[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

The Effect of Solvent on Spectra. II. Correlation of Spectral Absorption Data with Z-Values

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RECEIVED DECEMBER 19, 1957

A number of electronic transitions in different solvents are compared with **Z**-values, an empirical measure of solvent polarity based on the c.-t. band of 1-ethyl-4-carbomethoxypyridinium iodide. It is possible to identify certain specific interactions between solute and solvent by this means. With the aid of several reasonable assumptions, and a knowledge of the difference in the free energy of solution of the pyridinium iodide complex dipole between isoöctane and water, it is possible to estimate the excited state dipole moments resulting from certain electronic transitions. The effect of solvent on the spectra of several cyclopropyl ketones has been investigated, and a band resulting from cyclopropyl conjugation unequivocally identified in this way. Methyl cyclopropyl ketone has a maximum at 1931 Å. in water; this information casts doubt on previously reported maxima attributed to the interaction of a cyclopropyl ring with a carbonyl group.

The effect of solvent on absorption spectra is understood in a qualitative way[1]; McRae[2] has recently discussed the difficulties of making quantitative predictions. Previous attempts to correlate spectral shifts with solvent properties were invariably based on the refractive index,[3,4] excluding interactions due to hydrogen bonding. A more general treatment of solvent effects has been hindered by use of the model of a solute imbedded in a homogeneous medium of dielectric constant, *D*.[5,6] Bayliss and McRae[7] have demonstrated that *D* cannot account for the position of certain absorption bands. The dielectric constant is a *macroscopic* measure of solvent response to an electric field. For the purposes of chemistry, it is necessary to know the *microscopic* situation, the solute–solvent interaction.

The position of the charge-transfer (c.-t.) band of 1-ethyl-4-carbomethoxypyridinium iodide measures the extent of interaction of a dipole with a cybotactic region of a solvent.[8] The transition energies corresponding to the c.-t. bands were shown to be linear in **Y**, a kinetic measure of solvent polarity,[9] and were designated as **Z**-values, empirical measures of solvent polarity. We explore in the present paper the use of **Z**-values to correlate electronic transitions.

Experimental

Materials.—Acetone was treated with Drierite and fractionated. Infrared analysis showed the water content to be less than 0.1%.

Methyl cyclopropyl ketone was prepared according to the directions of Cannon[10] using 2-acetylbutyrolactone synthesized by the procedure of Johnson[11]; b.p. 110–111°.

Mesityl oxide (practical grade, Eastman Kodak Co.) was fractionated and a middle cut, very pale yellow in color, used, b.p. 127–128°.

Bicyclo[3.1.0]hexanone-2 was made available by Dr. N. A. Nelson. The slightly yellow liquid was redistilled at reduced pressure to give a colorless product, b.p. 65–66° (14 mm.) and $n^{25}\text{D}$ 1.4753. These properties and the infrared maxima were in good agreement with those recorded.[12]

Dicyclopropyl ketone[13] was purchased from the Aldrich Chemical Co., Milwaukee, Wis.

Solvents were purified or used as previously described.[8]

Spectra.—The Cary recording spectrophotometer model 14 can record spectra to wave lengths as short as *ca.* 1865 Å. if: (1) thin cells, 0.01-cm. path length, are used to minimize solvent absorption; (2) the phototube voltage is set at maximum (setting 5) and the slit control is fixed as low as possible (higher than during usual operation); and (3) appropriate solvents are chosen.[14] The absorption curves show some noise, but the maxima appear to be accurate within 10 Å., and all absorptions followed Beer's law.

The positions of both absorption bands of mesityl oxide are listed in Table I. The far ultraviolet absorptions for acetone and the cyclopropyl ketones are given in Table II; data for the long wave length region are included in Table III. New data for iodide ion in organic solvents are reported in Table IV. Absorption maxima at wave lengths longer than 2000 Å. are usually accurate to 5 Å. or better.

TABLE I

ABSORPTION DATA FOR MESITYL OXIDE

Solvent	λ_{max}, Å.	ϵ_{max}	λ_{max}, Å.	ϵ_{max}
Water	2426	9,700	..[a]	..
Methanol	2368	11,000	3088	57
Isopropyl alcohol	2362	10,400	3112	51
Isoöctane	2306	11,900	3210	38
Acetonitrile	2339	8,600	3140	33
Tetrafluoropropanol	2408	12,400	..[a]	..
n-Butyl alcohol	2372	10,200	3111	53
Ethylene glycol	2401	10,400	3074	61
95% ethanol	2371	10,500	3096	57
Ethanol	2364	10,600	3105	52
Dimethyl sulfoxide	..	....	3195	45
Chloroform (0.13 *M* EtOH)	2379[b]	10,800	3148	53
Chloroform, pure	2376[b]	....	3154	..
Ethylene dichloride	2357	10,600	3184	47

[a] Submerged. [b] 0.01-cm. cells required.

Discussion

Iodide Ion.—The absorption spectra of halide ions are of much interest since they are relatively uncomplicated.[15] We already have re-

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[1] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[2] E. G. McRae, *ibid.*, **61**, 562 (1957).

[3] A. Kundt, *Ann. Physik*, **4**, 34 (1878).

[4] K. Hirayama, THIS JOURNAL, **77**, 379 (1955).

