This scheme provides a convenient rationalization for the rearrangement of **1** to **2**. The intermediacy of radicals is supported by two observations. First, a strong esr signal is observed[5] in naphthalene at 160° which decays in time to a steady-state signal. Second, partial decomposition occurs during the rearrangement, giving the same products which are observed in the thermal racemization[2] of **1**. As in the racemization reaction, leakage *via* a direct, intramolecular pathway cannot be ruled out at present.

Generation of stable radicals such as benzyl and *p*-toluenesulfinyl appears to be a prerequisite for the rearrangement: Thus methyl *p*-toluenesulfenate does not rearrange to *p*-tolyl methyl sulfoxide but instead pyrolyzes at *ca.* 200°, and benzyl methanesulfenate ($CH_3SOCH_2C_6H_5$) does not rearrange to benzyl methyl sulfoxide but instead decomposes at *ca.* 150° to give benzaldehyde and methyl mercaptan.[6] The sulfoxide–sulfenate equilibrium may also be implicated in the β elimination of sulfoxides and sulfenates.[7]

The small value of ΔS^* is somewhat surprising for a radical dissociation mechanism which is expected to exhibit a large positive ΔS^*;[2,8] this suggests that bond breaking is not significantly advanced in the transition state. From the values of ΔH^* and ΔS^* for the rearrangement (**1** → **2**) and racemization (of **2**) reactions, assuming microscopic reversibility, the driving force for the rearrangement, $\Delta G = \Delta\Delta G^*$, is of the order of 3 kcal/mole at 130°, in agreement with observation (less than 5% of **1** at equilibrium). The startling reversal in direction of the present rearrangement, as compared with the formally analogous Meisenheimer rearrangement, has its source in the formation of the strong S–O sulfoxide bond.[9] The strength of this bond may reside in its multiplicity[10] which in turn arises from back donation of the lone electron pairs on oxygen into the vacant d orbitals on sulfur.[11] This mechanism of bond strengthening is not available to the amine oxides. Similar arguments may also account for the direction of other O → S 1,2-shifts, such as the sulfoxylate → sulfinate[12] and sulfinate → sulfone[13] rearrangements, and for the direction of the thermal O → P 1,2-shift in the phosphinite → phosphine oxide rearrangement.[14]

A fuller discussion of these and related[15] rearrangements is reserved for the detailed paper.

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[5] We thank Drs. E. Wasserman, M. Gueron, and J. Turkevich for helpful discussions.

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[16] Public Health Service Postdoctoral Fellow, on leave of absence from Manchester College, 1965–1966.

[17] Procter and Gamble Fellow, 1965–1966.

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Reversible Solvatochromic Shifts in Aqueous *t*-Butyl Alcohol Solutions[1,2] and Their Relationship to Thermochemical and Kinetic Properties

Sir:

We wish to report that certain electronic transitions show a solvent dependence in highly aqueous *t*-butyl alcohol that is closely related to the degree of structuredness of the medium and not to conventional solvent parameters. This medium effect produces reversible, bathochromic shifts which pass through an energy minimum at a composition of $X_{H_2O} \approx 0.96$.

Figure 1 portrays the most extreme effect of this kind which we have found so far: for one of Brooker's merocyanine dyes.[3] Adherence of ϵ_{max} to Beer's law was demonstrated in solvent compositions on both sides of the region of the reversal point.

In Table I are given data for various aromatic nitro compounds, most of which show the same effect to a smaller degree. Generally, these compounds have small, relatively soluble molecules with better characterized excited states than the larger dyes. To our knowledge, shift reversals have not been previously reported for these chemicals in any media. A number of other commercially obtained solvatochromic dyes of various kinds were examined. Some showed large spectral reversals and others showed none. Nearly all of them were so impure or badly characterized that we cannot say with confidence which component in the material was responsible for the inflection behavior and so will not report more than the qualitative result here. For example, a "quality" brand labeled naphthol blue yielded three components upon careful purification. All three of these unidentified materials gave shift inflections of over 29 mμ. Four blue-shifting (from *t*-butyl alcohol to water) dyes were examined: Brooker's dyes M-88[4] and IV,[5] quinaldine red, and sodium 2,6-dichlorobenzenone indophenol. None of these gave an inflection.

These observations are noteworthy because they are in harmony with a number of other facts about solvent–solute interactions in aqueous binary systems which have developed recently prompting us to perform the experiments described here.

