0.0405 mole) was dissolved in 10 ml. of 1,4-dioxane and 0.0648 (0.0162 mole) of NaOH dissolved in 10 ml. of 50% ethanol–water mixture was added. A precipitate formed immediately. The mixture was placed on a steam-bath for an hour. It was then filtered and washed repeatedly with distilled water. The solid was then dried and digested in boiling water for an hour. Again it was filtered and washed, then dried overnight in a drying pistol; yield 1.1 g. (86.5%).

Anal. Calcd. for $C_{14}H_{12}OSn$: C, 53.41; H, 3.81; Sn, 37.70. Found: C, 53.35; H, 3.88; Sn, 37.66.

Spectra.—Ultraviolet spectra were measured with a Beckman model DU spectrophotometer; isooctane was the solvent. Infrared spectra of all compounds but X were measured and will appear in the doctoral dissertation of O. F. Beumel, Jr.

DURHAM, NEW HAMPSHIRE

The Effect of Solvent on Spectra. I. A New Empirical Measure of Solvent Polarity: Z-Values

BY EDWARD M. KOSOWER

RECEIVED DECEMBER 19, 1957

The position of the charge-transfer (c.-t.) absorption band of 1-alkylpyridinium iodide complexes is remarkably sensitive to the nature of the solvent in which it is measured. The transition energies derived from the band positions are linear in the Winstein–Grunwald Y-value (a kinetic measure of solvent ionizing power) over a wide range of methanol–water, ethanol–water and acetone–water mixtures. The c.-t. bands can be measured in solvents for which it is not possible or convenient to seek a Y-value. It is proposed that the transition energies, in kcal./mole, be adopted as empirical measures of solvent polarity, and that they be called Z-values. The complex formed from 1-ethyl-4-carbomethoxypyridinium iodide was selected as a standard, and pyridine-1-oxide was used to extend the Z-value scale to isooctane, in which the salt is insoluble. As an initial check on the validity of the Z-values, the transition energies for the c.-t. bands of the 1-ethyl-4-cyanopyridinium iodide complex in six solvents have been found to be linear in Z. A theoretical analysis of the data based on a reasonable model for the 1-alkylpyridinium iodide complex provides the free energy of solution of the complex dipole. The difference in free energy of solution of the 1-ethyl-4-carbomethoxypyridinium iodide complex dipole between isooctane and water is 17.3 kcal./mole. Using the apparent absorption coefficient as a measure of the effect of the solvent on the association of the pyridinium and iodide ions into complex, it is found that certain solvents (dimethylformamide, dimethyl sulfoxide) are *dissociating*, and others are *associating* (acetic acid), in comparison with "normal" solvents (chloroform, alcohols, etc.).

In the course of an investigation of 1-alkylpyridinium iodide complexes[1], it was noted that the absorption attributable to the complex appeared to move to longer wave lengths in less polar solvents.[1b,2] 1 - Methyl - 4 - carbomethoxypyridinium iodide was chosen for further study because the salt had a deep orange color, in contrast with the colorless appearance of 1-methylpyridinium iodide, suggesting that the absorption band of interest might be more accessible than were those of the polymethylpyridinium iodides.[3]

In fact, a new absorption band did appear in many solvents and was clearly distinct from the absorption of the pyridinium ion. The position of the band was remarkably sensitive to the nature of the solvent, the maximum varying in a manner parallel with the ionizing power of the solvents used. In an effort to discover how precisely the charge-transfer absorption reflected the ionizing power of the medium, a series of mixtures of methanol, ethanol and acetone with water were used as solvents. An independent measure of solvent ionizing power, the Y-value of Winstein and Grunwald,[4] is available for these media.

(1) (a) E. M. Kosower and P. E. Klinedinst, Jr., THIS JOURNAL, **78**, 3493 (1956); (b) E. M. Kosower and J. C. Burbach, *ibid.*, **78**, 5838 (1956).

