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Electrostatic Modulation by Ionic Aggregates: Charge Transfer Transitions in Solutions of Lithium Perchlorate−Diethyl Ether[‡]

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Abstract: The ionic environment within solutions of lithium perchlorate−diethyl ether (LPDE) was probed by utilizing the extraordinary spectral shifts these media impart on various nitroanilines at 25 °C. These compounds all have UV−visible spectra that are sensitive to the polarity of the medium and the nitroanilines investigated all exhibited varying degrees of solvatochromatic behavior in LPDE solutions. In all cases, the low-energy absorbance band exhibited a dependence upon $\mathrm{LiClO_4}$ concentration throughout the entire solubility range investigated. For 4-nitroaniline and *N,N*-dimethyl-4-nitroaniline bathochromic shifts of 51.3 and 62.0 nm, respectively, were observed on going from pure ether to a 5.7 M LPDE solution, corresponding to a stabilization of 10.55 and 11.13 kcal mol^{-1}, respectively, for this transition. Thus, as the medium changes from diethyl ether to one containing ionic clusters of lithium perchlorate−diethyl ether, less energy is required to transfer the molecules from their ground states to their first excited states. For 2,6-dibromo- and 2,6-diiodo-4-nitroaniline smaller red shifts of 19.0 and 9.0 nm, respectively, were noted over the same concentration range of LPDE, resulting in stabilizations of 4.45 and 2.11 kcal mol^{-1}, respectively. Analysis of the observed molar transition energies indicates that for 4-nitroaniline and *N,N*-dimethyl-4-nitroaniline the stabilization of the zwitterionic excited states of such push−pull molecules is on the order of 2.0 kcal mol^{-1} per mol of added salt. Furthermore, such stabilization is *independent* of the composition of the media. Thus these compounds can act as solvent polarity indicators for LPDE solutions throughout the entire solubility range of $\mathrm{LiClO_4}$ in diethyl ether. As such, linear relationships are seen between the E_T values of 4-nitroaniline and *N,N*-dimethyl-4-nitroaniline and the log of the second-order rate constants for the [4+2] cycloaddition reaction of 9,10-dimethylanthracene and acrylonitrile in LPDE. We also observe linear relationships between the E_T values of 4-nitroaniline and *N,N*-dimethyl-4-nitroaniline and the keto−enol ratio of acetylacetone in LPDE.

Introduction

The solvent system composed of strictly anhydrous lithium perchlorate in diethyl ether, hereafter LPDE, has attracted much attention over the years and a number of physical organic studies have been carried out to assess the electrostatic effects governing these ionic media.[1−11] These highly polar concentrated salt solutions have been shown by conductivity and vapor pressure data to exist as complex ionic clusters composed of $\mathrm{LiClO_4}$ and ether, rather than simple aggregates of ions.[10,11] Solubility−temperature curves, NMR spectroscopy, and heats of solution measurements indicate that below 4.25 M LPDE, these solutions are composed of $\mathrm{Li(OEt_2)_2^+\ ClO_4^-}$ ions, while above 4.25 M, a mixture of $\mathrm{Li(OEt_2)_2^+\ ClO_4^-}$ and $\mathrm{Li(OEt_2)^+\ ClO_4^-}$ exists.[2] The limit of solubility, 6.06 M, corresponds to the ionic composition $\mathrm{Li(OEt_2)^+\ ClO_4^-}$.

Pocker and Buchholz used the ionization of triphenylmethyl chloride as a sensitive probe of the ionic environment present in these solutions, and observed a (7×10^9)-fold increase in trityl cation formation on going from pure ether to a 5.0 M LPDE solution.[2] Similarly, the rate of rearrangement of 1-phenylallyl chloride to cinnamyl chloride rises (8.56×10^4)-fold on going from ether to 3.39 M LPDE, while the aminolysis of

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[‡] For the previous paper in this series see: Pocker, Y.; Ciula, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4728.

