

Origin of the Z-Value Scale of Solvent "Ionizing Power". Solvation of the Ground and Franck-Condon Excited State of 1-Ethyl-4-cyanopyridinium iodide

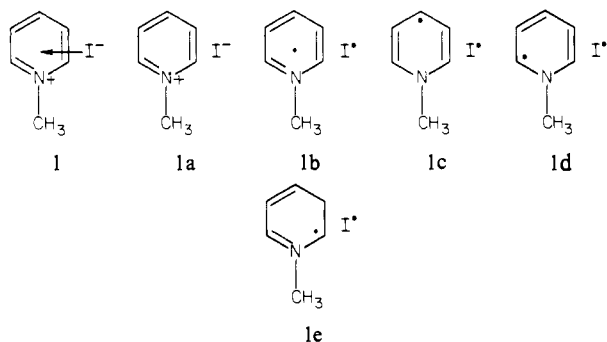
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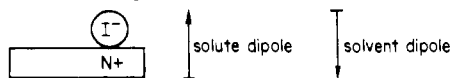
Abstract: Kosower's *Z* values serve successfully as one empirical measure of the microscopic polarity or ionizing power of solvents. An explanation of this phenomenon based on the stabilization of the ground state and destabilization of the excited state of the ion pair of 1-ethyl-4-(carbomethoxy)pyridinium iodide has been proposed. To test this proposal, we have studied the thermodynamics of solution and ionization of the closely related ion pair 1-ethyl-4-cyanopyridinium iodide in a series of solvents. The thermodynamic data obtained were combined with spectral data to obtain free energies, enthalpies, and entropies of transfer of the ground and Franck-Condon excited states. The experimental results show that, contrary to prediction, the ground-state ion pair is destabilized (ΔH) on transfer to more polar solvents. The excited state is also destabilized by the transfer by an amount greater than predicted.

A number of probes which purport to reflect changes in the microscopic nature of solvents have been developed in an attempt to understand and predict the effect of solvent changes on organic reactions. One of the most successful and widely used of these probes is the Kosower *Z*-value scale.¹ The *Z* value of a solvent is the energy of the long-wavelength, charge-transfer transition of 1-ethyl-4-(carbomethoxy)pyridinium iodide (ECMP) in that solvent expressed in kcal/mol. In order to gain a better understanding of the functioning of this probe, we have investigated the thermodynamics of solvation of both the ground and excited states of the closely related compound 1-ethyl-4-cyanopyridinium iodide (ECP) in several solvents.

A quantitative explanation for the strong dependence of *Z* on solvent was proposed by Kosower.² The 1-alkylpyridinium iodide salts were viewed as having the following contributing resonance forms:

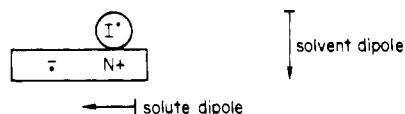


Form **1a**, representing a tight ion-pair complex, is the predominant resonance form contributing to the ground-state complex **1**. Form **1b**, with resonance structures **1c**–**e**, was viewed as being the predominant contributor to the excited-state structure. In the ground state the iodide ion resides in contact with the 1-alkylpyridinium ring, close to the center of positive charge—the nitrogen atom.³ The dipole moment of the ion pair, calculated as 13.9 D, is directed along a line joining the centers of charge and perpendicular to the plane of the ring.



When electron transfer from the iodide ion to the antibonding π^* orbital of the pyridinium ring occurs, the negative charge shifts

to the center of the ring and the dipole moment of the complex lies parallel to the plane of the ring and perpendicular to the direction of the ground-state dipole moment. If the group moment for the carbomethoxy group is considered, the dipole moment for the excited state is calculated as 8.6 D.



Kosower defined the cybotactic region as the volume of solvent molecules which were affected by the solute particle. The term is intended to apply to the first coordination shell of solvent molecules and to the transition region, separate from the bulk region of solvent molecules. The net dipole moment of the cybotactic region is antiparallel to the dipole moment of the ionic ground-state complex and orthogonal to the excited-state dipole.² Because solvent molecules are unable to reorient themselves during the time of an electronic transition (Franck-Condon principle) the solvent's net dipole does not interact with the solute's excited-state dipole because they are perpendicular to one another. Therefore, no electrostatic solute-solvent interaction should exist in the excited state. While this may not be strictly correct, at the very least the extent of solute-solvent interaction should be greatly decreased in the excited state.