(2) A preliminary communication of a portion of this work has appeared, *ibid.*, **78**, 5700 (1956). Certain conclusions derived from this paper and the two succeeding articles have been presented at a symposium "Solvent Effects and Reaction Mechanism," Queen Mary College, University of London, July 8-9, 1957, and at the XVIth International Congress of Pure and Applied Chemistry at Paris, July 18-24, 1957.

(3) *Cf.* F. Kröhnke, *et al.*, *Chem. Ber.*, **83**, 35 (1950); **86**, 1132 (1953); **87**, 1126 (1954); **88**, 851, 863 (1955).

(4) (a) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**,

Experimental

Pyridinium Salts.—1-Methyl-4-carbomethoxy iodide, orange crystals from methanol, m.p. 190–191° dec. (in bath at 184°) (reported[5] 176–179°); 1-ethyl-4-carbomethoxy iodide, bright orange-yellow crystals, crystallized by cooling a solution in acetone prepared at room temperature, m.p. 111–112°, equiv. wt. (by titration of the iodide ion) calcd. 293.1, found 293.2; 1-methyl-4-cyano iodide, bright orange-yellow crystals from cold water by addition of acetone, m.p. 197–198.5° dec. (in bath 180°), equiv. wt. (Ag I) calcd. 246.1, found 247.4; 1-ethyl-4-cyano iodide, bright yellow crystals from cold water by addition of acetone, m.p. 144.5–146° (evacuated sealed tube), equiv. wt. (titration) calcd. 260.1, found 260.0.

Pyridine-1-oxide was redistilled twice under reduced pressure, colorless, hygroscopic crystals, b.p. 146–147° (13 mm.).

Solvents.—Methanol, A.C.S. grade, was either used directly or dried with magnesium and redistilled; both solvents gave the same results. Ethanol, commercial absolute, was dried with magnesium and redistilled, or, 95% alcohol was dried with calcium oxide, then with magnesium. 1-Propanol, Eastman Kodak Co. white label was dried with calcium oxide and fractionated, b.p. 95–96°. 1-Butanol, C.P. was redistilled, b.p. 115–116°; isopropyl alcohol, C.P., was dried with magnesium and fractionated, b.p. 81–82°; *t*-butyl alcohol was dried with lithium aluminum hydride, and fractionated, b.p. 82–82.8°; dioxane was purified according to Fieser[6] and distilled from sodium, b.p. 100–101°; dimethylformamide, Eastman Kodak Co. white label was dried and redistilled, b.p. 80° (150 mm.); pyridine, Eastman Kodak Co. spectro grade was used directly; acetonitrile, Eastman Kodak Co. spectro grade was used directly; 2,2,3,3-tetrafluoropropanol was fractionated, b.p. 106–106.6°; 2,2,3,3,4,4,5,5-octafluoropentanol, as supplied; chloroform (0.13 *M* ethanol), A.C.S. grade, or purified according to Fieser[6]; dimethyl sulfoxide (Stepan Chemical Co.), was redistilled, b.p. 84° (16 mm.);

2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); **79**, 1597, 1602, 1608 (1957).

(5) C. A. Grob and E. Renk, *Helv. Chim. Acta*, **37**, 1672 (1954).

(6) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955.

isoöctane (2,2,4-trimethylpentane) Eastman Kodak Co. spectro grade was used directly; water, twice distilled.

Spectra.—Absorption curves were taken with Cary automatic recording spectrophotometers, either model 11 or model 14. The maxima usually were measured by running over the maximal absorption at the slowest speed three to five times, and averaging the maxima thus obtained. The maxima could normally be duplicated to at least ±6 Å. In a few cases, where the concentration used or the band location was unfavorably close to the pyridinium band, the errors might be larger, ±15Å. The c.-t. band for the complex from 1-methyl-4-carbomethoxypyridinium iodide in methanol was found to be 3416 Å., while a more extensive series of measurements on the same complex seven months afterward showed 3416 ± 5 Å.

