differs by slightly less than a factor of 2. Thus, the nature and position of the substituent on the pyridinium cation have little effect on the rate constant.

The polarographic half-wave potentials ($E_{1/2}$) for the pyridinium iodides in acetonitrile are also given in Table III. Plots of log $[i/(i_D - i)]$ *vs.* E, where i is the diffusion current, i_D the limiting diffusion current, and E the voltage, are linear with slopes corresponding to a one-electron transfer. Since the half-waves are cathodic, the electrode process is the reversible one-electron reduction of pyridinium ion to pyridinyl radical.

$$Py^+ + e^- \longrightarrow Py\cdot \qquad (2)$$

The reversibility of the half-wave is due to the relative stability of the radical in aprotic solvents, such as acetonitrile, as has been demonstrated by previous workers.[9] In addition, all of the salts examined possess sufficient solubility in acetonitrile, which has a good polarographic range when dry. The accuracy of the $E_{1/2}$ values will be less than the reported precision, since no correction was made for the ir drop.

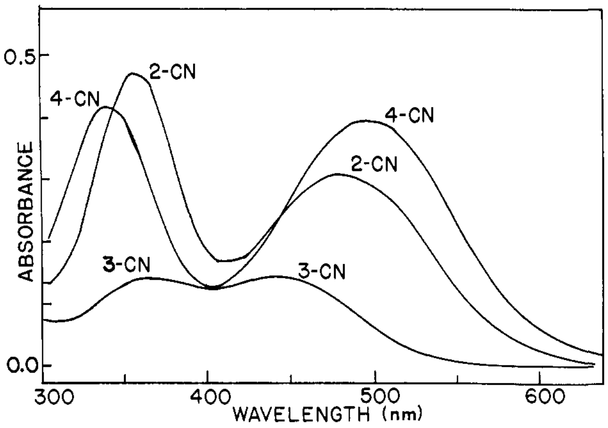

Figure 1. Charge-transfer spectra of 2-, 3-, and 4-cyano-1-methylpyridinium iodides in CH_2Cl_2. A 1-cm cell was used; each solution was saturated. The molar absorptivities are estimated to be on the order of 1000–1200 l. mol^{-1} cm^{-1} for the long-wavelength bands.

A plot of the first (E_{t1}) and second (E_{t2}) CT band energies *vs.* $E_{1/2}$ is shown in Figure 2. Although there is some scatter, it may be seen that there is a correlation between E_{t1} and $E_{1/2}$, while little if any correlation exists between E_{t2} and $E_{1/2}$. The correlation coefficients[10] for E_{t1} and E_{t2} are 0.872 and 0.522, respec-

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(9) W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Amer. Chem. Soc.*, **83**, 3164 (1961); W. M. Schwarz, Jr., Ph.D. Thesis, University of Wisconsin, 1961.

(10) The correlation coefficient (r) is calculated from the expression

$$r = \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})/ns_xs_y$$

where s_x and s_y are the standard deviations of the variables x and y, respectively.

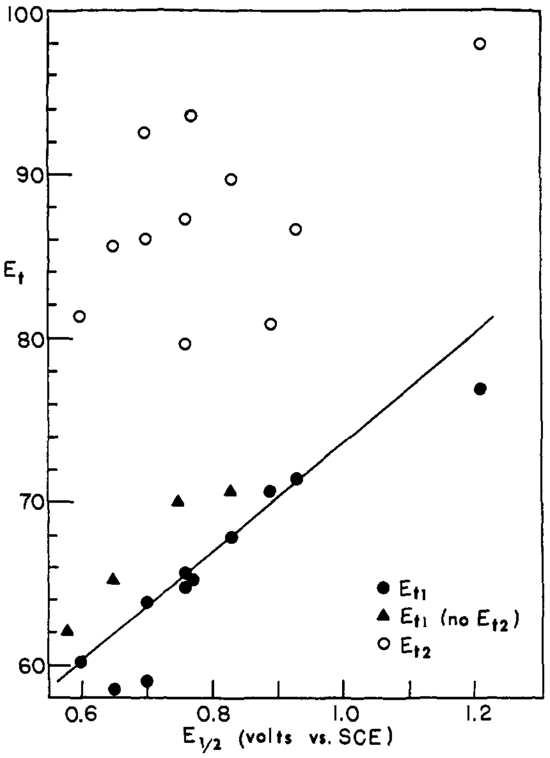


Figure 2. First and second CT band energies *vs.* polarographic half-wave potentials for various 2-, 3-, and 4-substituted pyridinium iodides. The E_{t1} (no E_{t2}) legend for the triangular symbols refers to data from the benzoyl derivatives and one of the cyanoformyloxime ethers. The shorter wavelength CT band (E_{t2}) was not observed with these compounds.