[5] F. A. Matsen, "Chemical Applications of Spectroscopy," Vol. 9, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 694.

[6] W. T. Simpson, THIS JOURNAL, **73**, 5359 (1951).

[7] N. S. Bayliss and E. G. McRae, *ibid.*, **74**, 5803 (1952).

[8] E. M. Kosower, *ibid.*, **80**, 3253 (1958).

[9] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956), and previous papers.

[10] G. W. Cannon, *Org. Syntheses*, **31**, 74 (1951).

[11] W. L. Johnson, U. S. Patent 2,443,827; *C. A.*, **43**, 677*i* (1949).

[12] N. A. Nelson, Chemistry Department, M.I.T., private communication; N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957).

[13] H. Hart and O. E. Curtis, Jr., THIS JOURNAL, **78**, 112 (1956).

[14] J. R. Platt, I. Rusoff and H. B. Klevens, *J. Chem. Phys.*, **11**, 535 (1943).

[15] (a) H. L. Friedman, *ibid.*, **21**, 319 (1953); (b) L. I. Katzin, *ibid.*, **23**, 2055 (1955); (c) M. Smith and M. C. R. Symons, *ibid.*, **25**, 1074 (1956); (d) E. M. Kosower, R. L. Martin and V. W. Meloche *ibid.*, **26**, 1353 (1957).

ported absorption data for iodide ion in a series of aqueous ethanol solutions and in acetonitrile.[15d] We are now able to show more clearly the experimental basis for our suggestion concerning the maxima observed in acetonitrile; included in the same category are dimethyl sulfoxide and acetone.

According to the view of Franck and Platzman,[16] light absorption by iodide ion is an ionization, $I^- \rightarrow I^{\cdot} + e^-$, the electron being transferred to a potential well formed by the dipoles of the solvent molecules. **Z** is essentially a measure of the ability of solvents to form this potential well. In fact, the transition energies for iodide ion in a series of seven solvents correlate with **Z** within the experimental error (Fig. 1). The transition in water requires 1.1 kcal./mole less than predicted from the correlation. Iodide ion as a solute is smaller than the pyridinium iodide complex used to measure the **Z**-value, and is able to produce a cybotactic region containing a larger number of the small water molecules than expected. Water deviates in the same direction for a number of other transitions (*vide infra*).

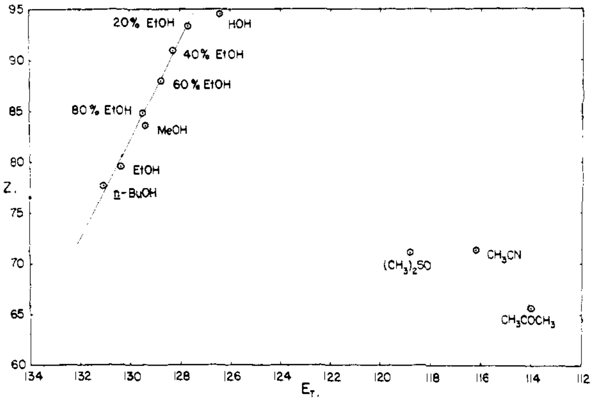

Fig. 1.—Transition energies for I^- in various solvents *vs.* **Z**; $E_T = -0.20260\mathbf{Z} + 146.625$.

Surprisingly, the transitions in acetonitrile, dimethyl sulfoxide and acetone require far *less* energy than predicted from the plot against **Z**-values, the deviations being, respectively, 16.0, 13.4 and 19.3 kcal./mole. The electron excited from the iodide ion must be transferred to a specific molecule, and the deviations must then be considered evidence of complex formation, *e.g.*, $I^- \rightarrow N{\equiv}CCH_3$. Acetone and acetonitrile possess polarized π-bonds which could easily accept an electron, and the same opportunity exists for the d-orbitals of the sulfur in dimethyl sulfoxide. Halide complexes with π-electron systems present an excellent opportunity for correlating electron donor and electron acceptor abilities.

Mesityl Oxide.—The sensitivity of the short wave length transition of α,β-unsaturated ketones to solvent is well known; Fieser and Fieser[17] have included in their discussion of the Woodward rules a table of factors for correcting absorption maxima measured in certain solvents to ethanol.

TABLE II

FAR ULTRAVIOLET ABSORPTION DATA

Solvent	10^2c_0	λ_{max},[a] Å.	ϵ_{max}	ϵ_{1900}
		CH_3COCH_3		
Isoöctane	2.26			1510
	11.3			1410
	2.61	1875	1,820	1500
	5.22	1878	1,860	1440
Water	12.5	..[b]		223
	8.99			309
		cyclo-$C_3H_5COCH_3$		
Isoöctane	0.404			4850
	1.36			5080
	1.44	1878	5,590	4870
Water	0.551	1935	5,990	
	1.10	1931	6,180	
	2.75	1927	6,330	
		bicyclo-C_6H_8O		
Isoöctane	1.49	1880	5,740	
	0.745	1883	5,670	
Water	2.39	1967	5,370	
	1.24	1969	4,990	
	0.62	1965	4,990	
		(cyclo-$C_3H_5)_2CO$		
Isoöctane	1.20	1879	10,100	
	0.60	1878	10,800	
Water	.227	1930 ± 15	12,700	
	.243	1943 ± 31	11,300	
	.486	1938	11,600	

[a] These maxima are *ca.* ±10 Å., except where otherwise noted. [b] The shape of the curve suggests that the maximum may be located somewhat below 1865 A.