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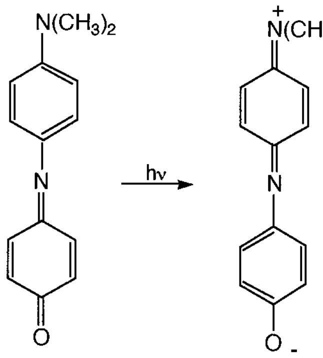
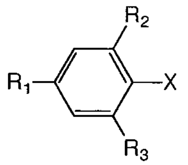
Scheme 1



4-nitrophenyl acetate by imidazole is accelerated by a factor of 5.8×10^4 from 0 to 4.49 M LPDE.[3,5,6]

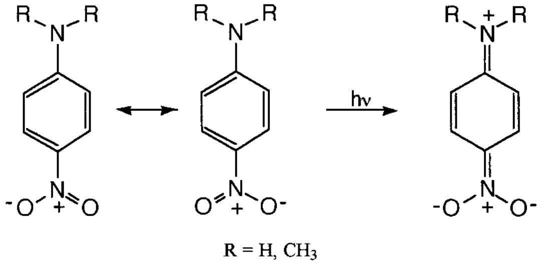
The ability of these solutions to facilitate proton transfer reactions has been extensively studied.[7,9b] The apparent equilibrium constant for the reaction of 4-nitrophenol with imidazole changes by ca. 10^7 when the solvent system is changed from pure ether to 5.0 M LPDE, while for the reaction of tropolone with pyridine, a (1.25×10^4)-fold increase occurs from ether to 2.95 M LPDE. Perhaps most striking of all is the change in the acidity order of substituted phenols in ether from 2,4-dinitrophenol > 3,5-dinitrophenol, 4-nitrophenol ≫ 2-nitrophenol to 2,4-dinitrophenol > 2-nitrophenol > 3,5-dinitrophenol > 4-nitrophenol in LPDE solutions. Recent work has focused on exploiting the synthetic utility of these media.[12]

Scheme 2



Aniline	X	R_1	R_2	R_3
2	NH_2	NO_2	H	H
3	$N(CH_3)_2$	NO_2	H	H
4	NH_2	H	NO_2	H
5	NH_2	H	NO_2	NO_2
6	NH_2	NO_2	Br	Br
7	NH_2	NO_2	I	I
8	NH_2	$4\text{-}O_2NC_6H_4$	H	H

Scheme 3



Previous work in these laboratories delineated the spectral changes that this solvent system imparts on 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye) and *N*,*N*-dimethylindoaniline (phenol blue, **1**, Scheme 1), as well as various 8,9-diacyl-substituted sesquifulvalenes, and apparent equilibrium constants were derived to describe the interaction of lithium ion with these indicators.[8] Reichardt's dye and the sesquifulvalenes were found to form either 1:1 or 1:2 complexes with lithium ion, complexes that were no longer susceptible to polarity changes in the environment upon further addition of $LiClO_4$. Indeed, Reichardt's dye was found to be exquisitely sensitive to the concentration of lithium ion present with an apparent equilibrium constant for 1:1 complex formation of 5.0×10^6 M^{-1}. Phenol blue, however, exhibited a dependence upon $LiClO_4$ concentration throughout the entire solubility range of the salt in diethyl ether. The increase in dipole moment of **1** upon absorbance of light produces a greater interaction between **1** and lithium ion. However, a plot of the molar transition energy (E_T, eq 1) for the low-energy absorbance band of **1** vs log-

$$E_T = hcN/\lambda = 28\,593 \text{ kcal mol}^{-1} \text{ nm}/\lambda \qquad (1)$$

[$LiClO_4$] revealed a break near 4.2 M that corresponds to the transition from dietherate, $Li(OEt_2)_2^+ \, ClO_4^-$, to monoetherate, $Li(OEt_2)^+ \, ClO_4^-$, clusters indicating that any increase in stabilization due to interaction with Li^+ is dependent on the number of solvent molecules coordinated to the lithium ion, that is, on the composition of the medium. Similar behavior was noted for **1** in solutions of $LiClO_4$ in THF.