Many physical properties of highly aqueous binary solutions pass through extrema in the region above

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[1] Solvent Effects in Organic Chemistry. IX. Previous paper is E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **88**, 1177 (1966).

[2] Supported by National Science Foundation Grant GP 2014.

[3] This is the compound referred to as dye VII in the paper by L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.*, *87*, *2443* (*1965*). *We are very grateful to* Dr. Brooker for a generous sample of this material.

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Table I. Spectral Properties of Various Compounds in the Aqueous *t*-Butyl Alcohol System

Compound	H_2O		Reversal point[c]			*t*-Butyl alcohol[d]		$\lambda_{H_2O} - \lambda_{rev}$	$(E_T)_{H_2O} - (E_T)_{rev}$[e]
	λ_{max}, mμ[a]	ε[b]	X_{H_2O}	λ_{max}, mμ[a]	ε[b]	λ_{max}[a]	ε[b]		
p-Nitroaniline	381.5	12.4	0.96	385.0	13.8	378.5	15.2	−3.5	0.7
4-Nitro-2-methylaniline	384.5	13.4	0.96	388.5	14.0	374.5	15.7	−4.0	0.8
2-Amino-5-nitrobenzene-sulfonic acid	366.8	14.0	0.96	372.0	14.7	372.5	16.3	−5.2	1.0
o-Nitroaniline	279.5; 408.5	5.4; 4.6	0.97; 0.96	281.5; 412.5	5.4; 4.8	274.5; 404.5	5.1; 5.5	−2.0; −4.0	0.7; 0.7
2-Nitro-4-methylaniline	286.0; 425.5	5.4; 4.2	0.97; 0.97	288.0; 431.5	5.0; 4.5	280.5; 421.5	5.3; 4.5	−2.3; −6.0	0.7; 1.0
2-Nitro-4-methoxyaniline	284.5; 447.5	4.7; 4.4	0.96; 0.96	286.0; 452.5	4.9; 4.8	... ; 444.5	...; 5.7	−1.5; −5.0	0.5; 0.7
2-Nitro-4-fluoroaniline	277.6; 422.5	4.7; 4.8	0.97; 0.96	278.4; 426.7	4.9; 5.3	271.5; 419.7	4.2; 5.9	−0.8; −4.2	0.3; 0.7
2-Nitro-4-fluoro-6-bromoaniline	285.5; 419.3	4.0; 5.2	0.97; 0.96	286.0; 423.0	4.0; 5.5	278.0; 411.3	3.7; 5.9	−0.5; −3.7	0.2; 0.6
p-Nitrophenol	316.7	9.9	0.97	318.1	9.7	314.5	10.9	−1.4	0.4
5-Nitro-2-methylaniline	291.8; 355.5	5.5; 2.0	0.95; none	293.8; none	5.2; none	287.2; 367.5	4.8; 1.4	−2.0; none	0.7; none
p-Nitrotoluene	285.0	9.1	0.98	285.5	8.9	271.5	9.4	−0.5	0.2
m-Nitroaniline	... ; 357	...; 1.4	...; none	...; none	...; none	...; 368.5	...; 1.4	...; none	...; none
3-Nitro-4-methylaniline	... ; 358.5	...; 1.5	...; none	...; none	...; none	...; 367.5	...; 1.4	...; none	...; none
Nitrobenzene	268; ...	7.8; ...	None; ...	None; ...	None; ...	258 ; ...	8.7;...	None	None
Aniline	230 ; 280.0	8.0; 1.4	None; none	None; none	None; none	234.5; 296.5	8.8; 1.6	None; none	None; none

[a] Listed values are corrected to ±0.5 mμ. [b] Values listed are for ε × 10^{-3}. [c] Where two values appear in a column, reversals were noted for two bands. [d] Solutions contained from 0 to 2% H_2O from stock aliquot. [e] Difference in transition energies[9] between solute in pure water and solute in reversal point composition.

0.80 mole fraction water and these have been related to the degree of solvent structuredness.[6,7]

In general, enthalpies and entropies of solution ($\Delta\overline{H}_s$) and of activation (ΔH^*) go through sharp inflections in these systems, but free energy terms are nearly linear functions of solvent composition.[6,7] Since solvent reorganization cannot occur during a Franck-Condon spectral transition, this should be a process in which the changes in free energy, enthalpy, and internal energy are nearly identical. Therefore, the solvent effects that produce large minima in ΔH^{*7} might cause reversible bathochromic shifts for appropriate electronic transitions. As shown above, the expected result is found.

