Solute–Solvent Interactions in the Ground State and in Electronic Excited States. The Dipolar Aprotic to Polar Protic Solvent Blue Shift of Nitroaromatics

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Abstract: The long-wavelength transition of some nitroaromatics was found to be uniformly blue shifted on transfer from dimethylformamide to methanol solvent. The enthalpies of transfer of the Franck–Condon excited states of these compounds were then determined by combining calorimetric and spectroscopic data. It was found that the enthalpies of transfer of the Franck–Condon excited states were uniformly endothermic into the hydrogen-bonding solvent and larger than the ground-state transfer enthalpies. As this is contrary to expectation for a transition that transfers negative charge to the nitro group, an estimate of the relaxed excited state transfer enthalpies was made using fluorescence measurements. It was found that the relaxed excited state has even more endothermic transfer enthalpies from the dipolar aprotic solvent to the polar protic solvent.

A solvent effect on the $\lambda_{\max}$ of the electronic spectrum of a compound can be caused by increased (or decreased) solvation of the ground state, by a change in the solvation of the excited state, or by a combination of these effects. By combining spectroscopic and calorimetric measurements these effects can be separated. Examination of the solvent transfer enthalpy of the ground state and the solvent transfer enthalpy of the excited state can then yield information concerning the nature of the electronic reorganization in the excited state and the nature of the solvation in the ground and excited states.

Recently we tried to dissect the solvation effects causing the well-known blue shift in the $n \rightarrow \pi^*$ transition of ketones and azo compounds on going to more polar solvents.[1,2] In the particular case of the blue shift of ketones on going from a dipolar aprotic to a polar protic solvent we found that the enthalpies of transfer of the ground states into the protic ("blue") solvent were endothermic. For the $n \rightarrow \pi^*$ transition, which involves a *decrease* in the carbonyl dipole moment, this fact alone would predict a red shift. The observed blue shift is caused by the fact that the orientation strain in the Franck–Condon excited state is evidently greater in the hydrogen-bonding solvents than it is in the dipolar aprotic solvents.[2]

It would be of interest to examine the dipolar aprotic to polar protic solvent effect on the ground and excited states of a dipolar molecule in which the excited-state dipole is *increased* relative to the ground state. The long-wavelength transition of nitroaromatics (corresponding to the 280-nm band of nitrobenzene) fills this requirement[3-5] and was therefore examined. The solvents used, dimethylformamide and methanol, have about the same dielectric constants (37 and 33, respectively)[6] and are therefore well suited for the study of specific solvation effects.

Results and Discussion

The enthalpy of solvent transfer of a compound, $\delta\Delta H^{\text{ground state}}_{\text{DMF}\rightarrow\text{MeOH}}$, is the difference between the heats of solution, $\Delta H_{\text{solvent}}$, of the compound in the two solvents of interest:

$$\delta\Delta H^{\text{ground state}}_{\text{DMF}\rightarrow\text{MeOH}} = \Delta H_{\text{MeOH}} - \Delta H_{\text{DMF}}$$

With the spectral solvent shift, $\delta\Delta E_{\text{DMF}\rightarrow\text{MeOH}}$, defined in the usual way as the difference in the excitation energies, ΔE^{abs}, in the two solvents

$$\delta\Delta E^{\text{abs}}_{\text{DMF}\rightarrow\text{MeOH}} = \Delta E^{\text{abs}}_{\text{MeOH}} - \Delta E^{\text{abs}}_{\text{DMF}}$$

the energy of transfer of the Franck–Condon excited state, $\delta\Delta H^{\text{F-C excited state}}_{\text{DMF}\rightarrow\text{MeOH}}$, is then readily calculated by the equation

$$\delta\Delta H^{\text{F-C excited state}}_{\text{DMF}\rightarrow\text{MeOH}} = \delta\Delta E^{\text{ground state}}_{\text{DMF}\rightarrow\text{MeOH}} + \delta\Delta E^{\text{abs}}_{\text{DMF}\rightarrow\text{MeOH}} \quad (1)$$

All the compounds examined exhibited a blue shift on going to the protic solvent, which amounted to 1–2 kcal/mol (Table I, column 2). As the reasonable expectation is that hydrogen bonding to the nitro groups will cause a red shift of a transition that moves negative charge toward the nitro group,[7] it is clear that other factors play a role here as well. The fact that the enthalpies of transfer of the ground states, $\delta\Delta H^{\text{ground state}}_{\text{DMF}\rightarrow\text{MeOH}}$ (Table I, column 3), are all endothermic indicates that the net interaction energy[8] between the nitro groups and the dipolar aprotic solvent is greater than that between the nitro groups[9] and the polar protic solvent. This is so because the only other contributions to the $\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}}$ values are the energies of solvent cavity formation in the two solvents[8] and the interaction energy between solvent and parts of the solute molecules other than the nitro group. That these two contributions are minor can be seen from the fact that the enthalpies of transfer of hydrocarbons of like size, such as toluene, biphenyl, and naphthalene, range from $\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}} = 0.3$ kcal/mol to $\delta\Delta H_{\text{DMF}\rightarrow\text{MeOH}} = 0.6$ kcal/mol,[10] as well as from a general overview of the substantial body of solvent transfer enthalpies for this pair of solvents determined by Fuchs and co-workers.[10,11]