The c.-t. bands were measured in quartz absorption cells of 0.0097, 0.050, 0.100, 1.00 and 10.0 cm. lengths. The short-path length cells were supplied by the American Instrument Co., Silver Spring, Md., and all but the shortest had matched blanks.

The values found are recorded in Table I (c.-t. bands) and Table II (pyridine-1-oxide).

The solutions were made up immediately before use and, in many cases, nitrogen was used to flush the air spaces of the cells and flasks. Lithium thiosulfate $(1-2 \times 10^{-4} M)$ was used in the alcohol–water and acetone–water solutions of 1-methyl-4-carbomethoxypyridinium iodide (see footnote f, Table I).

TABLE I

c.-t. BANDS OF PYRIDINIUM IODIDE COMPLEXES

Solvent		10^3c_0, moles/l.	λ_{max}, Å.	$\epsilon_{apparent}^g$	Y^a
1-Alkyl-4-carbomethoxy-(methyl, M; ethyl, E)					
Methanol:					
100%[b]	M	10.2	3416	129	−1.09
	E	8.00	3421	75	
97.5%	E	8.02	3401	..	$(−0.890)^c$
95%	M	13.2	3373	100	$(−0.701)^c$
	E	8.04	3385	63	
92.5%	E	8.06	3367	59	$(−0.514)^c$
90%	M	14	3340	95	−0.301
	E	8.08	3345	55	
87.5%	E	8.10	3331	51	$(−0.149)^c$
85%	M	17	3310	93	$(0.027)^c$
Ethanol:					
100%	M	8.78	3580	250	−2.033
	E	2.00	3591	100	
		4.00	3592	144	
		5.00	3590	173	
		6.00	3592	177	
98%	M	9.60	3557	240	−1.681
	E	5.04	3563	150	
96%	E	5.05	3537	127	$(−1.390)^c$
95%	M	9.89	3519	194	−1.287
	E	2.02	3521	63	
		4.04	3520	92	
		6.06	3523	122	
92%	E	5.06	3487	94	$(−0.932)^c$
90%	M	13.4	3458	172	−0.747
	E	5.07	3465	85	
85%	M	15.7	3420	150	$(−0.349)^c$
	E	5.08	3411	64	
80%	M	17.0	3375	131	0.000
	E	5.09	3372	49	
75%	M	14.4	3343	98	$(0.300)^p$
	E	10.2	3338	73	
70%	M	17.5	3305	99	0.595
	E	15.3	3311	78	
Isopropyl alcohol:					
100%	M	2.62	3735	561	
	E	2.61	3747	532	
95%	E	16.1	3604	404	
90%	E	22.4	3510	335	
80%	E	24.7	3406	202	
t-Butyl alcohol:					
100%	E	2.25	3960	753	
		0.102	4010	243	
95%	E	0.965	3739	425	
90%	E	1.96	3557	324	
80%	E	37.0	3431	343	
		3.92	3433	139	
Acetone:					
100%	M	1.83	4315[f]	200	
	E	2.00	4354	206	
99%	E	2.00	4200	163	
95.2%	M	3.40	3900	107	$−2.76^{4c}$
95%	E	2.00	3924	82	$(−2.973)^c$
93%	E	2.00	3824	61	$(−2.458)^c$
90%	M	5.95	3720	91	−1.856
	E	2.00	3735	39	
85%	M	17.9	3583	76	$(−1.185)^c$
	E	2.5	3633	29	
80%	M	13.7	3514	74	−0.673
	E	3.0	3544	23	
75%	M	16.6	3462	79	$(−0.266)^c$
	E	14.0	3482	19	
70%	M	19.3	3408	71	0.130
	E	16.0	3437	54	
65%	E	18.0	3391	52	$(0.453)^c$
60%	M	22.3	3331	61	0.796
	E	21.0	3343	55	
Dimethylformamide:					
100%	E	14.3	4172	70	
		24.7	4176	104	
90%	E	20.6	3869	57	
		38.8	3850	98	
80%	E	14.9	3676	31	
Formamide					
100%	E	116	3432	99	
		22.4	..[e]	21	
1-Propanol:					
100%	M	6.38	3625	370	
	E	10.0	3650	410	
1-Propanol–toluene					
1:9	M	0.48	3985	752	
1-Butanol:					
100%	E	3.31	3680	370	
Ethylene glycol:					
100%	M	48.5	3361	13	
Dioxane:					
90%	M	1.65	3717	665	−2.030
85%	M	2.19	3600	366	
80%	M	5.45	3556	280	−0.833
75%	M	9.39	3490	239	
70%	M	9.49	3444	160	0.013
Acetonitrile:					
100%	E	69.2	3975	312	
		16.1	3989	138	
		1.54	4005	23	
Pyridine:					
100%	E	82.0	4297	823	
		8.20	4421	622	