TABLE III

NEAR ULTRAVIOLET SPECTRAL DATA

Solvent	10^2c_0	λ_{max}, Å.	ε
	cyclo-$C_3H_5COCH_3$		
Water	0.63	2620	29
Methanol	1.11	2701	22
i-PrOH	1.17	2716	21
CH_3CN	1.17	2743	21
Isoöctane	1.23	2772	17
	bicyclo-C_6H_8O		
Water	1.24	2721	57
Isoöctane	1.49	2884	18
	(cyclo-$C_3H_5)_2CO$		
Water	0.486	2603	51
Isoöctane	3.61	2755	26

TABLE IV

IODIDE ION IN ORGANIC SOLVENTS[a]

Solvent	λ_{max}, Å.	ϵ_{max}
Dimethyl sulfoxide[b]	2417	11,400
Acetonitrile[c]	2461	12,500
Acetone[b]	2517	9,330
Water	2262[d]	13,500[d]

[a] Only long wave length maximum reported. [b] 0.01-cm. cells required. [c] *Cf.* ref. 15d. [d] E. Lederle, *Z. physik. Chem.*, B10, 121 (1930).

In order to examine the sensitivity of the maximum in greater detail, the spectrum of mesityl oxide (I) was measured in a series of solvents, varying in polarity from isoöctane (**Z** 60.1) to water (**Z**

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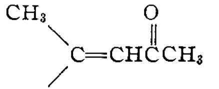
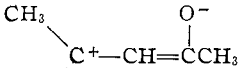
[16] R. Platzman and J. Franck, *L. Farkas Memorial Vol.* Jerusalem (1952).

[17] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publ. Corp., New York, N. Y., 1949, p. 184.

94.6).[18] The transition energies (from data, Table I) in ten solvents are plotted against **Z** in Fig. 2b. Except for chloroform, the points fall upon a straight line with an average deviation of ±0.37 kcal./mole, which corresponds to an error of ±8 Å. in the maximum over the range 2306 to 2426 Å., or about twice the experimental error. The marked difference between the calculated and actual transition energies in chloroform (3.33 kcal./mole) point to a specific interaction of mesityl oxide and chloroform. Complexes of olefins and aromatic molecules and chloroform have been reported from NMR studies.[19]



I



II

The behavior of the short wave length transition in mesityl oxide with solvent change is consistent with an increased contribution of the resonance form II to the excited state. Transitions with similar solvent sensitivity and relatively high intensities (ε, 1000–15000) were classified as π → π* by Kasha and McConnell.[20] The generality of the scheme proposed by McConnell[20] has been criticized by Pimentel[21] who pointed out that the Franck–Condon principle must not be neglected in the classification of bands according to solvent response. Nevertheless, the objection applies most strongly to the n → π*-transition (*cf.* Fig. 1b, ref. 21).[22] A more serious limitation is illustrated by the transition of merocyanine II (*vide infra*) for which the solvent response is *opposite* to that of mesityl oxide, even though the transition can scarcely be considered as anything but π → π*.

Other π → π*-Transitions.—As the solute molecules increase in size, correlation of electronic transitions with **Z** should become less precise. Specific solute–solvent interactions, self-association, and distortion of the cybotactic region would all contribute; additional studies on simple systems are needed (*e.g.*, a more complete solvent series for crotonaldehyde[24]).

Brooker[25] and LeRosen[26] have reported maxima for phenol blue (III) and McRae[2] has fitted much of their data with an equation relating the frequency to the refractive index and dielectric constant of the solvent and three adjustable parameters. The equation failed to account for the results in hydrogen-bonding solvents.

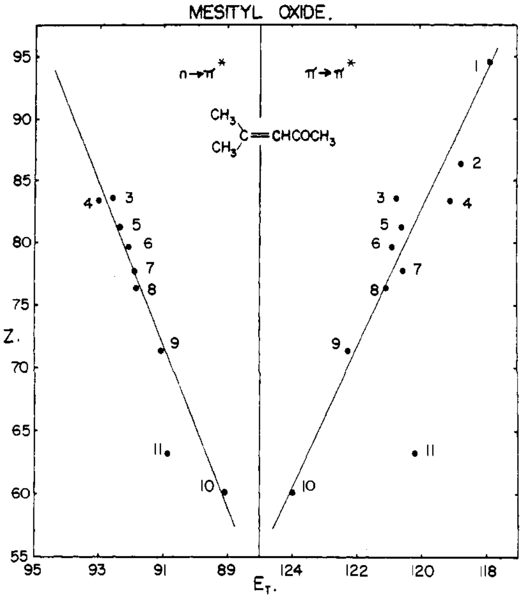
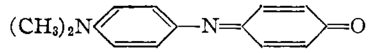
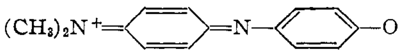


Fig. 2.—Right half (a), transition energies for π → π*-transition (2400 Å. region) of mesityl oxide *versus* **Z**; left half (b), transition energies for n → π*-transition (3100 Å. region) of mesityl oxide *versus* **Z**. The solvents are (1) water, (2) 2,2,3,3-tetrafluoro-1-propanol, (3) methanol, (4) ethylene glycol, (5) 95% ethanol, (6) ethanol, (7) 1-butanol, (8) 2-propanol, (9) acetonitrile, (10) isoöctane, (11) chloroform (0.13 *M* ethanol). The equation for the π → π*-transition is $E_T = -0.18258Z + 135.061$, for the n → π*-transition, $E_T = 0.15522Z + 79.839$.