It is this 90° swing of the dipole moment of the complex which causes the pronounced negative solvatochromism of 1-alkylpyridinium iodide salts. Kosower treated the energetics of this system by using Böttcher's electrostatic theory.⁴ Kosower assumed that the gas-phase transition energy of ECMP was equal to the *Z* value for benzene, while realizing that this approximation was not strictly correct because it ignored electronic polarization of the solvent by the dipoles. Nevertheless, by employing Böttcher's theory, one can calculate the energy involved in creating a spherical cavity in a uniform dielectric medium to accommodate a point dipole of magnitude μ . This energy is equal to $1/2 R\mu^2$, where R is the reaction field. When the dipole is taken from infinity and placed inside the cavity, a stabilization energy equal to $-R\mu^2$ is obtained. Thus moving the ground state from the gas phase to a solvent stabilizes the ground state by $-1/2 R\mu^2$. Now if the solute absorbs light and undergoes an electronic transition such that the excited-state dipole becomes perpendicular to the direction of the ground-state dipole and consequently to the direction of the solvent's overall dipole, solute-solvent electrostatic interaction is destroyed. The solvent molecules in the cybotactic region are now destabilized with respect to the bulk solvent and the resulting

(1) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(2) E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, 1968, pp 260-3, 293-302.

(3) S. Sakanque, Y. Kai, N. Ysoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **43**, 1306 (1970).

(4) C. J. F. Böttcher, "Theory of Electric Polarization", Elsevier, Amsterdam, 1952, pp 133-9.

Table I. Temperature Dependence of λ_{\max} , ϵ_{\max} , and K_D for 1-Ethyl-4-cyanopyridinium Iodide

| solvent | temp, °C | λ_{\max} , nm | ϵ_{\max} , L/(mol-cm) | $10^3 K_D$ | E_T , kcal/mol |
|--------------------|------------|-----------------------|--------------------------------|-------------|-------------------|
| ethanol | 15.0 ± 0.1 | 376 ± 2 | 515 ± 26 | 3.51 ± 0.34 | 76.0 ± 0.4 |
| | 25.7 ± 0.1 | 378 ± 2 | 529 ± 17 | 3.12 ± 0.18 | 75.6 ± 0.4 |
| | 35.4 ± 0.2 | 380 ± 2 | 549 ± 25 | 2.99 ± 0.24 | 75.2 ± 0.4 |
| | 44.9 ± 0.2 | 382 ± 2 | 560 ± 25 | 2.65 ± 0.24 | 74.8 ± 0.4 |
| acetonitrile | 25.6 ± 0.1 | 425 ± 2 | 336 ± 28 | 10.7 ± 1.1 | 67.3 ± 0.3 |
| | 35.2 ± 0.2 | 428 ± 2 | 338 ± 11 | 9.35 ± 0.35 | 66.8 ± 0.3 |
| | 44.7 ± 0.2 | 431 ± 2 | 345 ± 23 | 8.68 ± 0.63 | 66.3 ± 0.3 |
| acetone | 17.2 ± 0.1 | 455 ± 2 | 804 ± 10 | 2.31 ± 0.12 | 62.8 ± 0.3 |
| | 25.7 ± 0.1 | 460 ± 2 | 822 ± 11 | 2.15 ± 0.06 | 62.2 ± 0.3 |
| | 35.6 ± 0.2 | 464 ± 2 | 851 ± 11 | 1.94 ± 0.07 | 61.6 ± 0.3 |
| | 44.4 ± 0.2 | 467 ± 2 | 881 ± 19 | 1.59 ± 0.11 | 61.2 ± 0.3 |
| methyl formate | 15.7 ± 0.1 | 457 ± 2 | 1025 ± 9 | 0 | 62.6 ± 0.3 |
| | 20.0 ± 0.1 | 458 ± 2 | 1028 ± 8 | 0 | 62.4 ± 0.3 |
| | 24.7 ± 0.1 | 458 ± 2 | 1050 ± 12 | 0 | 62.4 ± 0.3 |
| | 28.2 ± 0.1 | 459 ± 2 | 1092 ± 29 | 0 | 62.3 ± 0.3 |
| methylene chloride | 16.2 ± 0.1 | 480 ± 2 | 1313 ± 10 | 0 | 59.6 ± 0.2 |
| | 20.3 ± 0.1 | 482 ± 2 | 1325 ± 10 | 0 | 59.3 ± 0.2 |
| | 25.0 ± 0.1 | 484 ± 2 | 1335 ± 10 | 0 | 59.1 ± 0.2 |
| | 30.3 ± 0.1 | 488 ± 2 | 1340 ± 5 | 0 | 58.6 ± 0.2 |
| | 34.8 ± 0.1 | 490 ± 2 | 1380 ± 10 | 0 | 58.4 ± 0.2 |
| chloroform | 25 | | 1040 | 0 | 57.8 ^a |