Therefore the solvent transfer enthalpies of ground and excited states, which range from 1.4 to 5.4 kcal/mol, clearly reflect differences between the solvation of the nitro group in the two solvents. This solvation is about 1–3 kcal/mol greater in the dipolar aprotic solvent for the ground state, and 2–5 kcal/mol greater in the dipolar aprotic solvent for the Franck–Condon excited state (Table I, column 3; Figure 1). The increase in the Ar–NO_2 dipole on going to the excited state evidently strengthens this solute–dipolar aprotic solvent interaction to a greater extent than it strengthens the solute–hydrogen bond donor interaction.[12] Transfer of electron density to the π^* orbital, although it involves a net increase of electron density on the NO_2 oxygens, may increase electron repulsion pushing some charge out of the oxygen σ lone pair orbital, thus actually weakening the hydrogen bond.[13] The dipole–dipole attraction between the nitroaromatics and dimethylformamide, on the other hand, increases when the solute dipole increases.

A second possible explanation lies in the more exact geometrical requirements of a hydrogen bond, thus introducing a greater Franck–Condon strain in the case of the hydrogen bond donor solvent. This explanation could be tested if the appropriate solvent transfer enthalpies of the *relaxed excited state* were available for comparison. If one makes the (rea-

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Table I. The Solvent Blue Shift ($\delta\Delta E^{\text{abs}}_{\text{DMF}\to\text{MeOH}}$ of the Long-Wavelength Transition of Nitro Compounds and the Enthalpy of Transfer of Their Ground States ($\delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}}$), Their Franck-Condon Excited States ($\delta\Delta H^{\text{F-C excited state}}_{\text{DMF}\to\text{MeOH}}$), and Their Relaxed Excited States ($\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}}$) from Dimethylformamide to Methanol (kcal/mol)

compd	$\delta\Delta E^{\text{abs}}_{\text{DMF}\to\text{MeOH}}$	$\delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}}$	$\delta\Delta H^{\text{F-C excited state}}_{\text{DMF}\to\text{MeOH}}$	$\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}}$
1-nitronaphthalene	1.43	1.4[a]	2.8	3.6
4-nitrobiphenyl	2.20	1.4[a]	3.6	4.3
4,4′-dinitrobiphenyl	2.20	2.0[a]	4.2	5.2
4-nitroanisole	2.07	2.11[b]	4.18	4.8
4-nitroacetophenone	1.09	2.2[a]	3.3	
4-nitro-α-bromotoluene	1.16	2.31[c]	3.46	
2,4-dinitroanisole	2.36	3.01[b]	5.37	
2,4-dinitroiodobenzene	0.94	3.5[d]	4.4	

[a] Reference 10. [b] P. Haberfield, *J. Am. Chem. Soc.*, **93,** 2091 (1971). [c] P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg, *J. Org. Chem.*, **36,** 1792 (1971). [d] P. Haberfield, L. Clayman, and J. S. Cooper, *J. Am. Chem. Soc.*, **91,** 787 (1969).

Table II. The Long-Wavelength Absorption Maximum ($\lambda^{\text{abs}}_{\text{max}}$) and the Corresponding Fluorescence Maximum ($\lambda^{\text{fl}}_{\text{max}}$) of Nitroaromatics in Dimethylformamide and Methanol Solvent (nm)

compd	$\lambda^{\text{abs}}_{\text{max}}$(DMF)	$\lambda^{\text{abs}}_{\text{max}}$(MeOH)	$\lambda^{\text{fl}}_{\text{max}}$(DMF)	$\lambda^{\text{fl}}_{\text{max}}$(MeOH)
4-nitro-α-bromotoluene	273.8	270.8		
2,4-dinitroiodobenzene	277.0	274.5		
4-nitroacetophenone	284.76	281.72		
2,4-dinitroanisole	297.92	290.77		
4-nitroanisole	312.61	305.70	397.4	380.1
4-nitrobiphenyl	312.94	305.57	379.6	362.1
4,4′-dinitrobiphenyl	314.1	306.7	380.4	359.9
1-nitronaphthalene	337.12	331.52	423.3	405.3