III



IV

The transition energies in a wide range of solvents give only a fair correlation with **Z** (Fig. 3), although the error in predicted transition energies is not very much larger than the prediction error for mesityl oxide. The maxima are predicted with an average deviation of ±80 Å. over the range 5500 to 6680 Å., excluding the points for chloroform and pyridine. The nature of the solvent response (shift to longer wave lengths in more polar solvents) is adequately rationalized by increased contribution from IV to the excited state.

Some years ago, Bayliss and McRae[7] studied the correlation of absorption maximum with solvent dielectric constant. In light of the theory depending on *D*, formamide was a particular *bête noire*. Although the *D* of formamide is 109.5 (25°),[27] its polarity with respect to the absorption band of Merocyanine II (V) was close to ethanol. A plot of transition energies against **Z** reveals that the point for formamide (Fig. 4) is located approxi-

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[18] In two respects, mesityl oxide was not a completely ideal choice. The equilibrium between *s-cis-* and *s-trans-*form is solvent dependent; private communication from Dr. M. C. Whiting, Oxford University. Second, mesityl oxide, after usual purification, contains *ca.* 9% of the non-conjugated isomer, 2-methyl-1-pentenone-4; F. H. Stross, J. M. Monger and H. de V. Finch, THIS JOURNAL, **69**, 1627 (1947). The absorption spectrum of the unconjugated isomer should not affect the correlation of the π → π* transition at all, and should have only a small effect on the n → π* transition in view of the observation that solvent effects on this transition for ketones appear to be approximately parallel; B. G. Ramsey, unpublished results.

[19] L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

[20] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[21] G. C. Pimentel, THIS JOURNAL, **79**, 3323 (1957).

[22] The maxima given by McConnell[20] and quoted by Pimentel[21] are not in agreement with ours in the 3100 Å. region. The value for water seems hardly credible. On the other hand, our results are very close to those recently reported by Nagakura.[23]

[23] S. Nagakura, A. Minegishi and K. Stanfield, THIS JOURNAL, **79**, 1033 (1957).

[24] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

[25] L. G. S. Brooker and R. H. Sprague, THIS JOURNAL, **63**, 3214 (1941).

[26] A. L. LeRosen and C. E. Reid, *J. Chem. Phys.*, **20**, 233 (1952).

[27] G. R. Leader, THIS JOURNAL, **73**, 856 (1951).

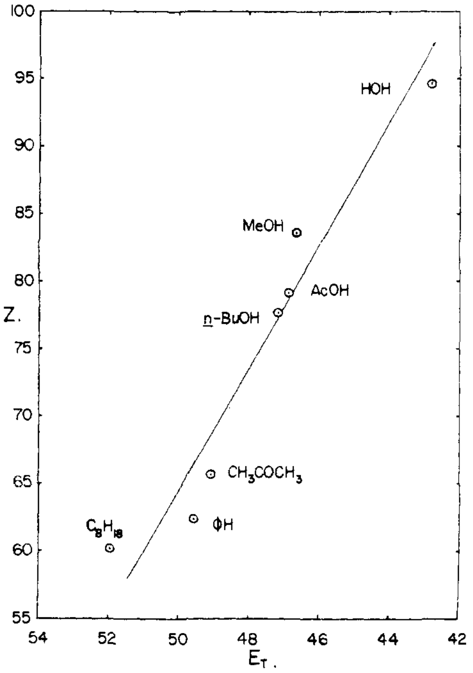


Fig. 3.—E_T (phenol blue, III) *versus* **Z**; $E_T = -0.22071\mathbf{Z} + 64.251$. **Z** (benzene) is taken as 62.3, estimated from a plot of the transition energies of certain betaines against **Z**; K. Dimroth, *et al.*, *Ann.*, **604**, 221 (1957).

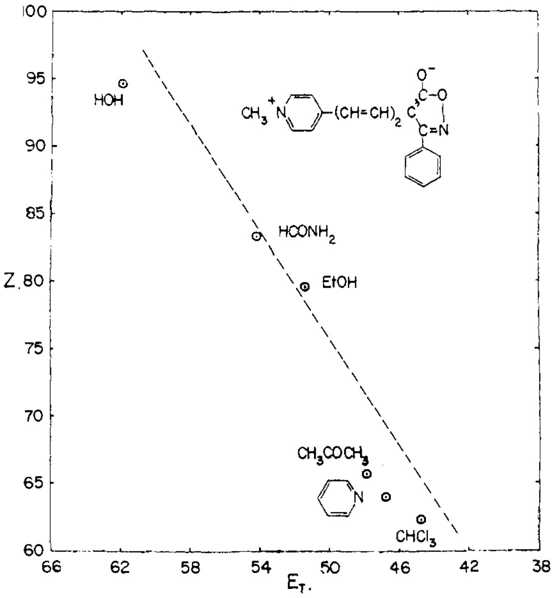
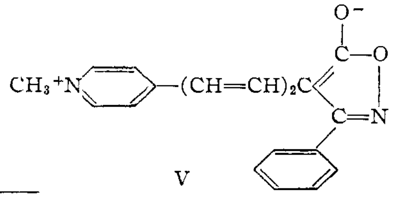


Fig. 4.—E_T (Merocyanine II, V) *versus* **Z** (dashed line indicates trend).

mately where one would expect it on the basis of its **Z**-value. The results of Hünig[28] afford the same conclusion.


