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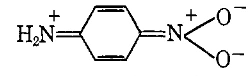
The Ground-State Solvation Contribution to an Electronic Spectral Shift[1,2]

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).

(4) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

(5) Thus, trimethylsulfonium chloride and trimethylamine oxide were used as models for the *t*-butyl chloride solvolysis transition state in a series of aqueous ethanol solutions.

(6) E. M. Arnett and D. Hufford, *J. Am. Chem. Soc.*, **88**, 3140 (1966).

(7) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1965, p 260.

(8) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **87**, 1393 (1965).

(9) See Table I and ref 3, 4, and 8.

(10) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 931 (1956).

A similar analysis of the solvent effect on E_T for the well-characterized n → π^* transition of ethyl acetate in aqueous ethanol[11] shows a steady monotonic drift of E_T from 140.0 kcal/mole in water to 138.38 kcal/mole in $X_{H_2O} = 0.582$, although the ethyl acetate ground state goes through a clearly defined maximum at $X_{H_2O} = 0.85$ in this system.[3,4]

Although we consider the above type of analysis of solvent effects on transition energies to be formally correct, several factors complicate interpretation of the results. Firstly, the position of λ_{max} on the broad well-separated spectral curves for these large molecules in solution is not purely a function of transition energy, but also of transition probability. There can be no change in solvation entropy during a Franck–Condon transition so that the entropy of transfer of the excited state from one solvent to another will be the same as that for the ground state. However, change in solvation entropy of the ground state, due to a change in solvent composition, can alter the position of the most likely frequency for energy absorption among a continuum of closely related transitions under the band envelope. Second, there is no guarantee that a solvent effect on the excited state ($\delta_M\Delta\overline{H}_s^{Ex}$) does not reflect a distortion of its potential function rather than a raising or lowering of the entire Morse curve. This factor is a clean breakdown of the analogy to molecules in quasiequilibrium with transition states.

The aqueous *t*-butyl alcohol system was chosen for the present study because prior experience with enthalpy behavior in aqueous binaries suggested that an easily dissected spectral shift would occur in this system. There is every reason to believe[12] that other binary mixtures also will give characteristic solvent enthalpy effects while dissolving a much wider range of organic solutes than do the aqueous ones. A practical consequence of such research could be a greater control over photochemical processes. We are pursuing this approach.

[11] W. Closson unpublished results. We are grateful to Professor Closson for making these data available to us.

[12] D. R. McKelvey, unpublished results.

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Evidence against an Exclusive Zwitterion Intermediate in Ozonide Formation

Sir:

The mechanism of ozonolysis of the carbon–carbon double bond is usually interpreted as involving formation of an unstable primary ozonide followed by its decomposition into zwitterion and carbonyl fragments.[1] Recombination of these fragments is then thought to lead to the normal ozonide. We wish to report results which clearly demonstrate that ozonide cannot arise exclusively through the intermediacy of the Criegee zwitterion and a carbonyl fragment. Specifically, we have found that the *cis*:*trans* ratio in the two symmetrical ozonides produced upon ozonolysis of an unsymmetrical olefin *is dependent upon olefin geometry.*

Contrary to Criegee's proposal that recombination of the zwitterion and carbonyl fragments takes place without exchange in a solvent cage,[2] a number of recent reports have demonstrated that unsymmetrical olefins do, in fact, yield a mixture of both symmetrical and unsymmetrical ozonides[3–6] whose composition, at least in the pentene-2 system,[5] was dependent on the olefin concentration and the nature of the solvent. Furthermore, *cis–trans* isomeric ozonides have been observed in the ozonolysis of several olefins, including di-*t*-butylethylene,[7] 1,4-dibromo-2,3-dimethylbutene-2,[8] methyl oleate and elaidate,[4,9] methyl *p*-methoxycinnamate,[10] and a number of simple alkenes.[5,6,11]

The observation of isomeric *cis–trans* ozonides has provided the basis for an important new probe with which to study, in detail, the mechanism of ozonolysis; that is, it has now become possible to evaluate the effect of olefin geometry on the course of the reaction through the determination of *cis*:*trans* ozonide ratios. There are several reported examples in which there seems to be a definite dependence of the *cis*:*trans* ozonide ratio on olefin geometry.[6–8,10,11] Indeed, recent work in this laboratory indicates that such dependence is a general phenomenon and appears to be related to steric factors in the olefin. The results reported by Greenwood[12] on the relative stabilities of the molozonides from *cis-* and *trans*-olefin isomers are undoubtedly also intimately involved in this olefin–ozonide relationship.

The finding that ozonide configuration is influenced by the geometry of the parent olefin, of course, raises serious questions about the validity of the Criegee zwitterion–carbonyl combination as the ozonide-producing reaction since such a process would lead to the same *cis*:*trans* ozonide ratio for either the *cis-* or the *trans*-olefin. A more exacting test of the Criegee zwitterion mechanism, however, is provided by examining the effect of olefin geometry on the *cis*:*trans* ratios of *cross-ozonides* since, in these cases, an intramolecular stereoselective pathway[13] from the olefin–ozone adduct would be obviated.

We have determined the ratio of the cross-products, *cis-* (**1**) and *trans*-2,5-dimethylhexene-3 ozonide (**2**), produced in the ozonolysis of *cis-* (**3**) and *trans*-4-methylpentene-2 (**4**). On the basis of the Criegee zwitterion mechanism the *cis*:*trans* ratio of the cross-ozonides would, of course, be expected to remain invariant with olefin geometry. In fact, the diisopropyl ozonide (**1, 2**)[14] ratio obtained from *trans*-4-

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[1] For a thorough discussion of the mechanism of ozonolysis, including the Criegee formulation, see P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[2] R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

[3] O. S. Privett and E. C. Nickell, *J. Am. Oil Chemists' Soc.*, **41**, 72 (1964).

[4] G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, *Rec. Trav. Chim.*, **82**, 1234 (1963).

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[6] O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).

[7] G. Schröder, *Chem. Ber.*, **95**, 733 (1962).

[8] R. Criegee, S. S. Bath, and B. V. Bornhaupt, *ibid.*, **93**, 2891 (1960).

[9] O. S. Privett and E. C. Nickell, *J. Lipid Res.*, **4**, 208 (1963).

[10] P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965).

[11] F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

[12] F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); **30**, 3108 (1965).

[13] This suggestion in very general terms has been offered to explain the observed stereochemical results for some *normal ozonides*.[5,6]

[14] Ozonolyses were carried out at *ca.* −70° and used 23.5 mmoles of olefin in 25 ml of pentane. Ozonolysis was continued to 75% of the