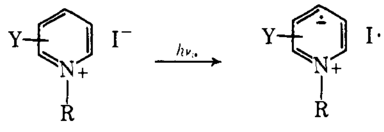
tively. A least-squares fit of the data to a straight line for the first CT band is given by

$$E_{t1} = 28.5E_{1/2} + 44.0 \tag{3}$$

The agreement of the $E_{1/2}$ values for 1-ethyl-4-cyanopyridinium iodide and perchlorate indicate that the anion has no appreciable effect on the half-wave potential.

Discussion

The electronic spectra of the pyridinium iodide salts studied show clearly two CT transitions. Actually, several transitions are possible, as shown by the following equations.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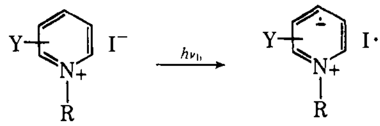
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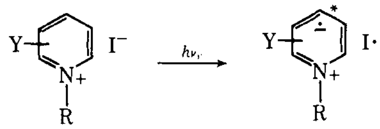
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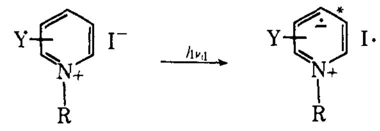
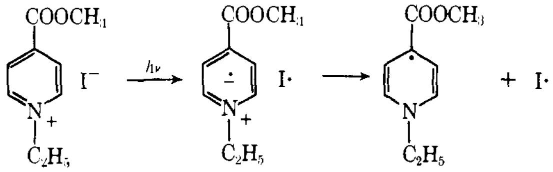

(7)

The transitions represent various combinations in which the pyridinium moiety has accepted an electron in one of two closely located vacant molecular orbitals and the iodine atom is left in its ground state or first excited state.

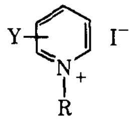
There is adequate evidence for the nature of the overall transition. It has been shown that one consequence of the photoexcitation of 4-carbomethoxy-1-ethylpyridinium iodide is dissociation to 4-carbomethoxy-1-ethylpyridinyl radical (eq 8).[11] This particular radical has been isolated in pure form.[12]


(8)

As mentioned, only two CT bands are evident in the electronic spectra of pyridinium iodides. It is reasonable to assign the long-wavelength band to eq 4, which represents the lowest energy transition. The transition represented by eq 7 would be expected to occur at energies too high to detect easily in our spectra.

For the mechanism represented by eq 5, the nature and position of the substituent would be expected to have little effect on ΔE_t, although they will, of course, affect the energies of the individual CT bands. From Table II it may be seen that ΔE_t varies between 10 and 28 kcal mol^{-1}, a range of about 1 eV. In addition, ΔE_t appears to be dependent primarily on the position, rather than the nature of the substituent, and decreases in the order 4 > 2, unsubstituted > 3. It is also interesting to note that ΔE_t values in solid-state spectra of pyridinium iodides appear to parallel those calculated from CH_2Cl_2 spectra.[13]

The only conceivable way in which the mechanism of eq 5 could produce effects on ΔE_t of these magnitudes is if there were extensive overlap of the involved orbitals.[14] If this is the case, then the ground-state (referring to the ion pair) stabilization energy should possess a large CT contribution. In other words, both the electrostatic (A) and CT (B) forms make substantial contribution to the ground-state ion pair.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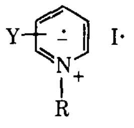
B

This difference in ion-pair stabilization energy should be reflected in the rate of reaction of the ion pair with methyl tosylate. Since there will be no CT interaction in the transition-state ion pair, and since it has been shown previously that the ground- and transition-state ion pairs have similar solvation properties,[5] any difference in the second-order rate constant (k_p) will be due to differences in ground-state stabilization energy. The entire range of k_p values in Table III corresponds to a free energy difference of only a few

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(11) E. M. Kosower and L. Lindqvist, *Tetrahedron Lett.*, 4481 (1965).

