Effects of Temperature and Solvent Polarity on the Interionic Charge-Transfer Interactions in Alkylpyridinium Bromide[1]

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Received October 5, 1970

Abstract: Beer's law is not obeyed by aqueous solutions of ethylpyridinium bromide. This is interpreted as being due to the formation of an interionic CT complex between ethylpyridinium and bromide ions. The CT band is shifted toward the red as the bulk polarity of the solvent is decreased and also as the temperature of the solution is increased. The temperature-induced red shift, also reported by earlier workers for alkylpyridinium iodides, but not understood so far, has now been interpreted as being largely due to a lowering of the solvent polarity at the higher temperature. The dissociation constant, K_d, of the ion pair complex decreases logarithmically, and the molar extinction coefficient, ϵ_{290}, increases linearly as the bulk dielectric constant, D, is decreased.

Hantzsch[2] had noticed about 60 years ago that Beer's law was not obeyed by aqueous solutions of alkylpyridinium iodides. In more recent years, Kosower and his coworkers[3–7] have interpreted this unusual spectral behavior as being due to the formation of a charge-transfer (CT) complex between the alkylpyridinium ion and the iodide ion. As opposed to molecular CT complexes,[8] the ground state of such an interionic CT complex is charged and the excited state is neutral. The remarkably high sensitivity of CT transition energy of such complexes to the polarity of the solvent has been studied in detail by Kosower and his coworkers.[5–7]

Ray and Mukerjee[9–12] have recently studied the interionic CT interactions in long-chain alkylpyridinium iodides in both ion pairs in solution and on the surface of micelles. In addition, they have demonstrated the existence of CT interactions of alkylpyridinium ions with a variety of other anions[9] on the micellar surface and with bromide and chloride ions in chloroform solutions as well. The ion pair CT bands in chloroform have been shown to appear at successively higher wavelengths in the order: $I^- > Br^- > Cl^-$.

Little studies have, however, been made on the effects of temperature on the CT interactions in alkylpyridinium halides. Although red shifts[5,12,13] of the iodide bands at higher temperatures were reported by earlier workers, the origin of such effects was not understood. The lack of any detailed studies on the effects of temperature in these systems may be attributed to the fact that the uv spectra of alkylpyridinium iodides are not consistent and not reproducible[3] due to the formation of triiodides. The latter have very intense absorbances in the wavelength regions of interest (ϵ 21,000 at 3625 Å and ϵ 35,000 at 2950 Å, in chloroform), and no accurate analytical method apparently exists to correct for any triiodide formation.[7] Dilute thiosulfate[3,4,12] solutions have often been used. This, however, cannot be recommended, as it has been shown by us that pyridinium thiosulfate[9,10] has CT bands similar to the iodide bands but lower in intensities.

We, therefore, decided to study the effects of temperature and solvent polarity on the CT interactions in ethylpyridinium bromide (EPB) in ion pairs in solution. Unlike the pyridinium iodides,[3] consistent and reproducible uv spectra are obtained with the bromide. As in the case of iodides,[3] most of the CT band of EPB in water is buried under the much more intense pyridinium absorption band, but its long wavelength end is sufficiently visible to be useful for the present study. No CT complex is presumably formed between the pyridinium ion and the perchlorate ion. Using 1.62 *M* methylpyridinium perchlorate solution, Kosower[3] has shown that the absorption of the free pyridinium ion is negligible above 288 mμ at this concentration. Since we worked at much lower salt concentrations (0.2 *M* or less) and since bromide ions do not absorb at these wavelengths, any absorbances above 288 mμ may be regarded as due to the pyridinium bromide CT complex. The bulk dielectric constant of the medium was varied from 78.5 to 37.7 at 25° by using water–ethylene glycol mixtures (0–100 vol %).