To date, highly aqueous *t*-butyl alcohol solutions have given the largest extrema of this kind[8] which is the reason why we chose that system for study in the present instance. In this binary solvent system, the dielectric constant[9] and refractive index,[10] which are the important macroscopic properties used in the usual formal treatments[11,12] of spectral shifts, are smooth, inflection-free functions of the composition.

As seen above, not all solvatochromic compounds show the reversible shift, and many of the compounds which do give it for one transition have other bands that exhibit monotonic red or blue shifts across the solvent range from water to *t*-butyl alcohol. However, in every case where we have observed a reversal in this medium, it has been located in the region of maximum structuredness of the solvent around $X_{H_2O} = 0.96$.

The selectivity of these shifts suggests that they could be used as empirical criteria for characterizing excited states. In suitable cases, they could be used to control photochemical reactions by shifting desired (or undesired) absorption bands into (or out of) the frequency of illumination. In any event, they emphasize the danger of indiscriminate use of spectral shifts as criteria of solvent polarity.

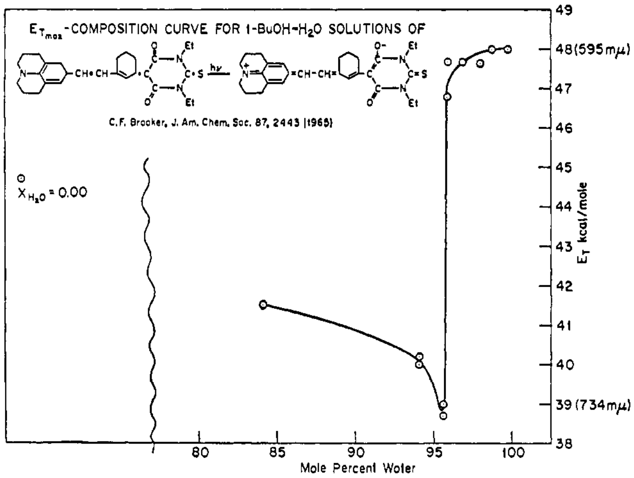

Figure 1.

Carefully purified solvents and compounds were used in a calibrated Cary Model 15 spectrophotometer. Most of the measurements were repeated several times with different batches at intervals of several weeks in order to detect errors from impurities. It is important to note that most solvatochromic compounds have very broad (although well-separated) absorption bands so that λ_{max} actually refers to the most intense of

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a continuum of closely related transitions covering a range of energies.

(13) On sabbatical leave from Seton Hill College, Greensburg, Pa.

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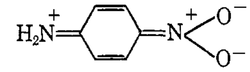
The Ground-State Solvation Contribution to an Electronic Spectral Shift[1,2]

Sir:

In several recent articles[3,4] we have shown how solvent effects on the enthalpy of activation (ΔH^*) for a simple reaction can be formally separated into the solvent effect on the ground state and that on the transition state. By means of this analysis, the solvent effect becomes a useful property through which the "transition state" (see below) may be compared with stable molecules and ions.[5]

The present article is concerned with the application of this type of analysis to solvent effects on electronic excited states. We recognize at the outset that there is no invariant species of ground, transition, or excited state. The formal treatment we employ merely factors the ground-state contribution from the solvent effect on a process of the ground state. The residual is then compared with the corresponding solvent effect on a model compound whose solvated species must also change as a function of composition. In the article previous to this,[6] we demonstrated that the long wavelength bands of *p*-nitroaniline and *p*-nitrophenol underwent reversible bathochromic shifts in highly aqueous *t*-butyl alcohol, the transition energy being minimized in a solution where $X_{H_2O} = 0.96$—exactly the same region where the solvent evidences a maximum degree of structuredness. The 381-mμ band of *p*-nitroaniline has been assigned[7] to an ^1L_a excited state approximated by the quinonoid structure



and a similar structure may be written for *p*-nitrophenol.