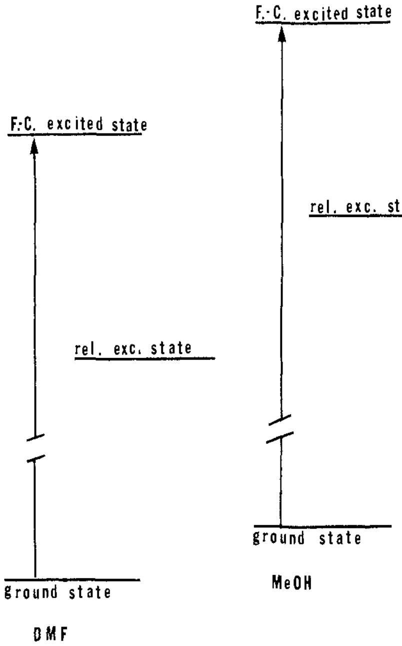

Figure 1. Relative energies of the ground states, the Franck-Condon excited states, and the relaxed excited states in a dipolar aprotic solvent (DMF) and a polar protic solvent (MeOH).

sonable) assumption[14] that the solvent (and other) relaxation processes in the excited and ground states, following excitation and fluorescence, respectively, are energetically about equal, then the enthalpy of solvent transfer of the relaxed excited state, $\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}}$, is given by the relation

$$\delta\Delta H^{\text{rel excited state}}_{\text{DMF}\to\text{MeOH}} = \delta\Delta H^{\text{ground state}}_{\text{DMF}\to\text{MeOH}} + \tfrac{1}{2}\delta\Delta E^{\text{abs}}_{\text{DMF}\to\text{MeOH}} + \tfrac{1}{2}\delta\Delta E^{\text{fl}}_{\text{DMF}\to\text{MeOH}}$$

where $\delta\Delta E^{\text{fl}}_{\text{DMF}\to\text{MeOH}}$ is the difference between the fluorescence energies in the two solvents. Using this assumption yields the enthalpies of transfer of the relaxed excited state from dimethylformamide to methanol shown in Table I, column 4, and depicted graphically in Figure 1. As can be seen, the enthalpies of transfer of the relaxed excited state are even more endothermic into the hydrogen bond donor solvent than are the enthalpies of transfer of the Franck-Condon excited state. Thus the second explanation, namely, Franck-Condon strain, is not the correct explanation for the blue shift. The conclusion that the long-wavelength excited state of nitroaromatics is solvated better by the dipolar aprotic solvent than by the polar protic solvent is therefore inescapable.

Experimental Section

Materials. All compounds were commercial samples and were recrystallized where necessary until their melting points agreed with the literature value. Solvents were dried and distilled before use.

Spectroscopic Measurements. Absorption spectra were determined using a Cary 17 spectrophotometer. The wavelength of each absorption maximum was corrected by measuring the spectrum of holmium oxide glass before or after each set of runs. The values are listed in Table II and are estimated to be accurate to ±0.1 nm or better. Fluorescence spectra were measured on a Perkin-Elmer MPF-2A fluorescence spectrometer. The instrument was calibrated periodically by means of the xenon 467.1-nm peak. Results are listed in Table II. Their accuracy is estimated to be ±1 nm or better.

Acknowledgment. This work was supported in part by the National Science Foundation, Undergraduate Science Education Program Grants GY-10689 and GY-11144.

References and Notes

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(5) Increase in proton affinity (substituent protonation) of nitrobenzene excited

states: B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 3214 (1977).

(6) A referee has pointed out that there is, of course, no reason to expect dielectric constants to correlate with UV transition energies. Thus F. W. Fowler, A. R. Katritzky, and R. J. D. Rutherford, *J. Chem. Soc. B*, 460 (1971), report that solvent effects on chemical and physical properties, including UV transition energies, are poorly correlated by *d* or functions of *d*, and there are few, if any, indications in the literature that absorption maxima (in the absence of H bonding) are linear with *d* or the $(d - 1)/(d + 2)$ function.

(7) E.g., (a) G. S. Hammond and F. J. Modic, *J. Am. Chem. Soc.*, **75**, 1385 (1953); (b) K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1964, p 189; (c) M. J. Kamlet, E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).

(8) The difference between the two net interaction energies ($\Delta H_{\text{solute-solvent}}$) is equal to the enthalpy of solvent transfer ($\delta\Delta H_{\text{DMF}\to\text{MeOH}}$) less the difference between the two solvent cavity formation energies ($\Delta H_{\text{solvent-solvent}}$), or

$$\delta\Delta H_{\text{DMF}\to\text{MeOH}} = \Delta H_{\text{solute-MeOH}} - \Delta H_{\text{solute-DMF}} + \Delta H_{\text{MeOH-MeOH}} - \Delta H_{\text{DMF-DMF}}$$

(9) In the case of the two anisoles, hydrogen bonding to the methoxyl oxygen might also make a significant contribution. See, however, the cogent argument of Kamlet (ref 7c) dismissing this possibility for the case of 4-nitroanisole. The 4-nitroacetophenone, on the other hand, undoubtedly has significant carbonyl group–solvent interaction contributions which complicate matters.