$CH_3{}^+N\langle C_5H_4\rangle{-}(CH{=}CH)_2C\langle C(O^-){-}O{-}C(C_6H_5){=}N\rangle$

V

The $n \rightarrow \pi^*$-Carbonyl Transition.—The long wave length absorption in saturated ketones is characteristically between 2600 and 3000 Å. On the basis of calculations of intensity[29] and solvent effects,[20] it is generally agreed that the Mulliken assignment of a formally forbidden $n \rightarrow \pi^*$-transition is correct. The transition is considerably displaced to longer wave lengths in α,β-unsaturated ketones.

The $n \rightarrow \pi^*$-transition of mesityl oxide correlates very well with **Z**; the maxima are predicted with an average error of ±5 Å. over the range from 3074 to 3210 Å., excluding the point for chloroform (Fig. 2a).

The carbonyl absorption band of methyl cyclopropyl ketone also correlates well with **Z** (±4 Å.) over the range from 2701 to 2772 Å. The observed transition energy for water is 1.94 kcal./mole higher than the correlation predicts (Fig. 5).

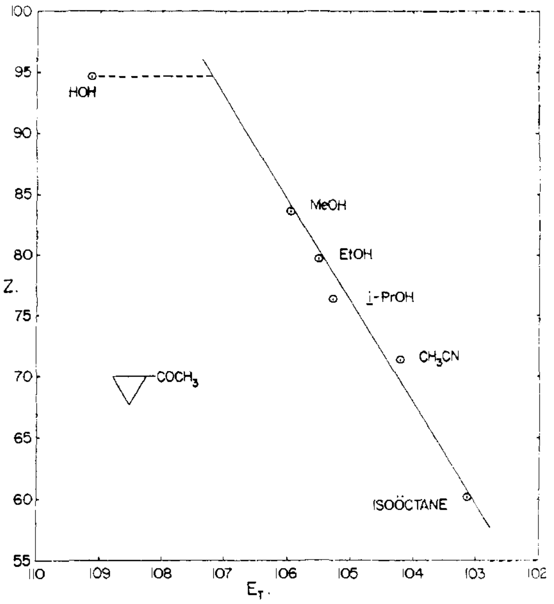


Fig. 5.—E_T (methyl cyclopropyl ketone) *versus* **Z** ($n \rightarrow \pi^*$-transition); $E_T = 0.11798\mathbf{Z} + 96.014$.

That this deviation is not due to the cyclopropyl group is shown by a plot of the transition energies for the carbonyl absorption of methyl isobutyl ketone against those for methyl cyclopropyl ketone, using the data of Mariella[30] (Fig. 6). The deviation for water is larger than that found for iodide ion, but probably arises from the same cause.

Pimentel[21] has shown, in his analysis of solvent effects, that the magnitude of the "blue shift" (shift to shorter wave lengths with increased solvent polarity) of the $n \rightarrow \pi^*$-transition is not a direct measure of the energy of hydrogen-bonding between the solute and the solvent. Although there are thermodynamic or infrared methods for determining the energy of interaction of solvent with the ground state of the solute, these are either laborious or unavailable for pure polar solvent. We should like to propose a simple model of the transition

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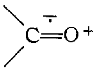
(28) S. Hünig and O. Rosenthal, *Ann.*, **592**, 161 (1955).

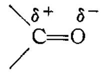
(29) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

(30) R, P. Mariella, *et al.*, *J. Org. Chem.*, **19**, 678 (1954).

which permits an estimate of the hydrogen-bonding energy from the ultraviolet spectral data.

If we consider the excited state of the $n \rightarrow \pi^*$-transition as represented by VI, and make the simplifying assumption that the polarization already present in the ground state, VII, is unaffected by the excitation, the resultant dipole moment for the excited state will be very close to zero (actually *ca.* 0.2 *D* in direction opposite to ground state, obtained by taking the electron from the oxygen and placing it in the center of the carbonyl bond). The situation is then analogous to that for the 1-alkyl-pyridinium iodide complexes


VI


VII

in which the destabilization of the excited state upon transfer of the complex dipole from one solvent to another was equal to the stabilization of the ground state.[8] The hydrogen-bonding energy is thus half of the change in transition energy from the gas phase (experimentally, isoöctane or hexane solution) to the polar solvent.