We have expanded on our earlier observations by investigating the effects of these room-temperature molten salt solutions on the UV−visible spectra of the nitroanilines **2**−**8** (Scheme 2). For nitroanilines the low-energy absorption band is the result of an intramolecular charge-transfer transition (Scheme 3) such that the excited state possesses more quinoid character than the ground state.[13,14] For example, 4-nitroaniline, **2**, has a ground-state dipole moment of 6.1 D while its first excited state has a dipole moment, in the same direction, of 15 D.[14c]

Experimental Section

UV−visible spectra were taken on a Cary 210 spectrophotometer interfaced to an Apple IIe computer through a bi-directional parallel interface. The cell compartment was maintained at 25.0 ± 0.1 °C with a Forma-Temp Junior Model 2095-2 constant-temperature bath. Stock solutions of the anilines investigated were prepared in dry diethyl ether

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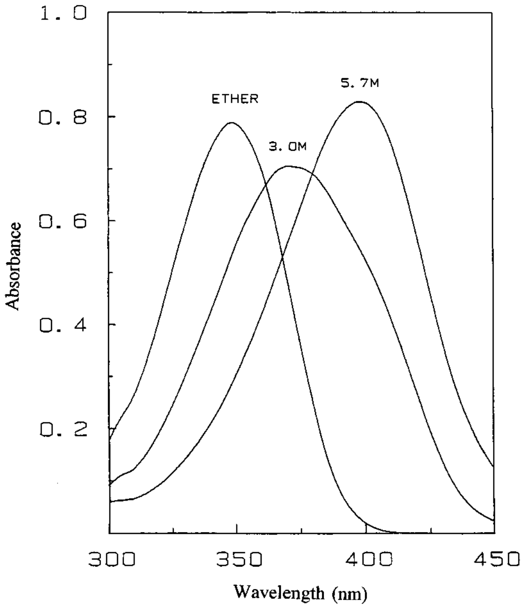

Figure 1. The UV−visible spectrum of 4-nitroaniline in ether, 3.0 M LPDE, and 5.7 M LPDE. In all media [4-nitroaniline] = 4.4 × 10^{-5} M.

and known amounts were injected into 3 mL of various LPDE solutions. Figure 1 depicts the UV−visible spectra of 4-nitroaniline, **2**, in various LPDE solutions.

Diethyl ether was distilled under dry nitrogen or argon from excess lithium aluminum hydride (Aldrich) just prior to use. Anhydrous lithium perchlorate (GFS Chemicals) was recrystallized twice from water and dried at 152 °C under high vacuum for at least 24 h. Care must be taken to ensure that the lithium perchlorate is strictly anhydrous, as the trihydrate, the only hydrate of $LiClO_4$ known, is only sparingly soluble in ether (0.139 g/100 mL of solution at 25 °C).[1] The anhydrous salt was stored under nitrogen or argon in a tightly sealed flask in a desiccator over P_2O_5 until used.

The indicators 4-nitroaniline, *N,N*-dimethyl-4-nitroaniline (**3**), 2-nitroaniline (**4**), and 2,6-dinitroaniline (**5**), were obtained from Eastman Kodak and recrystallized from either water or ethanol and then sublimed while 2,6-dibromo-4-nitroaniline (**6**) was chromatographed on silica gel with CH_2Cl_2.[15a−d] The aniline 2,6-diiodo-4-nitroaniline (**7**) was prepared by the method of Sy and chromatographed on silica gel with $CHCl_3$, with the first yellow band being collected.[15e−g] The biphenyl 4-nitro-4′-aminobiphenyl (**8**) was prepared by reducing 4,4′-dinitrobiphenyl with $Na_2S{\cdot}9H_2O$ and elemental sulfur and purified by chromatography on silica gel with CH_2Cl_2.[15h−15j]