Experimental Section

Reagent grade ethylpyridinium bromide was obtained from Matheson Coleman and Bell and was vacuum dried before use. Chromatoquality, reagent grade ethylene glycol, also supplied by the Matheson Coleman and Bell, was dried overnight with anhydrous sodium sulfate and distilled under reduced pressure before use.

The uv absorbance measurements were carried out in a Cary 14 spectrophotometer. The cell compartments and the cell holders were thermostated. Temperatures of solutions were kept constant within ±0.05°.

Results and Discussion

Absorbances at 290 mμ are plotted against the concentration of EPB in water and ethylene glycol at 25 and 45° (Figure 1). These and similar plots for longer wavelengths (not shown) indicate that Beer's law is not obeyed by EPB solutions at these wavelengths. This is similar to what was observed by Hantzsch[2] and confirmed by Kosower and coworkers[3] in pyridinium iodide

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[1] This work was supported by Grant No. GB-8410 of the National Science Foundation held by Dr. G. Némethy.

[2] A. Hantzsch, *Ber.*, **44**, 1783 (1911).

[3] (a) E. M. Kosower, *J. Amer. Chem. Soc.*, **77**, 3883 (1955); (b) *ibid.*, **78**, 3493 (1956).

[4] E. M. Kosower and J. C. Burbach, *ibid.*, **78**, 5838 (1956).

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

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

[7] E. M. Kosower and J. A. Skorcz, *ibid.*, **82**, 2195 (1960).

[8] R. S. Mulliken, *ibid.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[9] A. Ray and P. Mukerjee, *ibid.*, **70**, 2138 (1966).

[10] P. Mukerjee and A. Ray, *ibid.*, **70**, 2144 (1966).

[11] P. Mukerjee and A. Ray, *ibid.*, **70**, 2150 (1966).

[12] P. Mukerjee and A. Ray, *ibid.*, **67**, 190 (1963).

[13] A. Hantzsch, *Ber.*, **52**, 1544 (1919).

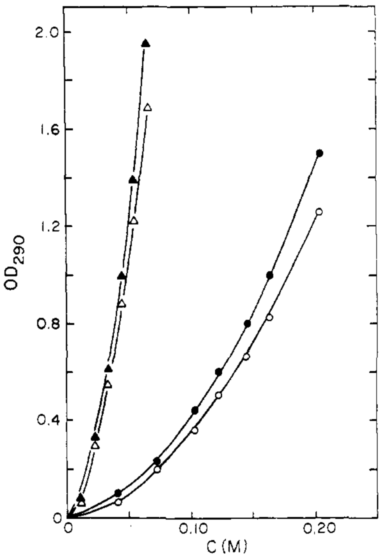

Figure 1. Absorbance data as a function of EPB concentration in water: (○) 25°, (●) 45°; in ethylene glycol: (△) 25°, (▲) 45°.

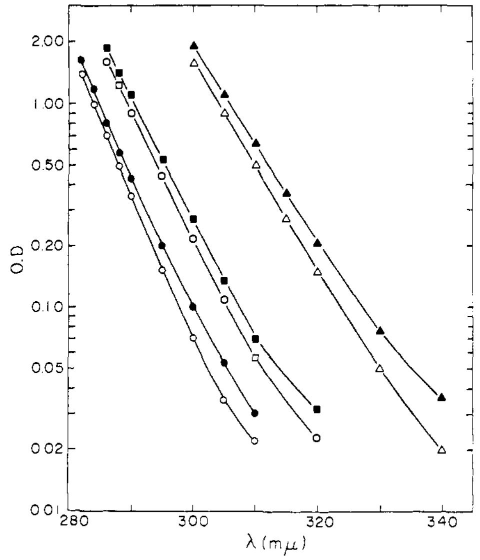

Figure 2. Absorption spectra of EPB in water, 0.1021 *M*: (○) 25°, (●) 45°; in 40 vol % ethylene glycol, 0.1190 *M*: (□) 25°, (■) 45°; in ethylene glycol, 0.1266 *M*: (△) 25°, (▲) 45°.

solutions. By analogy to the iodide systems, therefore, it can be postulated that the absorbing species involved is the CT complex in ethylpyridinium bromide ion pairs. This conclusion is supported by our previous observations[9] of pyridinium bromide CT bands both in chloroform and on the micellar surface in water.