The following hydrogen-bonding or, more simply, interaction energies have been estimated for water: methyl cyclopropyl ketone, 3.0 kcal./mole; acetone, 2.5 kcal./mole; bicyclo[3.1.0]hexanone-2, 3.0 kcal./mole; dicyclopropyl ketone, 3.1 kcal./mole; and methyl isobutyl ketone, 2.2 kcal./mole. The same kind of estimate for pyridazine[31] leads to a value of *ca.* 5.8 kcal./mole.

It is more difficult to estimate the interaction energy for mesityl oxide, since VI does not represent the excited state. Since the ground state dipole moment of mesityl oxide is 2.80 *D*,[32] and that for acetone 2.74 *D*,[33] we can estimate the interaction energy for mesityl oxide (*s-trans*, $\mu \sim 3.7$ *D*) and water as being approximately 3.4 kcal./mole (3.7/2.74 × 2.5).

Excited State Dipole Moments.—The dipole moment of an excited state is of considerable interest since it should be related to the charge distribution within the excited molecule, and might permit more precise evaluation of certain theoretical calculations for the energies of such states.[34]

McRae[2] estimated the excited state dipole moment of phenol blue (III) from his empirical equation and an assumed cavity radius for the moment, arriving at a figure between 7.5 and 9.1 *D*, depending upon the radius used. He concluded that this moment, increased from 5.80 *D* in the ground state, did not represent strong support for the suggestion that the zwitterionic structure IV contributes greatly to the excited state. If this estimate is valid, it should be remembered that it applies only to non-polar solvents.

Two other recent attempts to estimate excited state dipole moments both depend upon the ability of certain excited molecules to survive for a length of time sufficient to attain equilibrium with the solvent. The fluorescence emission which is then observed reflects the dipole moment of the excited state by its variation with solvent change. This information may be combined with other data concerning variation in the absorption maximum with solvent change. The method of Lippert[35] suffers from assumptions concerning the nature of the interaction between the solvent and the solute, in particular, from using the Onsager equation for the point dipole in a homogeneous dielectric for molecules which are far too large to conform. The treatment of Mataga, Kaifu and Koizumi[36] is similar, but unfortunately was applied to a number of molecules where the excited state dipole differed only slightly from that of the ground state.

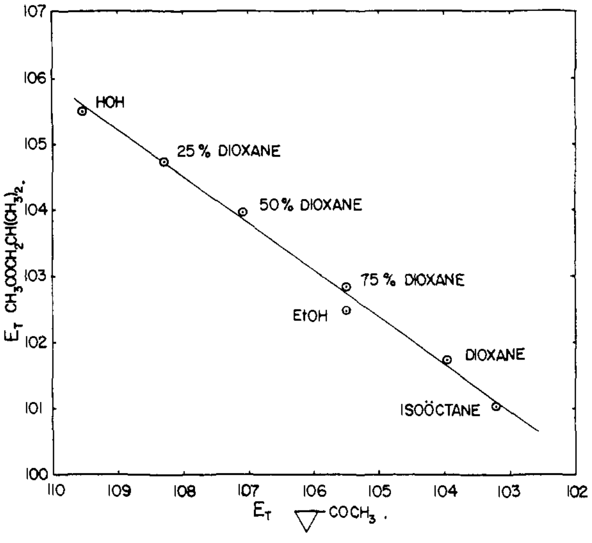


Fig. 6.—E_T (methyl cyclopropyl ketone) *versus* E_T (methyl isobutyl ketone), $n \rightarrow \pi^*$-transition; E_T (MIBK) = 0.70624 E_T (MCK) + 28.2097.

We wish to propose a method which is essentially an estimate of the difference in excited state stabilization for a transition in two solvents and then a comparison of this energy with that found[8] for the ground state of the pyridinium iodide complex dipole. We shall illustrate with mesityl oxide. The assumptions made are (a) that the *s-trans*-form exists in all solvents,[18] (b) that the interaction of the excited state dipole with the cybotactic region is directly proportional to the interaction of another somewhat larger dipole with the same solvent and (c) that the ground state interactions are those given in the previous section.[37]

Figure 7 is a diagrammatic representation of the relationship of the ground and excited state energy levels in isoöctane and water for the $\pi \rightarrow \pi^*$-transition of mesityl oxide. Equations (1), (2) and (3) apply

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[31] F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

[32] Landolt-Börnstein, "Zahlenwerte und Funktionen," 6th edition, Vol. 1, Part 3, Springer-Verlag, Berlin, 1951, p. 421; *cf.* ref. 18.

[33] R. J. W. Le Fèvre, "Dipole Moments," John Wiley and Sons, Inc., New York, N. Y., 1953.

[34] *Cf.*, for example, a recent analysis of the carbonyl group; J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

[35] E. Lippert, *Z. Naturforsch.*, **10A**, 541 (1955); *Z. physik. Chem.*, **6**, 125 (1956).

[36] N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Japan*, **28**, 690 (1955); **29**, 469 (1956); *cf.* R. A. Marcus Abstracts, 133rd meeting, American Chem. Soc., San Francisco, April, 1958, p. 430.