TABLE I (continued)

Solvent		$10^3 c_0$, moles/l.	λ_{max}, Å.	$\epsilon_{apparent}{}^g$	Y^a
		0.82	4425	415	
		0.082	4472	122	
95%	E	8.09	4088	267	
90%	E	41.1	3877	280	
		20.4	3895	206	
		9.52	3900	151	
80%	E	38.6	3703	146	

Pyridine–benzene

1:9	E	0.82	4442	955	
1:99	E	0.082	4475	1000	

Chloroform:

(0.13 M Ethanol)

	E	54.8	3990	1410	
		6.07	4150	1021	
		5.48	4150	1186	
		1.26	4338	1090	
		0.548	4418	1113	
		0.110	4470	1136	
		0.0219	4489	1233	

Chloroform–acetic acid:

1:1	E	8.9	3750	280	

Methylene chloride:

100%	E	5.12	4381	1147	
		8.53	4347	1212	
		17.1	4294	1254	

Methyl cyclopropyl ketone:

100%	E	16.1	4371	352	

Acetic acid:

100%	E	2.05	3610	∼600	

Dimethyl sulfoxide:

100%		2.51	. . ᵉ	ca. 8	
		8.77	4019	21	
		14.0	4020	33	
		33.5	4021	63	

Methanol–isoöctane:

95%ᵈ	E	7.99	3428	84	
90%	E	7.99	3435	95	
85%	E	7.99	3442	108	
80%	E	7.98	3447	122	

Chloroform–isoöctane:

1:1	E	0.63	4100	1238	

1-Alkyl-4-cyano- (methyl, M; ethyl, E)

Methanol:

100%	E	14.6	3613	130	

2,2,3,3-Tetrafluoropropanol (TFP):

100%	M	8.45	3463	118	

2,2,3,3,4,4,5,5-Octafluoropentanol (OFP):

100%	M	7.80	3530	364	

Dioxane:

65%ᵇ	M	9.18	3610	153	

Acetonitrile:

100%	E	3.00	4271	60	

Chloroform:

(0.13 M Ethanol)

	E	0.0385	4912	922	

Dimethyl sulfoxide:

100%	E	18.9	4265	46	

Ethanol:

100%	E	4.05	3776	215	

Pyridine

100%	E	1.46	4740	644	
90%	M	17.8	4120	270	
		25.0	4121	308	

Acetone:

100%	E	2.00	4625	322	

ᵃ See reference 4c.   ᵇ Volume per cent. organic component in mixture with water.   ᶜ Calculated from the equations given by Fainberg and Winstein, ref. 4c.   ᵈ Volume per cent. methanol.   ᵉ Not observed.   ᶠ Possibly anomalous due to thiosulfate-1-alkylpyridinium complex.   ᵍ Calculated from observed optical density and c_0.