Figure 2 shows the absorption spectra of EPB in water, 40 vol% ethylene glycol, and ethylene glycol at 25 and 45°. Since the absorbances due to both pyridinium ions[3] and bromide ions are negligible at wavelengths above 288 mμ, at concentrations 1.62 *M* or less, any absorption above this wavelength is taken to be due to the CT interaction in the ion pair only.

It is evident from Figure 2 that as the polarity of the solvent is decreased, the log OD *vs.* λ plot moves out into longer wavelengths. The observed increase in OD at any given wavelength can be due to two factors: an increase in the concentration of ion pairs in the less polar medium, and a red shift of the actual CT band due to a decrease in the solvent polarity.[5]

Interestingly, an increase in the temperature of each solution from 25 to 45° also results in an increased OD in all the cases (Figures 1 and 2), although a decrease in OD may actually be expected because of an increase in the dissociation of the ion pair complex at the higher temperature.

Hantzsch[13] had noted that the color of an ethylpyridinium iodide solution in chloroform changes from yellow at 25° to colorless at −75°. Over the same temperature range, a red-orange solution of 1-ethyl-4-carbomethoxypyridinium iodide in chloroform was found by Kosower[5] to turn pale yellow. Also, it has been observed by Kosower[5] that the "Z-value," defined as the CT transition energy (kcal/mol) at the wavelength of maximum absorption for the latter compound, decreases with increasing temperature and the apparent molar extinction coefficient, calculated on the basis of total salt concentration, increases. A shift in the red by 2 mμ has been observed in the micellar CT band of dodecylpyridinium iodide[11] as the temperature was raised from 25 to 45°.

Thus, although all the past observations mentioned above, made in pyridinium iodide systems, actually confirm the present observations, no attempt seems to have been made so far to interpret this temperature effect.

The strong dependence of the pyridinium iodide CT band position on the solvent polarity is now well established.[5–7] The pyridinium bromide band also appears to be dependent on solvent polarity both from the present study as well as from our previous observation[9] that in chloroform ($D = 5$) solution the pyridinium bromide band appears much further toward the red than the CT band on the micellar surface or in ethylene glycol ($D = 37.7$) (this work). Also, it is a well-known fact that the dielectric constant, D, of a solvent is a decreasing function of the temperature,[14] t, *i.e.*, dD/dt is negative. In the present paper it is postulated that the observed temperature effect on the CT absorption is, at least in part, a result of the decrease in the bulk polarity of the solvent at the higher temperature.

To test this hypothesis, the dissociation constant, K_d, and the molar extinction coefficient, ϵ, of the ion pair complex are determined as a function of the dielectric constant of the medium at 25 and 45°.

It is conceivable[9] that several kinds of ion pairs, such as "intimate," "solvent sharing," or "solvent separated," may exist in solution, but owing to the short-range nature of the CT forces, only the "intimate" ion pairs are likely to be involved in the CT interactions. Since the "intimate" ion pairs are in equilibrium with the other kinds, the former may be regarded as a constant fraction of all ion pairs, independent of concentration. The equilibria can be written as

$$(\mathrm{RPy^+Br^-}) \rightleftharpoons (\mathrm{RPy^+Br^-})_{\text{solvent sharing}} \rightleftharpoons (\mathrm{RPy^+Br^-})_{\text{solvent separated}} \rightleftharpoons \mathrm{RPy^+} + \mathrm{Br^-} \qquad (1)$$

The dissociation constant, K_d, is given by

$$K_d = (C - C_2)^2/C_2 \qquad (2)$$

where C = total salt concentration and C_2 = concentration of all ion pairs. Assuming that the absorbance is

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[14] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, pp 159–162.