[37] Each of the factors composing the estimate probably can be obtained with more precision. Thus, (a') a molecule which is small and always *s-trans* can be used, (b') a more refined calculation can improve the comparison with the larger dipole and (c') the ground state interactions can be measured directly.

$$(a - c) = E_T\text{ (isoöctane)};\ (b - d) = E_T\text{ (water)} \quad (1)$$

$$(a - c) - (b - d) = 6.1 \quad (2)$$

$$(a - b) = (c - d) + 6.1 = 3.4 + 6.1 = 9.5\text{ kcal./mole} \quad (3)$$

The stabilization of the mesityl oxide excited state dipole on transfer from isoöctane to water is 9.5 kcal./mole; for the pyridinium iodide complex dipole of 13.9 D, the stabilization was 17.3 kcal./mole.[8] By assumption (b), the dipole moment of the excited state of mesityl oxide produced by the $\pi \rightarrow \pi^*$-transition is 7.6 D in water.

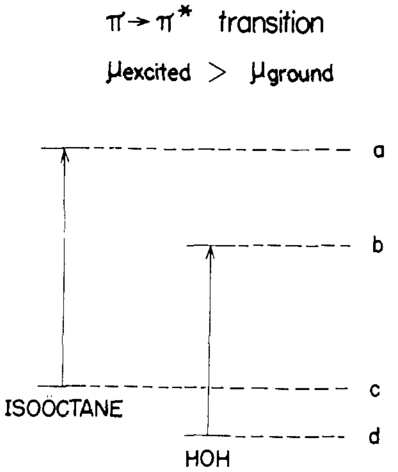
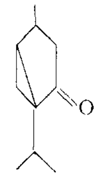


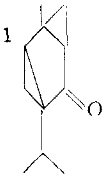
Fig. 7.—Energy level diagram for $\pi \rightarrow \pi^*$-transition in isoöctane and water.

Using the method outlined above, and assuming that the interaction of phenol blue with water in the ground state will be no less than that for mesityl oxide, the minimum dipole moment calculated for the excited state of phenol blue in water is 10.2 D. The latter is considerably higher than the moment found by McRae.[2] Water would increase the contribution of the charged form IV to the excited state, and increase the dipole moment.

Cyclopropyl Ketones.—The "unsaturated" character of the cyclopropane ring has been recognized for many years, but the circumstances of electron delocalization have only been *clearly* delineated for transition states, and not for ground and electronically excited states. The successful correlation of $\pi \rightarrow \pi^*$-transition energies with **Z** suggested an extension of the method of solvent variation to cyclopropyl ketones. In this way, one can decide how much more electron delocalization occurs in the excited state than in the ground state.

Rogers[38] and Klotz[39] have reported that cyclopropyl ketones show materially greater end absorption in the ultraviolet than saturated ketones. Maxima have actually been recorded for a number of cyclopropyl ketones; *e.g.*, β-dihydroumbellulone (VIII), λ_{max} 2100 Å. (ϵ 2470)[40a] and the tricyclic ketone IX, λ_{max} 2140 Å. (ϵ 2990).[40a] It has even been stated that the cyclopropyl carbonyl absorption occurs between 2100 and 2150 Å.[40b] However, the location of these maxima must be considered doubtful in view of their proximity to the wave length limit of the spectrophotometer used.


VIII


IX

The Cary recording spectrophotometer, model 14, permits observation of maxima at wave lengths as low as 1870 Å. Three cyclopropyl ketones, methyl cyclopropyl ketone (X), dicyclopropyl ketone (XI) and bicyclo[3.1.0]hexanone-2 (XII) were studied in water (**Z** 94.6) and isoöctane (**Z** 60.1). The simplest saturated ketone, acetone, also was examined. The results are summarized in Table V.

▷ COCH$_3$
X

▷ CO ◁
XI

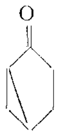

XII

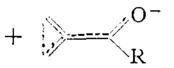
TABLE V

SPECTRA OF KETONES

Compound	Water λ_{max},[a] Å.	Water ϵ_{max}	Isoöctane λ_{max},[a] Å.	Isoöctane ϵ_{max}
X	1931	6,160	1878	5,600
XI	1938	11,900	1878	10,800
XII	1967	5,120	1880	5,700
CH_3COCH_3	..	....	1876	1,840
		230[b]		1,470[b]

[a] ±10 Å. [b] At 1900 Å.

Although all of the ketones have approximately the same maximum in isoöctane, the three cyclopropyl ketones shift to considerably longer wave lengths in the polar solvent, water. The change in transition energy for X and XI for this change in solvent is 4.5 kcal./mole, compared to 6.1 kcal./mole difference for the same solvent change for mesityl oxide. The change in dipole moment on light absorption for the cyclopropyl ketones must be comparable to that for mesityl oxide, and comparison of the spectral data for the cyclopropyl ketones with that for acetone demonstrates that the cyclopropane ring must be contributing electronic charge to the carbonyl group. Delocalization may be indicated through such structures as XIII. *The present set of data appears to be the first which reports maxima with positions which must be ascribed to the interaction of a cyclopropyl ring with a π-electron system.*[41]



XIII

The absorption maximum for acetone in hexane has been found to be 1870 Å.[42] and this value has

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[38] M. T. Rogers, THIS JOURNAL, **69**, 2544 (1947).

[39] I. M. Klotz, *ibid.*, **66**, 88 (1944).