Results and Discussion

Table 1. The Dependence of the Wavelength of Maximum Absorbance on the Species Present in Solution at 25 °C for Nitroanilines **2**−**8**

aniline	λ_{max} Et_2O^a	λ_{max} LPDE^{a,b}	$\Delta\lambda^c$	$\Delta E_T{}^d$
2	348.0	399.3	51.3	10.55
3	369.3	431.3	62.0	11.13
4	391.8	424.3	32.5	5.59
5	415.3	424.8	9.5	1.54
6	340.0	359.0	19.0	4.45
7	345.0	354.0	9.0	2.11
8	372.0	378.0^e	6.0	1.22

[a] In nm. [b] 5.7 M LPDE. [c] $\Delta\lambda = \lambda_{max\ LPDE} - \lambda_{max\ ether}$ in nm for the low-energy visible band. [d] $\Delta E_T = E_{T\ ether} - E_{T\ LPDE}$ in kcal mol^{-1} for the low-energy visible band. [e] 3.0 M LPDE.

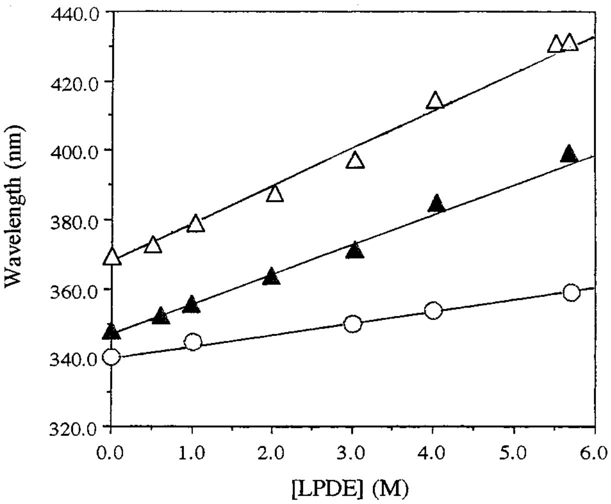

Figure 2. Plot of λ_{max} (nm) vs [LPDE] (M) for 4-nitroaniline, **2** (▲), *N,N*-dimethyl-4-nitroaniline, **3** (△), and 2,6-dibromo-4-nitroaniline, **6** (○). The equation of the line for 4-nitroaniline is λ_{max} = 364.64 + 9.10[LPDE] (*r* = 0.996). The equation of the line for *N,N*-dimethyl-4-nitroaniline is λ_{max} = 366.73 + 11.27[LPDE] (*r* = 0.994). The equation of the line for 2,6-dibromo-4-nitroaniline is λ_{max} = 340.50 + 3.25[LPDE] (*r* = 0.996).

The nitroanilines investigated all exhibited varying degrees of solvatochromatic behavior in LPDE solutions as shown in Table 1. Bathochromic shifts were observed for all the indicators studied, indicating that as the medium changes from diethyl ether to one containing ionic clusters of lithium perchlorate−diethyl ether, less energy was required to transfer the molecules from their ground states to their first excited states. In all cases, the low-energy absorbance band exhibited a dependence upon $LiClO_4$ concentration throughout the entire solubility range investigated as illustrated in Figure 1 for **2**, similar to the behavior of **1** in LPDE solutions

The anilines **2** and **3** produced the largest shifts on going from pure ether to a 5.7 M LPDE solution (Table 1). This is consistent with the dimethylamino group being a more powerful electron donor than the amino group.[16] There is a ca. 20 nm decrease in the bathochromic shift when the aniline changes from **2** to its ortho isomer, **4**, and a ca. 42 nm drop in red shift on going from **2** to 2,6-dinitroaniline. This is indicative of the smaller difference in dipole moments between the ground and excited states in ortho-substituted aromatic rings relative to their para isomers, as well as steric crowding around the amino group in **5**.[17] In LPDE, the wavelength of maximum absorbance for the indicators **2**, **3**, and **6** exhibited a linear dependence on $[LiClO_4]$ (Figure 2). Slopes of 9.10, 11.27, and 3.25 nm mol^{-1} were noted for **2**, **3**, and **6**, respectively. A plot of E_T vs LPDE