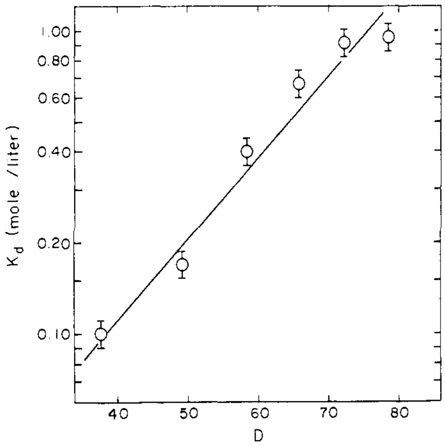

Figure 3. The variation of the dissociation constant of the EPB CT complex with the dielectric constant at 25°.

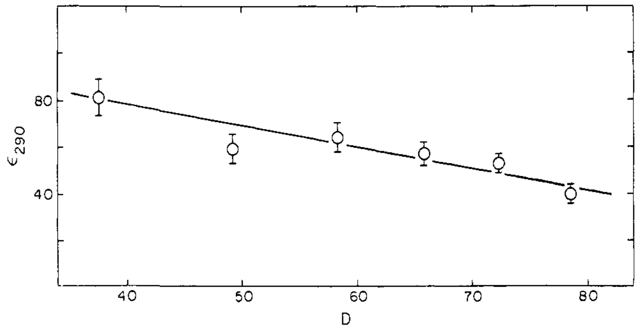

Figure 4. The variation of the molar extinction coefficient at 290 mμ of the EPB CT complex with the dielectric constant at 25°.

due only to the ion pairs and not the free ions, the molar extinction coefficient, ϵ, can be defined as $\epsilon = a/C_2$, where a = OD and ϵ is the average for all ion pairs. As before,[9] the following equations can be written

$$(K_dC_2)^{1/2}/C = 1 - C_2/C = 1 - a/\epsilon C = (1/C)(K_d a/\epsilon)^{1/2} \quad (3)$$

and

$$a/C = \epsilon - (K_d\epsilon)^{1/2}(a^{1/2}/C) \quad (4)$$

Since the calculations are of an approximate nature, the activity coefficients are considered to be unity.

The plots of a/C *vs.* $a^{1/2}/C$ are indeed found to be linear. The slopes and the intercepts of these straight lines are calculated by the least-squares method. The values of K_d and ϵ_{290} so obtained are listed in Table I.

Table I. Dissociation Constants and Molar Extinction Coefficients of EPB CT Complexes in Water–Ethylene Glycol Mixtures

Solvent (vol % EG)	Temp, °C	Dielectric constant[14]	K_d, mol/l.	ϵ_{290}
0	25	78.5	0.95	40
	45	71.7	0.95	48
20	25	72.3	0.91	53
40	25	65.8	0.67	57
	45	59.9	0.67	71
60	25	58.3	0.40	64
80	25	49.2	0.17	59
100	25	37.7	0.10	81
	45	33.9	0.10	93