(12) E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, 86, 5515 (1964).

(13) E. J. Poziomek and R. A. Mackay, unpublished results.

(14) This refers to the highest filled and lowest vacant orbitals of the donor (iodide) and the acceptor (pyridinium), respectively.

Table IV. Pyridinium Iodides

	Melting point, °C	
Substituent	Found[a]	Reported
1-CH_3	118.5–119	116–117.2,[f] 117,[g] 115–117[h]
1-CH_3, 2-$COCH_3$	162–163 dec	163–164,[i] 159–160,[j] 158–159[k]
1-CH_3, 3-$COCH_3$	165.5–166	162,[l] 166,[m] 163–164,[j] 163.5,[k] 154.4–155.2[n]
1-CH_3, 4-$COCH_3$	175–175.5 dec	176,[m] 177–178,[j] 175[k]
1-CH_3, 2-$COOC_2H_5$	106.5–107.5	108.3–109.3[o]
1-CH_3, 3-$COOC_2H_5$	97–99	100[l]
1-CH_3, 4-$COOC_2H_5$	121–121.5	122–124[p]
1-CH_3, 2-CN	175 dec	183–184,[q] 175–176 (vacuum) dec,[o] 175.5–177[k]
1-CH_3, 3-CN	197.5–198 dec	198,[r] 196,[l] 200.5,[k] 154.5–155.2[n]
1-C_2H_5, 3-CN	192.5–193.5 dec	192.5–193.5 dec[s]
1-CH_3, 4-CN	197–197.5 dec	197,[r] 197–198.5 dec,[t] 195–198,[u] 197.5–198.5[k]
1-C_2H_5, 4-CN	140–141 dec	144.5–146,[t] 140–141,[u] 142–144,[h] 139–140 dec[s]
1-C_2H_5, 4-CN[b]	163.5–165.5	166–170[v]
1-CH_3, 2-COC_6H_5[c]	145–146	Syrup[w]
1-CH_3, 3-COC_6H_5[d]	151.5–152	
1-CH_3, 4-COC_6H_5	181.5	80–180,[w] 174–176[x]
1-CH_3, 4-$C(CN){=}NO(CH_2)_2CH_3$[e]	119–119.5	114–118 dec[y]
1-CH_3, 4-$C(H){=}NO(CH_2)_2CH(CH_3)_2$[e]	95–96	111–114 dec[y]
1-CH_3, 4-$C(CN){=}NOCH_2C_6H_5$[e]	149.5	148–150 dec[y]

[a] Corrected. [b] Perchlorate. [c] *Anal.* Calcd for $C_{13}H_{12}INO$: C, 48.0; H, 3.7; N, 4.3. Found: C, 48.1; H, 3.7; N, 4.4. [d] *Anal.* Calcd for $C_{13}H_{12}INO$: C, 48.0; H, 3.7; N, 4.3. Found: C, 48.0; H, 3.7; N, 4.3. [e] These samples were obtained from Dr. B. C. Tyson, Jr., and were recrystallized prior to the spectral measurements. [f] Reference 1. [g] A. B. Prescott, *J. Amer. Chem. Soc.*, **18,** 91 (1896). [h] J. F. Biellmann and H. Callot, *Bull. Soc. Chim. Fr.*, 397 (1967). [i] I. B. Wilson, S. Ginsburg, and D. Nachmansohn, U. S. Patent 2,816,113 (Dec 10, 1957); *Chem. Abstr.*, **52,** 10212*h* (1958). [j] S. Ginsberg and I. B. Wilson, *J. Amer. Chem. Soc.*, **79,** 481 (1957). [k] P. Böger, C. C. Black, and A. San Pietro, *Biochemistry*, **6,** 80 (1967). [l] G. Pfleiderer, E. Sann, and A. Stock, *Chem. Ber.*, **93,** 3083 (1960). [m] J. Tirouflet and E. Laviron, *C. R. Acad. Sci.*, **247,** 217 (1958). [n] M. R. Lamorg, R. M. Burton, and N. O. Kaplan, *J. Amer. Chem. Soc.*, **79,** 617 (1957). [o] Reference 8. [p] J. Kapcho, U. S. Patent 2,759,942 (Aug 21, 1956). [q] R. I. Ellin, *J. Amer. Chem. Soc.*, **80,** 6588 (1958). [r] J. H. Blanch and O. T. Onsager, *J. Chem. Soc.*, 3729 (1965). [s] Reference 5. [t] Reference 2. [u] D. Eilhauer, W. Hoefling, and K. H. Meinicke, German Patent 1,188,601, (March 11, 1965); *Chem. Abstr.*, **63,** 4263*a* (1965). [v] Reference 9. [w] N. Sugimoto and H. Kugita, *Yakugaku Zasshi*, **73,** 66 (1953); *Chem. Abstr.*, **47,** 10532*a* (1953). [x] R. E. Lyle, S. A. Leone, H. J. Troscianiec, and G. H. Warner, *J. Org. Chem.*, **24,** 330 (1959). [y] B. C. Tyson, Jr., Ph.D. Dissertation, University of Delaware, June 1969.