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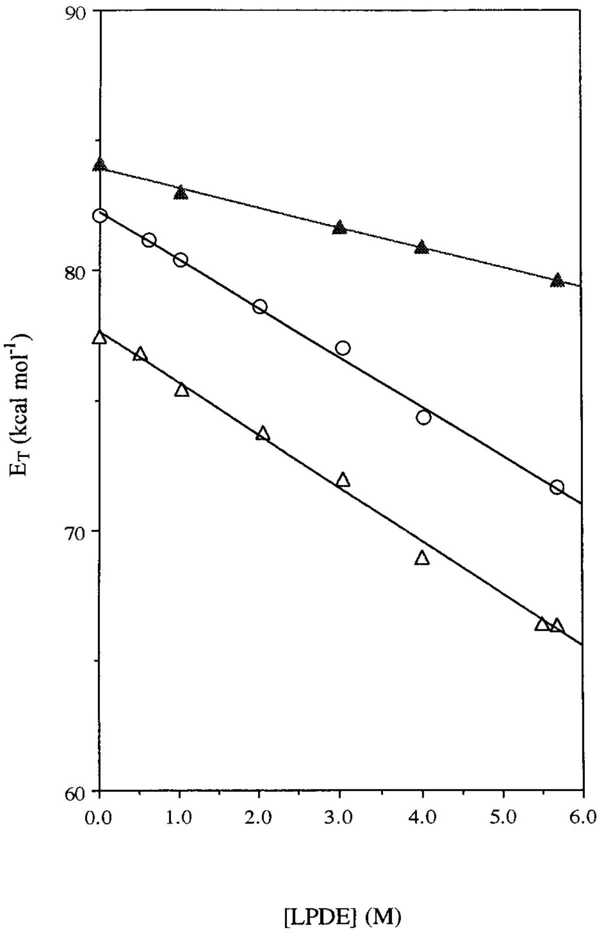


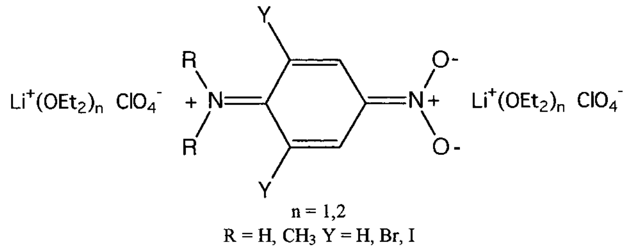
Figure 3. Plot of E_T (kcal mol^{-1}) vs [LPDE] (M) for 4-nitroaniline (○), *N*,*N*-dimethyl-4-nitroaniline (△), and 2,6-dibromo-4-nitroaniline (▲). For 4-nitroaniline the slope of the line is 1.88 kcal mol^{-1} per mol of LPDE (r = 0.993). For *N*,*N*-dimethyl-4-nitroaniline the slope of the line is 2.02 kcal mol^{-1} per mol of LPDE (r = 0.995). For 2,6-dibromo-4-nitroaniline the slope of the line is 0.76 kcal mol^{-1} per mol of LPDE (r = 0.996).

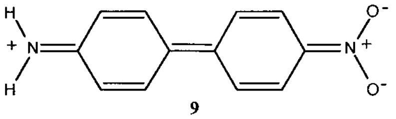
concentration (Figure 3) illustrates that the addition of LiClO$_4$ to diethyl ether decreases the energy gap between the ground state and the first electronic excited state by ca. 2.0 kcal mol^{-1} per mole of added salt for **2** and **3** and by 0.76 kcal mol^{-1} per mole of salt for **6**.