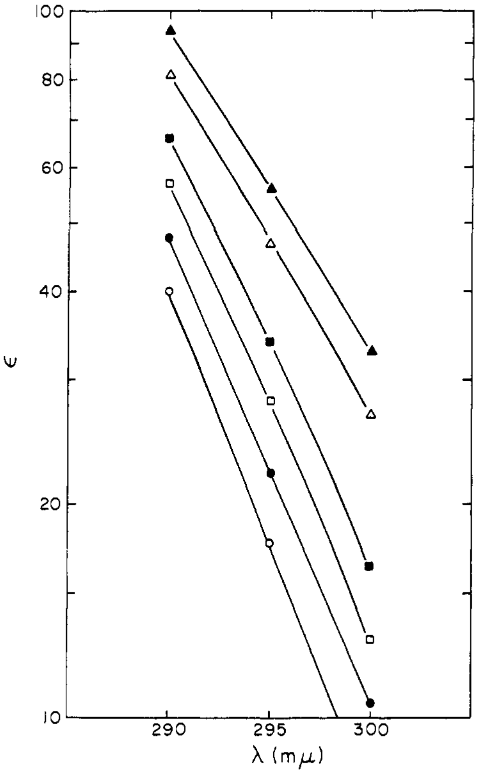

Figure 5. Plot of the molar extinction coefficient of the EPB CT complex against wavelength in water: (○) 25°, (●) 45°; in 40 vol % ethylene glycol: (□) 25°, (■) 45°; in ethylene glycol: (△) 25°, (▲) 45°.

At 25°, K_d is found to increase by about a factor of ten as the bulk D is increased by slightly more than a factor of two. A plot of log K_d against D^{14} is found to be linear (Figure 3). On the other hand, the molar extinction coefficient, ϵ_{290}, is found to decrease by about a factor of two over the same range of D, at the same temperature, the decrease being approximately linear with D (Figure 4). The K_d value for EPB in water, 0.95 (mol/l.), may be compared with that of methylpyridinium iodide[4] in water, 0.43. The higher K_d value for EPB indicates that the bromide complex is weaker than the iodide complex, which may be expected. Similarly, the K_d values, 0.10 and 0.041, for EPB and dodecylpyridinium iodide[9] in ethylene glycol (D = 37.7) and 80% methanol (D = 40.1), respectively, show a similar order in the magnitude which is further indicative of the relative strengths of the bromide and the iodide complexes. The corresponding molar extinction coefficients at 290 mμ for the latter two solvents are 81 and 430, respectively. A lower ϵ_{290} value for EPB is actually expected, as the bromide band appears at a lower wavelength than the iodide band.

The measurements are extended to 45° in 0, 40, and 100 vol% ethylene glycol in water. The K_d values and the ϵ_{290} values are calculated in a similar manner for this temperature and listed in Table I. The K_d values at 45° are found to be the same as at 25° for all three solvents. Even though the calculations are rather approximate, this invariance of K_d with temperature is interesting and can be explained if it is assumed that any dissociating effect due to the higher temperature is counterbalanced by an associating effect of a comparable magnitude due to a lowering of the bulk polarity of the solvent at the higher temperature. The molar extinction coefficients, on the other hand, are found to increase at the higher temperature (Table I and Figure 5), which would be expected if the polarity of the medium is decreased.

In dioxane–water mixtures[14] (0–50 wt %), the dielectric constant is known to decrease by a constant fraction, *viz.* 9–10%, as the temperature is increased from 25 to 45°, the value of this fraction being almost independent of the composition of the solvent mixture. Assuming that similar decreases occur in ethylene glycol–water mixtures, values of D at 45° may be estimated to be 71.7, 59.9, and 33.9 for 0, 40, and 100 vol % ethylene glycol, respectively. The observed increases in ϵ_{290} at 45° are about those expected from Figure 4, for 0 and 40 vol % ethylene glycol; the increase for pure ethylene glycol is somewhat higher than the expected value. In view of the approximate nature of the calculations involved, the above agreements may be considered to be fair. Thus, the observed temperature effect can be explained largely in terms of the decrease in the polarity of the bulk medium at the higher temperature.

If it is assumed that the shape of the pyridinium bromide CT band, when log ϵ is plotted against λ, remains unchanged over the temperature range 25–45°, as has been observed for pyridinium iodide[9] bands, then the magnitudes of the red shifts for the same temperature range are 1.3–1.4 mμ for the three solvents. This is comparable to the 2-mμ shift in the red observed for the micellar CT band in dodecylpyridinium iodide.[11] The blue shifts in the pyridinium iodide CT bands, reported by earlier workers,[5,13] due to cooling may be at least partly because of an increase in the dielectric constant of the medium at the lower temperature.