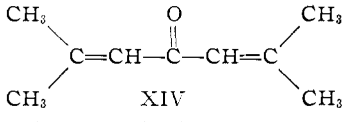
[40] (a) R. H. Eastman, *ibid.*, **76**, 4115 (1954); R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954); (b) R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955).

[41] M. F. Hawthorne, *J. Org. Chem.*, **21**, 1523 (1956), has reported maxima for dinitrophenylhydrazones of cyclopropyl ketones which cannot be due simply to the interaction under discussion because the cyclopropyl compounds absorb at *longer* wave lengths than the vinyl derivatives.

[42] H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 194 (1932).

been confirmed by Mohler.[43] Both authors reported an absorption intensity of only 800. It is remarkable that the maximum for acetone shifts to *shorter* wave lengths in water, although Goodman[44] has suggested that a 2-center $\pi \rightarrow \pi^*$-transition might show this behavior.

Rowe has concluded that there may be a steric factor in cyclopropyl interaction in excited states,[45] although a previous suggestion to this effect for transition states in solvolysis[46] does not appear to be correct.[47] In open-chain systems, attaching another double bond to a carbonyl, has a considerable effect upon absorption characteristics although the system is "cross-conjugated." For example, phorone (XIV) in water has a maximum at 2700 Å. (ϵ 17800)[23] as compared with a maximum of 2426 Å. (ϵ 9700) for mesityl oxide in the same solvent.

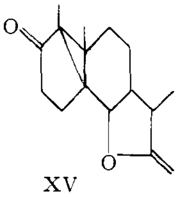


$$(CH_3)_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH{=}C(CH_3)_2$$

XIV

Dicyclopropyl ketone (XI), in contrast, absorbs at almost the same wave length as methyl cyclopropyl ketone, but with *twice the intensity.* Crude models suggest that both cyclopropyl groups cannot have the same orientation with respect to the carbonyl group at the same time. The implication is that there *may* be a steric factor in cyclopropyl conjugation.

The additional shift in absorption maximum (in water) which occurs when the cyclopropyl ring is fused to a five-membered ring probably is due to the extra strain in such systems (XII). It is possible, but improbable, that the compound XV reported by Barton[48] actually has a maximum at 2140 Å. (ϵ 4600) in alcohol in light of its resemblance to XII.



XV

Acknowledgments.—I wish to acknowledge the assistance of Mr. J. W. Marr, who prepared the methyl cyclopropyl ketone, and Mr. B. G. Ramsey, who measured a number of solution spectra. A portion of the work was carried out with assistance of funds provided by the Research Committee of the Graduate School of the University of Wisconsin.

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[43] H. Mohler, *Helv. Chim. Acta*, **20**, 285 (1937).

[44] Dr. L. Goodman, Chemistry Department, Pennsylvania State University, University Park, Pa., personal communication.

[45] J. W. Rowe, "Homoallylic π-Complexes and Related Cyclopropyl Conjugation," Thesis, Swiss Federal Institute of Technology, Zurich, 1957.

[46] J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

[47] S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950).

[48] D. H. R. Barton, P. de Mayo and M. Shafiq, *Proc. Chem. Soc.*, 205 (1957).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Effect of Solvent on Spectra. III. The Use of Z-Values in Connection with Kinetic Data

BY EDWARD M. KOSOWER

RECEIVED DECEMBER 19, 1957

The correlation of solvent effects on reaction rates can be extended to non-hydroxylic solvents with **Z**-values, which are based on the position of the charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide in a given solvent. In the case of the exchange of radioactive iodide ion with methyl iodide, specific interaction between iodide ion and acetone in the transition state and initial state accounts for the unusually rapid reaction observed in acetone. The **Z**-value correlations offer an opportunity of separating electrostatic and specific solvent effects. The analogy between the "intimate ion-pair" solvolysis intermediate and the pyridinium iodide complex is discussed, and the value of this point of view is illustrated by application to some data for tri-(p-nitrophenyl)-methyl derivatives.

Recent studies by Fainberg and Winstein[1] have demonstrated that a single empirical measure of solvent polarity, **Y**,[2] does not correlate very well the solvolysis rates of alkyl derivatives in different solvent mixtures, but that excellent correlation is found with **Y** for many cases, if the solvent-pairs are treated *separately*.[3] In view of the failure of treatments which consider the solvent as a continuous medium (*e.g.*, $1/D$, etc.[2]), and the necessity for dealing with binary pairs, it seems clear that further advances will depend on an understanding of the solvent–solute interaction on a microscopic level. The volume of solvent concerned with the solute has been called "frozen" or an "iceberg"[4]; we have favored the name, *cybotactic region*.[5]

The position of the charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide in a given solvent has been shown to be a linear function of **Y** over a wide range of solvent polarities[5a]; solvent pairs are clearly differentiated by this measure, called **Z**.[5a] **Z**-Values can be measured in non-hydroxylic solvents. In this paper, we show that correlation of rate with **Z** in both hydroxylic and non-hydroxylic solvents leads to certain insights

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[1] A. H. Fainberg and S. Winstein, THIS JOURNAL, **79**, 1597, 1602, 1608 (1957).

[2] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

[3] S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (957).

[4] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[5] E. M. Kosower, THIS JOURNAL, **80**, (a) 3253 (1958); (b) 3261 (1958).