From Figure 3 we see that E_T values for 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline, as well as 2,6-dibromo-4-nitroaniline, are *independent* of the composition of the medium: $[\mathrm{Li(OEt_2)_2^+,ClO_4^-}]$ or $[\mathrm{Li(OEt_2)^+,ClO_4^-}]$, unlike the behavior of **1** in LPDE, as well as **1** in lithium perchlorate−THF.[8] Thus, **2** and **3**, and to a lesser degree **6**, are excellent candidates for use as solvent polarity indicators for solutions of lithium perchlorate in diethyl ether as their molar transition energies are not dependent on the number of solvent molecules coordinated to the lithium ion.

In LPDE solution, the dipole moment of the nitroanilines produces an orientation of LiClO$_4$−Et$_2$O clusters about the indicator molecules such that Li$^+$ is situated at the nitro pole while ClO$_4^-$ is located at the amino end (Scheme 4).[14] From the Franck−Condon principle, the solvent molecules have no time to reorganize during excitation and charge redistribution, so Li$^+$ remains at the nitro pole of the aniline.[18] As the excited states of these indicator dyes possess larger dipole moments than the ground states, it is reasonable to conclude that stabilization of the aniline's excited state by LPDE is occurring to a much greater degree than stabilization of its ground state. For **6** and **7** the sensitivity of the nitroaniline toward its ionic environment is not as great as that of 4-nitroaniline or *N*,*N*-dimethyl-4-nitroaniline. The crystal structure of **6** reveals that the amino group is coplanar with the aromatic ring.[19] The decreased sensitivity may be the result of steric crowding between the amino moiety and ClO$_4^-$ in conjunction with a decrease in the excited-state dipole moment due to the ortho-substituted bromines. Such steric crowding is occurring to a much larger degree in the diiodonitroaniline, **7**, which exhibits a red shift of only 9.0 nm on going from pure ether to 5.7 M LPDE, similar to the 9.5 nm red shift of **5**. The biphenyl **8** shows only a 6 nm red shift on going from 0.0 to a 3.0 M LPDE solution. Crystallographic studies by Graham and co-workers reveal that the biphenyl ring system of **8** is essentially planar, possessing a dihedral angle of only 5°, unlike other 4,4′-disubstituted biphenyls.[20] From the small bathochromic shift noted in LPDE solutions, the quinoid structure, **9**, must make only a small contribution to the structure of the excited state, in contrast to **2** and **3**.

Scheme 4





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The ability of LPDE solutions to enhance the reaction rates of some pericyclic reactions has been the subject of some debate over the nature of the catalysis.[12,21−25] Grieco has proposed that the increase in diethyl ether's internal pressure upon addition of LiClO$_4$ is behind the observed rate accelerations while recent work by Springer et al. has shown that this rate acceleration

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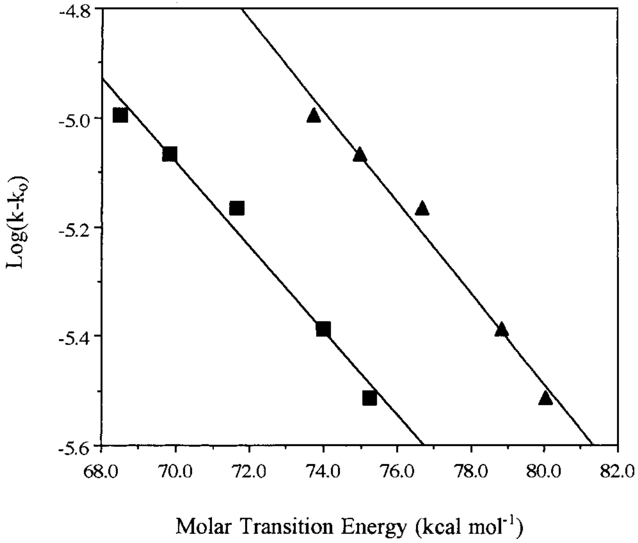