Assuming that the pyridinium bromide band shape remains unaltered also over the dielectric constant range 78.5–37.7, the total red shift in going from water to ethylene glycol is only 8.5 mμ (Figure 5), considerably less than the 30-mμ red shift observed in the case of pyridinium iodide.[10] This indicates that the effect of solvent polarity is actually less on the position of the bromide band than on that of the iodide band.

The uv absorption behaviors at 25 and 45° for the long-chain compound, dodecylpyridinium bromide[15] (DPB), in 100% ethylene glycol are found to be very similar to those of EPB at these temperatures. The observed OD's are, however, slightly higher for DPB. This might be due to some premicellar association effects in DPB which presumably forms micelles[16] in pure ethylene glycol.

Acknowledgment. It gives the author great pleasure to thank Dr. G. Némethy for his interest in this work.

(15) A. Ray, unpublished observation.
(16) A. Ray, *J. Amer. Chem. Soc.*, **91**, 6511 (1969).

Structure and Stability of the Nitric Oxide Dimer

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Abstract: Approximate nonempirical SCF–MO calculations using a minimum basis of Slater atomic orbitals have been made on the most likely structures of the nitric oxide dimer. The planar trans configuration has been found to have the lowest energy, with the following optimum geometry: $R(\text{NO}) = 1.23$, $R(\text{NN}) = 1.53$ Å, NNO = 104.6°. The optimum cis geometry has an energy 3.5 kcal/mol higher, and the near-rectangular structure suggested by X-ray evidence has an energy 66 kcal/mol higher. The dissociation energy of the dimer has been estimated by calculating the energy for the reaction $(\text{NO})_2 + \text{H}_2 \rightarrow 2\text{HNO}$ and using an experimental energy for $\text{HNO} \rightarrow 0.5\text{H}_2 + \text{NO}$. The resulting value of 3.6 kcal/mol is near the upper limit of the experimental estimates.

In this paper we report the results of *ab initio* minimal-basis SCF calculations for the nitric oxide dimer and for the molecule HNO. Our aim is to calculate reliable bond lengths and angles of $(\text{NO})_2$ at equilibrium in the gas phase, and assign a structure. Calculations on the closed-shell molecule HNO are carried out first to test the reliability of the method for a species containing the N–O bond, and second to estimate the energy of $(\text{NO})_2$ by calculating the energy of

$$(\text{NO})_2 + \text{H}_2 \longrightarrow 2\text{HNO}$$

and using an experimental energy for the reaction

$$\text{HNO} \longrightarrow 0.5\text{H}_2 + \text{NO}$$

The nitric oxide dimer has been postulated as an important intermediate in several gas-phase reactions of nitric oxide, most recently in a study of the chemiluminous NO + O reaction.[2] It was inferred some years ago from X-ray crystallography of the solid[3] and from the magnetic susceptibility[4a] and vibrational spectra[4] of the liquid and solid that nitric oxide in its condensed phases consists almost entirely of dimer molecules. Only recently, however, has the gas-phase dimer been observed directly, by mass spectroscopy[5] and in the infrared spectrum of NO gas.[6]

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(1) U. S. Air Force Office of Scientific Research–National Research Council postdoctoral fellow, 1969–1970.

(2) D. Golomb and R. E. Good, *J. Chem. Phys.*, **49**, 4176 (1968).
(3) W. J. Dulmage, E. A. Meyers, and W. N. Lipscomb, *Acta Crystallogr.*, **6**, 760 (1953).
(4) (a) A. L. Smith, W. E. Keller, and H. L. Johnston, *J. Chem. Phys.*, **19**, 189 (1951); (b) W. G. Fateley, H. A. Bent, and B. Crawford, *ibid.*, **31**, 204 (1959).
(5) T. A. Milne and F. T. Greene, *ibid.*, **47**, 3668 (1967).
(6) C. E. Dinerman and G. E. Ewing, *ibid.*, **53**, 626 (1970).