TABLE II

ABSORPTION DATA FOR PYRIDINE-1-OXIDE

Solvent	λ_{max}, Å.	ϵ_{max}
2,2,3,3-Tetrafluoropropanol	2539	11,100
Water	2544	11,800
Methanol	2633	14,200
Ethanol	2651	13,200
Isopropyl alcohol	2660	13,300
90% Dioxane	2681	12,000
Chloroform (0.13 M EtOH)	2746	13,700
Chloroform, pure	2761	15,000
Acetonitrile	2758	14,000
Dimethylformamide	2763	13,000
Isoöctane	2817	12,600
n-Butyl alcohol	2662	13,300
Dimethyl sulfoxide	2777	13,500
t-Butyl alcohol	2668	13,800
Ethylene glycol	2618	13,000

Results

After a considerable number of spectra had been measured for 1-methyl-4-carbomethoxypyridinium iodide, it was found that the greater solubility of the 1-ethyl salt, especially in non-polar media, made it more suitable for the purposes of this investigation. Table I lists the charge-transfer absorption maxima in numerous solvents for 1-methyl- and 1-ethyl-4-carbomethoxy- and 1-methyl- and 1-ethyl-4-cyanopyridinium iodides.

In some of the least polar solvents (chloroform, pyridine), a second band appeared near 3100 Å. for the 1-ethyl-4-carbomethoxypyridinium iodide. Details on this band, which is the second c.-t. band expected for a charge-transfer transition involving iodide ion as donor,[7] have not been included in the table. It is planned to discuss these absorption bands in a future publication.

New absorption data for pyridine-1-oxide in various solvents are listed in Table II. Solvent sensitivity of the absorption spectrum of pyridine-1-oxide was previously reported by Ito.[8]

Discussion

In order to compare the observed maxima with Y-values, and for reasons of convenience in later use, the maxima were converted into transition energies by means of the relation (derived from E

(7) L. E. Orgel, Quart. Revs., 8, 422 (1954).
(8) M. Ito and N. Hata, Bull. Chem. Soc. Japan, 28, 260 (1955); J. Chem. Phys., 23, 495 (1956).

$= h\nu$), E_T (kilocalories/mole) $= 2.859 \times 10^{-3} \bar{\nu}$ (in cm.$^{-1}$). The transition energies in the mixtures of water with methanol, ethanol and acetone were plotted against **Y**. Straight lines were obtained in every case for solvents containing at least 5% water. The lines for the different binary mixtures (Fig. 1) converged with increasing water con-
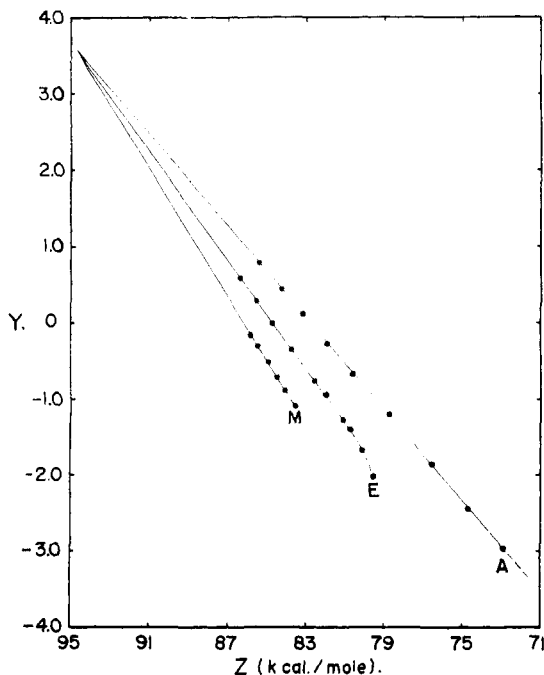

Fig. 1.—**Z** vs. **Y** in methanol–water (M), ethanol–water (E) and acetone–water (A). The equations for the lines are $Y_M = 0.41632Z - 35.877$, $Y_E = 0.35338Z - 29.946$, and $Y_A = 0.29887Z - 24.758$.

tent and gave *identical transition energies, within the experimental error, at the independently determined* **Y**-*value for water*.[4c] The value for the transition energy required to excite 1-ethyl-4-carbomethoxypyridinium iodide in water is 94.6 ± 0.1 kcal./mole, the values for the three mixtures being 94.6 (methanol–water), 94.6 (ethanol–water) and 94.5 (acetone–water). A less complete set of similar measurements for 1-methyl-4-carbomethoxypyridinium iodide led to a transition energy of 94.4 ± 0.2 kcal./mole in water. Thus, the positions of the c.-t. absorption bands of the 1-alkylpyridinium iodide complexes reflect accurately the ionizing power of the solvent as measured by the rate at which *t*-butyl chloride solvolyzes.