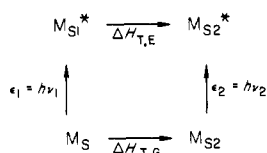
^a Data from ref 12.

Figure 1. Cycle used in analyzing excited-state solvation.

destabilization is equal to $1/2 R\mu^2$. Thus Kosower has predicted that on transfer of the ion-pair dipole to more polar solvents, a blue shift in λ_{\max} occurs because the ground state is stabilized and the excited state is destabilized *each to the same degree*. A consequence is that plots of Z vs. the heat of transfer of the ground state and excited state should be straight lines having slopes of $-1/2$ and $+1/2$, respectively.

This explanation for the operation of the Z -value scale can be tested easily by using a thermodynamic cycle which has been used by others in studying excited-state solvation⁵⁻⁸ (Figure 1). When applied to excited-state reactions, this is the Forster cycle, whose thermodynamics have been well developed.^{9,10} Combination of the heats of transfer of M from solvent 1 to solvent 2 with the observed transition energies in these solvents yields the "heat of transfer of the excited state". It is important to realize that the Franck-Condon excited states in question are not at equilibrium and thus it is not correct to speak of their "heats of transfer". It would be more correct to couch the discussion in terms of the "energy of transfer of the excited state", but we shall follow the conventions developed by our predecessors and associate $\Delta H_{T,E}$ with a quantity which is not readily treatable by equilibrium thermodynamics. For all its thermodynamic elusiveness, it does have a clear and readily perceived physical meaning and significance.¹¹

We elected not to use the defining compound for the Z scale in our studies and chose 1-ethyl-4-cyanopyridinium iodide (ECP) instead. The reason for this choice was that solubility data for

Table II. Comparison of Experimental Data with Literature Values

| solvent | temp, °C | ϵ_{\max} , L/(mol-cm) | $10^3 K_D$ | E_T , kcal/mol |
|--------------------|-------------------|--------------------------------|-------------------|-------------------|
| ethanol | 27 ^a | 429 ^a | 2.13 ^a | 75.8 ^a |
| | 25.0 ^b | | | 75.7 ^b |
| acetonitrile | 25.7 | 529 | 3.12 | 75.6 |
| | 25 ^a | 330 ^a | 10.4 ^a | 68.1 ^a |
| acetone | 25.0 ^b | | | 66.9 ^b |
| | 25.6 | 338 | 10.7 | 67.3 |
| methyl formate | 27 ^a | 816 ^a | 2.64 ^a | 62.2 ^a |
| | 25.0 ^b | | | 61.8 ^b |
| methylene chloride | 25.7 | 822 | 2.15 | 62.2 |
| | 26 ^a | 810 ^a | 0 ^a | 66.6 ^a |
| chloroform | 24.7 | 1040 | 0 | 62.4 |
| | 27 ^a | 1200 ^a | 0 ^a | 59.3 ^a |
| | 25.0 | 1335 | 0 | 59.1 |

^a Data from ref 12. ^b Data from ref 2.