Figure 4. Plot of log($k - k_o$) for the second-order rate constants, k, for the reaction of 9,10-dimethylanthracene and acrylonitrile at 28.0 °C in LPDE solutions vs E_T (kcal mol^{-1}) values for 4-nitroaniline (■) and *N,N*-dimethyl-4-nitroaniline (▲). For 4-nitroaniline the equation for the line is log($k - k_o$) = 0.313 − (7.71 × 10^{-2})E_T (r = 0.982). For *N,N*-dimethyl-4-nitroaniline the equation for the line is log($k - k_o$) = 1.15 − (8.30 × 10^{-2})E_T (r = 0.982). The kinetic data are from ref 21.

can instead be attributed to Li$^+$ ion acting as a Lewis acid in conjunction with an increase in solvent polarity of the medium as the LiClO$_4$ concentration increases.[22,23] Forman and Dailey observed an 8.9-fold increase in rate for the [4+2] cycloaddition reaction between 9,10-dimethylanthracene and acrylonitrile on going from pure ether to a 4.55 M LPDE solution.[21] They attributed this increase in rate to Li$^+$ acting as a Lewis acid and coordinating with the cyano nitrogen. We observe linear correlations between the E_T values of **2** (r = 0.982), as well as **3** (r = 0.982), and the log of the second-order rate constants for the [4+2] cycloaddition reaction of 9,10-dimethylanthracene and acrylonitrile in LPDE (Figure 4), results consistent with lithium ion functioning as a Lewis acid and that are in accord with previous observations.[2−9,21,23−26] Linear relationships are also seen between the E_T values of **2** (r = 0.977) and **3** (r = 0.977) and the keto−enol ratio of acetylacetone in LPDE media (Figure 5).[26] These results can be attributed to preferential stabilization of the more polar keto tautomer via Li$^+$ ion coordination coupled with an increase in intensity of the electrostatic field present as the number of ionic aggregates in solution expands as more LiClO$_4$ is added. Major advances in LPDE systems in this laboratory have been stimulated by elegant interdisciplinary studies pertaining to ionic interactions during enzyme catalysis, biomolecular recognition, and control.[27,28] For example, Dunn, et al. have reported a 97 nm bathochromic shift when 4-(*N,N*-dimethylamino)cinnaminaldehyde (DACA) forms a ternary complex with LADH and NAD$^+$, as well as a 66 nm red shift upon DACA•LADH•NADH complex formation.[29] Dunn has argued that the large red shift in the visible spectrum of DACA is the result of the combined effects of complexation with Zn^{2+} and the close proximity of the positively charged nicotinamide ring of NAD$^+$. We have observed a 47 nm bathochromic shift on going from pure diethyl ether to a 5.0 M LPDE solution, corresponding to a ΔE_T of 8.94 kcal mol^{-1}, consistent with increased stabilization of the excited state over the ground state by Li$^+$.[26] It is hoped that these observations, when taken as a whole, will shed light on the nature of the ionic clusters present in these media.

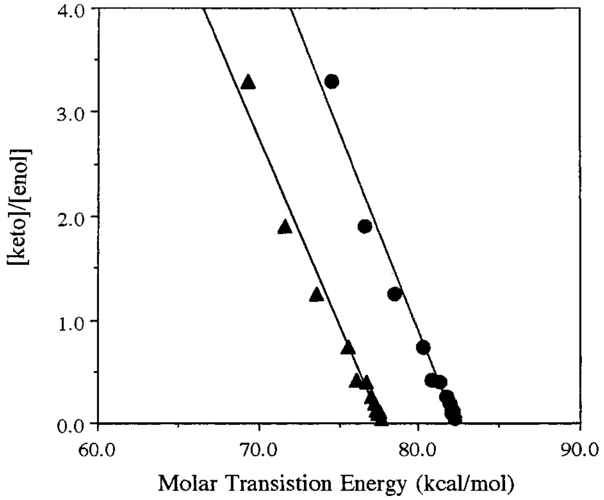

Figure 5. Plot of the equilibrium constant, K = [keto]/[enol], for the ketonization of acetylacetone at 25.0 °C in LPDE solutions vs E_T (kcal mol^{-1}) values for 4-nitroaniline (●) and *N,N*-dimethyl-4-nitroaniline (▲). The equilibrium data are from ref 26.

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