Z-Values.—Although **Y**-values can be measured with great precision, rates of this type cannot be measured routinely for a large number of different solvents. In addition, there is a large group of solvents for which **Y** cannot be found. On the other hand, c.-t. bands of the pyridinium iodide complexes can be determined rapidly in solution. By the use of secondary standards, transition energies can be estimated for solvents ranging from isooctane to water. These transition energies constitute a quantitative empirical measure of the ionizing power of this broad range of solvents. We propose that the transition energies for the 1-ethyl-4-carbomethoxypyridinium iodide

complex be called **Z**-values, and utilized as standards of solvent polarity.

Brooker[9] proposed the use of "merocyanine" dyes as solvent polarity indicators. For this purpose, they suffer from two disadvantages. These dye molecules possess large π-electron systems which are subject to specific interaction with solvent molecules, especially in the low polarity region. Secondly, the maxima change less in position with solvent change than the 1-alkylpyridinium iodide complexes.[10a,24] Although their response to solvent is extremely interesting, the nature of the electronic transition is such that they cannot provide the same information as the pyridinium iodide complexes (*vide infra*).

Z-Values have been measured with the standard complex for solvents ranging from chloroform (**Z** 63.2) to 70% ethanol (**Z** 86.4). Interference from the strong absorption of the 1-ethyl-4-carbomethoxypyridinium ion precludes direct determination of higher **Z**-values, but these are obtainable for mixtures of methanol, ethanol and acetone with water from the linear relationship of **Z** and **Y**. The pyridinium salts are insoluble in paraffin hydrocarbons, and a secondary standard has been adopted. Suitable secondary references should make it possible to find the **Z**-value for almost any solvent. Pyridine-1-oxide was chosen on the grounds that it (a) has a molecular shape close to that of the pyridinium iodide complexes, (b) possesses a strong, solvent sensitive ultraviolet absorption band and (c) is soluble in all solvents tried.
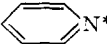
The absorption maximum for pyridine-1-oxide was measured in thirteen solvents, and the transition energies for these maxima plotted against **Z** (Fig. 2). Although there was some scatter about the calculated line, the order of points was more or less that expected. The region around the flat pyridine-1-oxide molecule is probably differently organized from that around the pyridinium iodide complex, accounting for the lack of strict linearity (compare with Fig. 4), and suggesting that apparently small changes in solute shape can be important. The **Z**-value for isooctane was obtained from the equation for the straight line and the measured transition energy in isooctane. The value found was 60.1 kcal./mole, a number which seems satisfactory for other uses.[10] The **Z**-values currently available are listed in Table III.

The **Z**-value depends somewhat upon electrolyte concentration and, in general, the lower the **Z**-value the greater its sensitivity to the electrolyte concentration. No effect could be noted in methanol and only a relatively small effect was found in ethanol. A substantial change was observed in chloroform in which the **Z**-value was 71.6 kcal./mole at a salt concentration of 0.055 M and 63.2 kcal./mole at zero salt concentration. The latter figure was obtained by measuring a series of band positions at varying low concentrations and extrapolating to infinite dilution with a plot of **Z** against $c^{1/2}$. In contrast, the **Z**-value for dimethylsulfoxide seemed independent of salt concentration. For those solvents in which the effect of varying 1-

(9) L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, THIS JOURNAL, **73**, 5350 (1951).

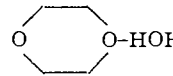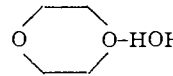(10) E. M. Kosower, *ibid.*, (a) **80**, 3261 (1958); (b) **80**, 3267 (1958).