Table III. Thermodynamic State Functions of Ion Pair Dissociation for 1-Ethyl-4-cyanopyridinium Iodide at 25 °C

| solvent | $10^3 K_D$ | ΔH_{ion}° , kcal/mol | ΔG_{ion}° , kcal/mol | ΔS° , eu |
|---------------|-------------|-----------------------------------|-----------------------------------|-----------------------|
| ethanol | 3.14 ± 0.41 | -1.61 ± 0.21 | 3.42 ± 0.13 | -16.8 ± 0.8 |
| aceto-nitrile | 10.8 ± 1.7 | -2.09 ± 0.33 | 2.68 ± 0.16 | -16.0 ± 1.2 |
| acetone | 2.17 ± 0.42 | -2.42 ± 0.40 | 3.63 ± 0.19 | -20.3 ± 1.5 |

this compound are available,¹² enabling a more complete thermodynamic picture of the solvation of this ion pair to be developed. An additional complication is that this ion pair dissociates to different degrees in different solvents so that the measured heats of solution must be corrected to account for this dissociation.

Results

Ground-State Solvation. As pointed out earlier, the heats of transfer of ECP cannot be derived directly from the measured heats of solution because the salt is dissociated to different degrees in different solvents. The observed heat of solution is composed of the heat of solution to give the ion pair and an additional component which is some fraction of the molar heat of dissociation of the ion pair. Our interest is in the solvation of the ion pair and of the excited state derived from it, so we must remove the con-

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(11) M. Jauquet and P. Lasflo in "Solutions and Solubilities", M. R. J. Dack, Ed., Wiley, New York, 1975.

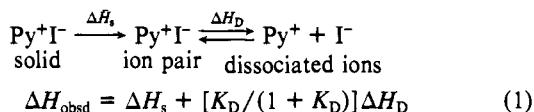
(12) R. A. Mackay and E. T. Poziomek, *J. Am. Chem. Soc.*, **92**, 2432 (1970).

Table IV. Thermodynamics of Solution and Transfer for 1-Ethyl-4-cyanopyridinium Iodide at 25 °C

| solvent | ΔS_s , kcal/mol | $\delta_m \Delta H_s$, kcal/mol | $\delta_m \Delta G_s$, kcal/mol | $\delta_m \Delta S_s$, eu |
|------------------------|----------------------------|-------------------------------------|-------------------------------------|-------------------------------|
| ethanol | 6.70 ± 0.18 | 7.53 ± 0.26 | -2.01 | 32.0 |
| acetonitrile | 1.15 ± 0.20 | 1.98 ± 0.27 | -3.26 | 17.6 |
| acetone | 0.46 ± 0.10 | 0.37 ± 0.21 | -2.05 | 8.1 |
| methyl formate | 1.78 ± 0.23 | 2.61 ± 0.30 | -2.59 | 17.4 |
| methylene chloride | 1.18 ± 0.08 | 2.01 ± 0.21 | -0.79 | 9.4 |
| chloroform | -0.83 ± 0.19 | 0.0 | 0 | 0 |
| isopropyl alcohol | | | -0.70 | |
| <i>n</i> -amyl alcohol | | | +0.21 | |

tribution made by the ion-pair dissociation. To make the necessary corrections, we measured the equilibrium constants for ion-pair dissociation (K_D) at a series of temperatures and obtained the heat of dissociation of the ion pair, using standard van't Hoff techniques. The temperature dependence of λ_{max} , ϵ_{max} , and K_D is given in Table I, where K_D was determined spectrophotometrically by the technique of Mackay and Poziomek.¹² Agreement of our results with those of previous workers is good, as shown by the data in Table II. Finally, the free energy, enthalpy, and entropy of ionization of the ECP ion pair are given in Table III. In methyl formate and methylene chloride, K_D is less than 1×10^{-4} . For our purposes, in these two solvents the salt can be treated as if it does not dissociate and no corrections to the observed heats of solution are necessary.

The dissolution of the solid pyridinium iodide salt can be viewed as the sequential process



The observed heat of solution is comprised of the heat of solution to give an ion pair and a fraction of the molar heat of dissociation of the ion pair. The values measured are given in Table IV.