The minimum in transition energy indeed occurs at just the solvent composition where a minimum in energy of activation may be expected for reactions involving an increased polarization on going from ground to transition state,[3,4,8] a process which is in some ways analogous to excitation. It is, therefore, of interest to see how the solvation enthalpies of these molecules in their ground states vary as a function of the medium.

p-Nitrophenol is soluble enough to permit accurate calorimetric determination[4] of its partial molal heat of solution ($\Delta\bar{H}_s$) in highly aqueous *t*-butyl alcohol solutions. However, *p*-nitroaniline is not. If we assume that functional groups in similar molecules make additive contributions to $\delta_M\Delta\bar{H}_s$ within our experimental error,[9] we may estimate $\delta_M\Delta\bar{H}_s$ for *p*-nitroaniline by subtracting the values for phenol from those for *p*-nitrophenol and adding the value for aniline to the difference.

Table I.[a] Solvent Effects on Transition Energies and Heats of Solution in Aqueous *t*-Butyl Alcohol

		$\Delta\bar{H}_s$			$\delta_M\Delta\bar{H}_s^g$			*p*-Nitrophenol				*p*-Nitroaniline[b]				
X_{H_2O}	Vol. %	*p*-Nitrophenol	Aniline	Phenol	*p*-Nitrophenol	Aniline	Phenol	λ_{max}	E_T	$\delta_M E_T$	$\delta_M\Delta\bar{H}_s^{Ex}$	λ_{max}	E_T[a]	$\delta_M E_T$	$\delta_M\cdot\Delta\bar{H}_s^g$	$\delta_M\cdot\Delta\bar{H}_s^{Ex}$
1.000	100	5.30	0.46	3.16	0	0	0	316.5	90.41	0	0	381.5	75.1	0	0	0
0.979	90	7.33	1.62	4.19	2.03	1.16	1.03	317.4	90.22	−0.19	1.84	383.5	74.7	−0.4	2.16	1.8
0.955	80	10.50	3.55	6.45	5.20	3.09	3.29	317.5	90.19	−0.22	4.98	385.0	74.4	−0.7	5.00	4.3
0.925	70	7.55	3.48	5.31	2.25	3.02	2.15	317.1	90.30	−0.11	2.14	383.5	74.7	−0.4	3.12	2.7
0.888	60	5.10	2.46	3.81	−0.20	2.00	0.65	317.8	90.36	−0.02	−0.22	382.5	74.9	−0.2	1.15	1.0
0.841	50	4.15	1.92	3.03	−1.15	1.46	−0.13	316.3	90.53	+0.12	−1.03	380.5	75.3	+0.2	0.44	0.5
0.694	30	3.06	1.46	2.22	−2.24	1.00	−0.94	316.2	90.55	+0.15	−2.09	...	...	...	−0.30	...
0.370	10	...	1.34	...	...	0.88	...	315.0	90.90	+0.49	...	...	...	...	...	...
0	0	2.41	2.63	1.59	−2.89	2.17	−1.57	...	...	...	...	378.5	75.8	+0.6	0.85	1.5

[a] All measurements at 25°. All enthalpies and transition energies in kcal/mole. All wavelengths in mμ. The maximum error in the calorimetric measurements is ±0.20 kcal/mole and for the spectral measurements is ±0.2 mμ. [b] $\delta_M\Delta\bar{H}_s^g$ for *p*-nitroaniline was estimated from values for *p*-nitrophenol, phenol, and aniline.

In Table I, we have treated the solvent effect δ_M on the transition energy E_T as the difference between the solvent effect on the heats of solution of the excited state $\Delta\bar{H}_s^{Ex}$ and ground state $\Delta\bar{H}_s^g$, *i.e.*, $\delta_M E_T = \delta_M\Delta\bar{H}_s^{Ex} - \delta_M\Delta\bar{H}_s^g$. $\delta_M\Delta\bar{H}_s^{Ex}$ is easily obtained then by combining the spectral shifts with the heats of solution. The data in Table I show plainly that only a small part of the increased energy of these two ground states ($\delta_M\Delta\bar{H}_s$) on going from water to $X_{H_2O} = 0.96$ is reflected in the spectral shift.

On the basis of thermodynamic and kinetic precedents, the small change in E_T compared to $\Delta\bar{H}_s^g$ for the ground states suggests that there is not a large increase in polarity during excitation; that is to say the excited state is rather similar to the ground state. This is quite reminiscent of the small change in ΔH^* compared to ΔH_s^g for methyl benzenesulfonate hydrolysis in aqueous alcohols.[3,10]

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(1) Solvent Effects in Organic Chemistry. X.

(2) Supported by National Science Foundation Grant GP 2014, for which we are most grateful.

(3) See E. M. Arnett and D. R. McKelvey, *Record Chem. Progr.*, **26**, 185 (1965).

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