tenths of a kilocalorie per mole. The CT contribution to the ground state of the ion pair must be quite small. This same conclusion was reached for several pyridinium iodides on the basis of appropriate comparisons of dissociation constants.[15,16]

Assuming that the solvation energies are approximately the same for the various pyridinium ions, the polarographic half-wave potential ($E_{1/2}$) should be a measure of the electron affinity of the ion. The correlation of $E_{1/2}$ and E_{t1} values is consistent with the CT nature of the process. The scatter is likely due in great part to the differences in "vertical" and "adiabatic" excited-state solvation energy, which should be quite large in this system. The lack of a correlation with E_{t2} is consistent with the mechanism of eq 6 since $E_{1/2}$ is only a measure of the ground-state electron affinity of the pyridinium ion.

As mentioned above, Verhoeven, Dirkx, and de Boer[6] suggested that eq 4 and 6 represent the correct mechanism since two CT bands were observed in the spectrum of a solution of 3-cyano-1-methylpyridinium ion and *N*,*N*-dimethylaniline. Verhoeven[17] has performed some simple Hückel LCAO-MO calculations which give energy separations between the lowest (first) and next-highest (second) vacant molecular orbitals of the pyridinium ion in the order 4-CN > 2-CN > 3-CN, in support of the observed separation of the double CT band pattern found for cyanopyridinium iodides.

However, it then remains to explain why a third band corresponding to iodine being left in the $^2P_{1/2}$ state (eq 5) is not seen. For at least some of the salts, the states represented by eq 5 and 6 can be close in energy, since ΔE between I· and I·* should be about 21 kcal mol^{-1} and ΔE between Py· and Py·* can vary from about 10 to 30 kcal mol^{-1}, depending on the substituent. If the excited states of eq 5 and 6 were mixed to any considerable extent, then both bands might be expected to be observed since, even if the transition of eq 5 were forbidden, the mixing should provide intensity. In the event that both transitions were allowed but the mixing was sufficient to cause a splitting of about 10 kcal mol^{-1} or more, then the higher energy band would become hidden under the intense ring absorptions. However, in this event ΔE_t should always be less than 22 kcal mol^{-1}. Thus, it seems likely that the transitions are fairly well represented by eq 4–6, and that the transition of eq 5 is forbidden (relative to 4 and 6; *i.e.*, much less intense). At present we have no explanation for the apparent lack of intensity of this transition. Since two bands of about equal intensity are observed for iodide ion in water or acetone, it appears that the magnitude of the transition moments for each of the two possible CT bands involving a given acceptor orbital and I^- as donor will depend upon the nature of the acceptor orbital and the geometrical relationship between iodide and the acceptor. Molecular orbital calculations are currently in progress.

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(15) E. M. Kosower and J. C. Burbach, *J. Amer. Chem. Soc.*, **78,** 5838 (1956).

(16) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3,** 85 (1965).

(17) J. W. Verhoeven, Thesis, Laboratorium voor Organische Scheikunde der Universiteit van Amsterdam, 1969.

We conclude that the CT mechanisms given by eq 4 and 6 best explain the available experimental data, and that the CT contribution to the ground state of the ion pair is quite small. The ground-state stabilization of the CT complex is thus primarily electrostatic. In this regard the complex behaves as would any ion pair.