The partial molar free energies of transfer of the ion pair were calculated by using the solubility data of Mackay and Poziomek.¹² The standard state used is the hypothetical 1 M solution (Henry's law) and it was assumed that the activity coefficient of the ion pair in each solvent at the concentrations used was 1. For the solvents in which the ion pair does not dissociate, methylene chloride and methyl formate, the standard free energy of transfer ($\delta_m \Delta G$) was calculated by eq 2. For solvents in which the ion

$$\delta_m \Delta G = RT \ln ([\text{Py}^+\text{I}^-]_{s1}/[\text{Py}^+\text{I}^-]_{s2}) \quad (2)$$

pair is partly dissociated, eq 3 was used, where $X = [\text{Py}^+\text{I}^-] +$

$$\delta_m \Delta G = RT \ln \{([\text{Py}^+\text{I}^-]_{s1}/X) - [-K_D + (K_D^2 + 4K_D)^{1/2}]/2\} \quad (3)$$

$[\text{Py}^+]$ and is the measured solubility of the pyridinium iodide. Equation 3 is useful only when the ion pair does not dissociate in the reference solvent, in this case, chloroform. The partial molar heats of solution, the free energies of transfer, and the entropies of transfer derived from them are given in Table IV. The salt concentrations used for the UV measurements were lower than those used for the calorimetric measurements. It has been suggested that no ion aggregates larger than ion pairs can exist at these salt concentrations¹³ but no careful study of this salt has been found. It is possible that the results reported may be effected by the concentration difference, although we would expect such effects to be small.

Excited-State Solvation. The excited-state thermodynamics of transfer were calculated by using the cycle shown in Figure 1. Since we are dealing with a Franck-Condon excited state, we will

Table V. Thermodynamic State Functions of Transfer of the Excited State of 1-Ethyl-4-cyanopyridinium Iodide in Selected Solvents at 25 °C

| solvent | $\delta_m \Delta \bar{G}_{\text{ex}}$, kcal/mol | $\delta_m \Delta \bar{H}_{\text{ex}}$, kcal/mol | $\delta_m \Delta \bar{S}_{\text{ex}}$, eu |
|--------------------|---|---|---|
| ethanol | 15.8 ± 0.4 | 24.9 ± 0.5 | 32.0 |
| acetonitrile | 6.24 ± 0.3 | 11.5 ± 0.4 | 17.6 |
| acetone | 2.35 ± 0.3 | 4.77 ± 0.37 | 8.1 |
| methyl formate | 2.01 ± 0.3 | 7.21 ± 0.42 | 17.4 |
| methylene chloride | 0.51 ± 0.2 | 3.31 ± 0.29 | 9.4 |
| chloroform | 0.00 | 0.00 ± 0.27 | 0.00 |

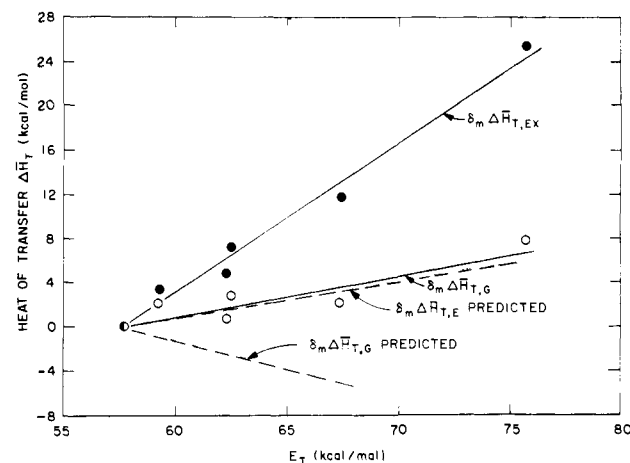


Figure 2. Dependence of the heats of transfer of the ground and excited states of ECP on E_T .

make the customary assumption that the solvation entropies of the ground and excited states are the same. The band shapes in the various solvents were quite similar, suggesting that the medium effects on the population distribution of the excited states are negligible. The thermodynamics of transfer of the excited state are given in Table V.

Discussion

The model developed by Kosower to rationalize the solvatochromism of pyridinium iodides predicts that plots of the heats of transfer of the excited and ground states vs. E_T should have slopes of +0.5 and -0.5, respectively. The data to test this model are plotted in Figure 2. The agreement between experiment and prediction for the excited state is not unreasonable, given the approximations made in the model. However, the model fails for the ground state. The slope is actually positive, rather than the predicted negative value.