TABLE III

	Z-Values[a]
ROH	
HOH	94.6
CH₃OH*	83.6
CH₃CH₂OH*	79.6
CH₃CH₂CH₂OH	78.3
CH₃CH₂CH₂CH₂OH	77.7
(CH₃)₂CHOH	76.3
(CH₃)₃COH*	71.3
HOCH₂CH₂OH[b]	85.1
HCF₂CF₂CH₂OH[c]	86.3
HCF₂(CF₂)₃CH₂OH[c]	84.8

Other compounds	
CHCl₃ (0.13 M EtOH)*	63.2
CH₃COCH₃	65.7
(CH₃)₂NCHO*	68.5
CH₃CN*	71.3
⟨benzene ring⟩N*	64.0
(CH₃)₃CCH₂CH(CH₃)₂	(60.1)[d]
CH₃SOCH₃*	71.1
NH₂CHO	83.3
cyclo-C₃H₅COCH₃	65.4
CH₃COOH	79.2
CH₂Cl₂*	64.2

Mixtures, ROH–HOH

CH₃OH	Z-value	(CH₃)₂CHOH	Z-value
97.5	84.1	95	79.3
95	84.5	90	81.5
92.5	84.9	80	83.9
90	85.5		
87.5	85.8		

CH₃CH₂OH		(CH₃)₃COH	
98	80.2	95	76.5
96	80.8	90	80.4
95*	81.2	80	83.3
92	82.0		
90	82.5		
85	83.8		
80	84.8		
75	85.7		
70	86.4		

Other mixtures

CH₃COCH₃–HOH			
99	68.1		
95	72.9		
93	74.8	⟨dioxane ring⟩ O-HOH	
90	76.6	90[b]	76.7
85	78.7	85[b]	79.2
80	80.7	80[b]	80.2
75	82.1	75[b]	81.7
70	83.2	70[b]	82.8
65	84.3		
60	85.5		

[a] Transition energies at 25°, 1 atm. for the c.-t. band of the complex from 1-ethyl-4-carbomethoxypyridinium iodide, corrected where feasible (indicated by *) to lowest (or zero) electrolyte concentration. [b] Based on 1-methyl-4-carbomethoxypyridinium iodide complex (for which transition energies are usually 0.0–0.4 kcal./mole higher). [c] Transition energy measured for 1-methyl-4-cyanopyridinium iodide complex and Z-value derived from linear relation of such transition energies with Z. [d] Figure derived from E_T (pyridine-1-oxide) vs. Z.
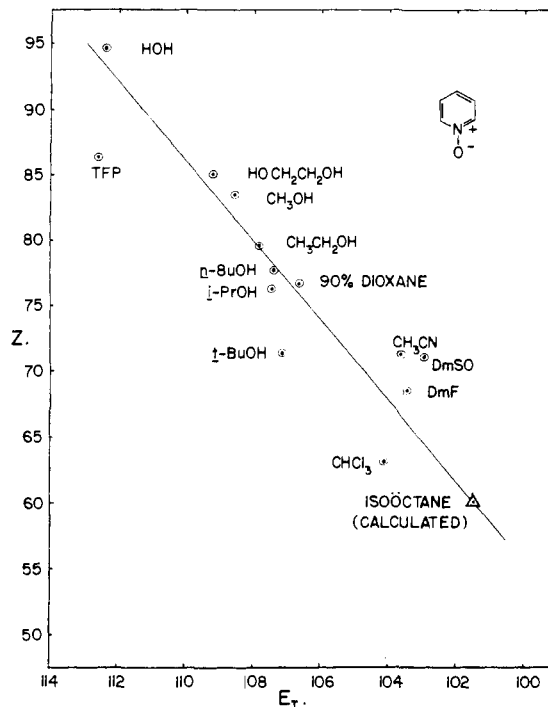
Fig. 2.—E_T (pyridine-1-oxide) vs. Z in fourteen solvents; $E_T = 0.32975Z + 81.693$; TFP = tetrafluoropropanol, DMSO = dimethyl sulfoxide, DMF = dimethylformamide.

alkylpyridinium iodide concentration has been investigated, an asterisk has been placed in Table III. It is planned to continue the investigation of salt effects in a number of selected solvents.