Two CT bands have also been observed in spectra of tropylium[18] and pyrylium[19] iodides. The ΔE_t for tropylium iodide in CH_2Cl_2 was found to 19.9 kcal mol^{-1}; the energy difference for 2,4,6-trimethylpyrylium iodide CT bands ($CHCl_3$ solvent) was found to be 14.5 kcal mol^{-1}. More work is needed before assigning the two-band pattern in these ring systems to properties of either the donor or acceptor.

Experimental Section

Compounds. Most of the compounds used for this study were reported previously (Table IV). They were prepared by reaction of the appropriate pyridine compound with either methyl or ethyl iodide. The absence of trace amounts of triiodide in each compound was confirmed spectrophotometrically in methylene chloride. 1-Ethyl-4-cyanopyridinium perchlorate was prepared according to the procedure of Schwarz.[9]

Polarography. The polarographic studies were performed using a Leeds and Northrup Electro-Chemograph, Type E, and a dropping mercury electrode (dme). The reference electrode was aqueous saturated calomel (sce); a three-compartment cell was employed to prevent water from entering the sample (dme) compartment. The middle compartment contained the nonaqueous solvent (CH_3CN) and 0.1 *M* $[CH_3(CH_2)_3]_4N^+ClO_4^-$ electrolyte only. The acetonitrile was dried over Na_2CO_3 and then distilled from molecular sieve. The polarographic grade $[CH_3(CH_2)_3]_4N^+ClO_4^-$ was obtained from Southwestern Chemical Co. and was dried overnight at 110° before use. The pyridinium salt concentrations were approximately 10^{-3} *M*.

Kinetics. All visible absorption data were obtained on a Cary 14 spectrophotometer using 1-cm cells with the solvent as reference. Temperature control was maintained using a constant-temperature bath with the water circulating through a metal block cell holder. Kinetic studies were performed by mixing the reagents, placing a sample in the spectrophotometer, and scanning optical density as a function of time at a fixed wavelength corresponding to the first CT band maximum. A methyl tosylate concentration of 0.1 *M* was used throughout; the initial pyridinium iodide concentrations were about 10^{-4} *M*.

Analyses. Elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood, Arsenal.

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A Nuclear Quadrupole Resonance Investigation of Iodine Monochloride Complexed with Pyridines[1a]

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Abstract: The ^{35}Cl and ^{127}I nqr absorption frequencies of pyridine–ICl and 4-methylpyridine–ICl have been measured as a function of temperature. Their respective values at 273.2°K are 21.136 ± 0.01, 21.175 ± 0.01, 464.28 ± 0.04, and 462.76 ± 0.04 MHz. Their temperature coefficients were +2.2, +2.5, −28, and −24 kHz/°K. Application of the Townes and Dailey theory with neglect of s hydridization at the halogen atoms results in the following charge densities in each complex: pyridine (or 4-methylpyridine), +0.26; iodine, +0.35; and chlorine, −0.61 electron. A valence-bond interpretation indicates a 57% contribution of the "no-bond" wave function to the ground state. A representation in which the charge-transfer and electrostatic wave functions are explicitly included contains a maximum of 26% charge-transfer character in the ground-state wave function. Classical electrostatic forces thus appear to play a dominant role in the stabilization of these complexes. The charge-transfer contributions are nonnegligible, but a picture of the complex structure based completely on the charge-transfer model is likely to give misleading results.

In many instances stable molecules have been found to interact to form associated species, called molecular, charge-transfer, or donor–acceptor complexes. The literature concerning these complexes is voluminous, and the reader is referred to a number of books[2,3] and reviews[4–7] treating the subject in greater detail.

The properties of these complexes have usually been interpreted within the context of the charge-transfer (CT) model developed by Mulliken.[8] This model not only accounted for the "CT band" observed in many of these complexes, but also provided a theoretical basis for interpreting their ground-state properties. As is well known, this model proposes that the ground-state wave function for a donor–acceptor complex may be represented by

$$\psi_G = a\Phi_0(D,A) + b\Phi_1(D^+\text{-}A^-) \qquad (1)$$

where Φ_0 represents a "no-bond" structure and Φ_1 represents a "dative" structure in which an electron has been transferred from the donor to the acceptor molecule. The inclusion of Φ_1 in ψ_G results in a reso-

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