(10) R. Fuchs and R. F. Rodewald, *J. Am. Chem. Soc.*, **95**, 5897 (1973).

(11) P. P. Saluja, T. M. Young, R. F. Rodewald, F. H. Fuchs, D. Kohli, and R. Fuchs, *J. Am. Chem. Soc.*, **99**, 2949 (1977).

(12) This observation is in agreement with the findings of M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977), who found that DMF is a more polar solvent (has a larger π^* value) than methanol.

(13) L. C. Allen, *J. Am. Chem. Soc.*, **97**, 6921 (1975).

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Replacement of the Nitro Group by Hydrogen[1]

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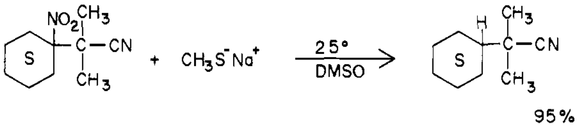
Abstract: The reaction of an aliphatic nitro compound with the sodium salt of methanethiol can occur with clean replacement of the nitro group by hydrogen. This is so despite the existence of a competitive process—replacement of nitro by thiomethyl. Evidence in support of the view that both transformations are electron transfer processes is presented and a radical anion-free radical chain mechanism is proposed. The factors which control the course of reaction of a nitro compound and the sodium salt of methanethiol are described and a simple rationale is presented.

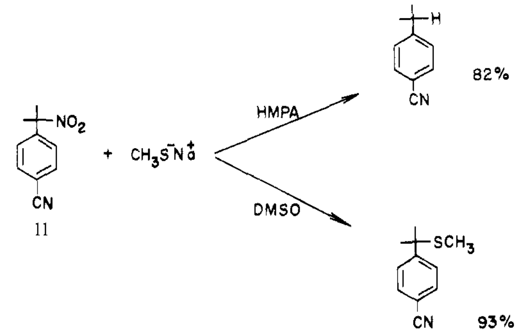
Until 1954 a synthetically useful method for the preparation of tertiary nitroparaffins did not exist. Since that time a number of reactions have been discovered which give excellent yields of pure aliphatic and alicyclic tertiary nitro compounds;[2-11] these reactions employ mild conditions and most of them are carbon-carbon bond forming processes. It is noteworthy that they give rise to highly branched compounds—many of them virtually unobtainable by other means—and that they are capable of providing tertiary nitro compounds in which other functional groups are present, e.g., cyano, keto, and ester.

With such a wide variety of unusual structures readily available it is apparent that any process which results in the replacement of a nitro group by other atoms or groups of atoms has considerable value. In this paper we describe a new reaction—the replacement of a nitro group by hydrogen. This occurs at room temperature when the nitro compound is treated with the sodium salt of methyl mercaptan. Equation 1 is illustrative and Table I summarizes our results; it should be emphasized that yields refer to pure, isolated products.



(1)

Although matters are easily arranged so that the handsome yields of Table I are readily achieved, this is so despite the existence of a competitive process—the replacement of a nitro group by the thiomethyl group. Indeed, in certain systems replacement by thiomethyl can be made overriding simply by the proper choice of solvent. An example is shown in eq 2. The "proper" choice of solvent depends on the structure of the nitro compound and in order to facilitate discussion of this, and related matters, we shall consider tertiary nitro compounds as falling into three groups.



(2)

The first group consists of compounds **1–6** (Table I); except for **6** they are all purely aliphatic or alicyclic systems. (It is of interest that **6** is the only β-arylated nitro compound which falls into this group; note will be taken of this in the accompanying paper.) The common characteristic of compounds **1–6** is that on treatment with the sodium salt of methyl mercaptan the nitro group is replaced by hydrogen—regardless of the solvent employed. In no instance is a detectable amount of the methyl thioether produced. (Here, and indeed with the other two groups as well, the solvent has a large influence on rate; in all cases studied the reaction of a nitro compound with the sodium salt of methyl mercaptan is much faster in hexamethylphosphoramide (HMPA) than in dimethylformamide (DMF) or in dimethyl sulfoxide (Me_2SO).)

Compounds **7–10** comprise the second group which, it will be noted, consists of β-arylated nitroparaffins. Here, as with the preceding group, the reaction with sodium thiomethoxide in DMF results in replacement of the nitro group by hydrogen; the yields are excellent and, once again, the methyl thioether cannot be detected. However, in contrast to what is observed with the first group, when the reaction is conducted in HMPA substantial amounts of the thioether are produced, e.g., as in

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