The deviation of the experimental results from prediction is probably due to the simplicity of the model used. Kosower's solvation theory is based on Böttcher's⁴ formulation of the energetics of solution of a point dipole at the center of a spherical cavity in a homogeneous dielectric medium. The treatment of a molecule as a point dipole is a common assumption for theoretical molecular calculations and not unreasonable. However, an examination of X-ray evidence³ indicates that due to the shape of the molecule, the cavity occupied by it in solution is probably not spherical. Further, the molecule's dipole moment is not in the center of the molecule. The X-ray evidence indicates that the iodide ion sits close to the nitrogen atom over the pyridinium ring. The relative direction of the dipole in the excited state (i.e., perpendicular to the ground-state dipole) is probably valid. Perhaps the most unjustifiable simplifying assumption in the model is that the point dipole is transferred from infinity to a homogeneous dielectric. The individual dipole moments of the various atoms in the ion pair would produce an uneven polarization of the solvent molecules surrounding the cavity. Different solvation of the anion and cation portions of the pair and the presence of specific solute-solvent interactions are not considered.

It is obvious from this work that the model proposed by Kosower is not entirely correct. It works reasonably well for the excited

(13) M. Mohammad and E. M. Kosower, *J. Phys. Chem.*, **74**, 1153 (1970).

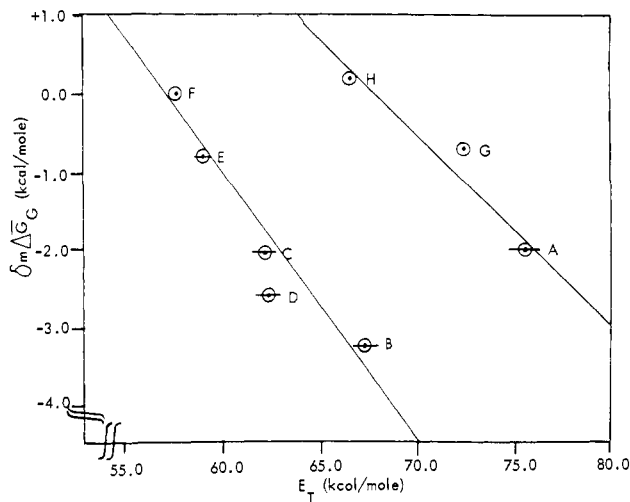


Figure 3. Dependence of $\delta_m \Delta G_G$ on E_T . Solvents plotted: (A) ethanol; (B) acetonitrile; (C) acetone; (D) methyl formate; (E) chloroform; (F) methylene chloride; (G) isopropyl alcohol; (H) *n*-amyl alcohol.

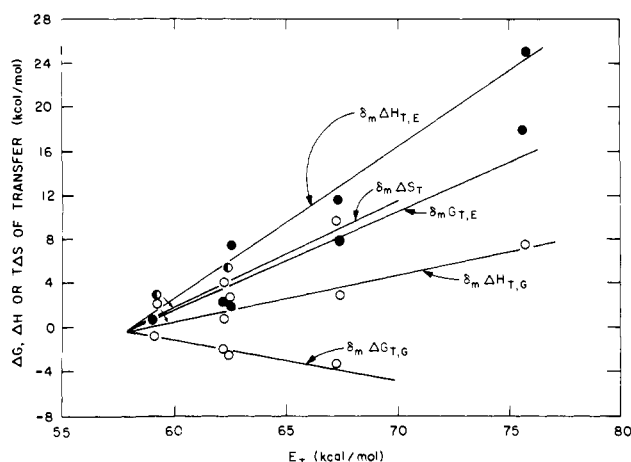


Figure 4. Dependence of the thermodynamics of transfer of the ground and excited states of ECP on E_T .

state but fails for the ground state. This is a particularly complex case, and the model should be tested further by obtaining similar data for other systems before it can be considered to have been reasonably well tested.

The thermodynamics of transfer of the ground and excited states show quite different patterns. The analysis of these data, shown in Figure 4, is complicated by the fact the $\delta_m \Delta G_G$ behaves differently in alcoholic and nonalcoholic solvents, as shown in Figure 3. A plot of $\delta_m \Delta G_G$ vs. E_T gives two nearly parallel lines, one for alcohols and one for the other solvents. The differences presumably are due to hydrogen bonding. In Figure 4, the line shown is that for the nonalcoholic solvents. The entropy of transfer is assumed to be the same for ground and excited states since this is a Franck-Condon excitation. The band shapes in the various solvents are nearly identical, suggesting that the distribution of populated excited states is solvent independent. This supports the assumption of an identical $\delta_m \Delta S$ for the two states.

It is clear from Figure 4 that the transfer of the excited-state ion pair is dominated by the enthalpy term while the ground-state transfer is entropy controlled. While the experimental results for the ground state were contrary to our expectations, the entropy change is in the expected direction, more positive in more structured solvents.¹⁴ The increasingly endothermic heat of transfer of the excited state to more polar solvents is not surprising since the excited state is less polar than the ground state and should not interact as strongly with the surrounding oriented medium.

Table VI. Enthalpy of Solute-Solvent Interactions in the Ground and Excited States of 1-Ethyl-4-cyanopyridinium Iodide at 25 °C

| solvent | $(\Delta \bar{H}_{cav})_G = (\Delta \bar{H}_{cav})_{ex}$, kcal/mol | $(\Delta \bar{H}_{int})_G$, kcal/mol | $\delta_m(\Delta \bar{H}_{int})_{ex}$, kcal/mol |
|--------------------|---|---------------------------------------|--|
| ethanol | 24 | -17 | 14 |
| acetonitrile | 22 | -21 | 3 |
| acetone | 15 | -15 | 3 |
| methyl formate | 16 | -14 | 4 |
| methylene chloride | 15 | -14 | 2 |
| chloroform | 13 | -14 | 0 |

Ramos et al. have pointed out the importance of the cavity term when interpreting solvatochromic effects.¹⁵ Crude estimates of the cavity term were made by using regular-solution theory.¹⁶ Assuming a molar volume of 154 cm³ mol⁻¹ for ECP, the data in Table VI were calculated. The interaction effects are more important for the excited than for the ground state. If the dipole rotates by 90° in the excited state, the interaction should be nearly 0. The results of the cavity treatment are not reasonable and this may be due to the crudeness of the approach. Little credence should be given to these results until both a larger set of data is available and a more sophisticated analysis is carried out.

The combination of spectroscopic studies with thermodynamic measurements to generate data on the solvation of Franck-Condon excited states is a very interesting probe of solvent-solute interactions which, with the exception of Haberfield's⁸ and Arnett's⁷ work, has not been much exploited. It is possible, even easy, to find substrates in which dipoles grow larger, smaller, or change direction, all without altering the position of the surrounding solvent. This approach to understanding solvent-solute interactions is clearly powerful and deserves further work. Applied to the Kosower Z values, it reveals a need for an improved theoretical treatment of the observed solvatochromism. Clearly more data are needed and a thorough evaluation of cavity effects in this and other systems seems necessary.

Experimental Section

UV Absorption Measurement. All volumetric glassware was calibrated volumetrically with water. Samples for absorption measurements were prepared by diluting stock solutions. All measurements were made in a Cary Model 17 spectrophotometer in cells thermostated with an external circulating bath. The temperature of the circulating water emerging from the thermostated cell was measured and used to determine the cell temperature via a calibration curve prepared by simultaneously measuring the temperatures of the circulating water and of the cell contents. Temperature control in the cell was ± 0.02 °C. Usually, 16 measurements at different ECP concentrations at each temperature were made. A computer program kindly supplied by Dr. R. Mackay was used to calculate equilibrium constants from the absorption measurements. The program has been described elsewhere.¹² Heats of dissociation were obtained from the equilibrium constants by the usual van't Hoff procedure. Data obtained at temperatures between 15 and 45 °C were used for the ΔH determination.

Calorimetry. A calorimeter of the Arnett design was used as described.¹⁷

Purification of Compounds. Solvent purification procedures recommended by Perrin and Perrin¹⁸ were used. Purity was monitored by NMR, IR, and UV spectroscopies as well as by gas chromatography.

1-Ethyl-4-cyanopyridinium Iodide. This was prepared by the method of Mackay and Poziomek,¹² crystallized from acetone/benzene (2:1 v/v), dried over P₂O₅ under vacuum, and stored in the dark. Potentiometric titration with AgNO₃ gave a molecular weight of 261.1 (theoretical 260.08).

Acknowledgment. We thank Dr. R. A. Mackay for providing advice and a copy of his computer program for calculating dissociation constants.

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