The Z-values vary with temperature, decreasing with increasing temperature. At the same time, the apparent absorption intensity increases[11] (i.e., the ε calculated on the basis of the concentration of 1-alkylpyridinium salt). The visible effects can be quite striking. A red-orange solution of 1-ethyl-4-carbomethoxypyridinium iodide in chloroform at 25° becomes pale yellow when cooled to −75°. Hantzsch[12] had previously reported that 1-ethyl-pyridinium iodide changed from yellow to colorless over the same temperature range. At this time, it is not clear what portion of the change observed with higher temperature can be attributed to a decrease in the intrinsic transition energy and what portion to a decrease in solvent–solute interaction.

In the series ROH the largest change in Z occurs when the H of water is replaced by a methyl group. Z decreases from 94.6 for water to 83.6 for methanol. Successive insertions of methylene groups lead to still smaller Z-values, but the changes rapidly become small as the alkyl group becomes longer. For the compounds R₃COH replacement of H by CH₃ lowers Z by 4.0 (ethanol, Z 79.6), while further substitution has a similar effect, Z changing by 3.3 to isopropyl alcohol (Z 76.3), and by 5.0 more to t-butyl alcohol (Z 71.3).

Substitution of fluorine for H has a large effect on Z; 2,2,3,3-tetrafluoropropanol-1 has a Z-value of 86.3, 8.0 higher than 1-propanol. Ethylene

(11) W. M. Schwarz, Jr., unpublished results.
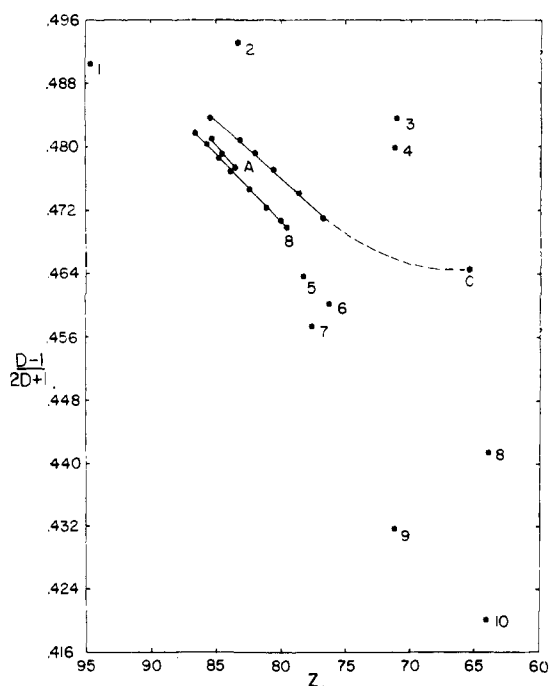
(12) A. Hantzsch, Ber., **52**, 1544 (1919).

Fig. 3.—Z vs. D − 1/2D + 1. Lines A, B and C connect the points for methanol–water, ethanol–water and acetone–water, respectively. Other points are 1, water; 2, formamide; 3, dimethyl sulfoxide; 4, acetonitrile; 5, 1-propanol; 6, isopropyl alcohol; 7, 1-butanol; 8, pyridine; 9, t-butyl alcohol; 10, methylene dichloride. Dielectric constants are taken from ref. 14 or from H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950.

glycol (Z 85.1) is considerably more polar than ethanol.

It will be noted that the hydroxylic solvents vary from Z 71.3 (t-butyl alcohol) to Z 94.6 (water), while the non-hydroxylic solvents, with the single exception of formamide (Z 83.3), only vary from Z 60.1 (isoöctane) to Z 71.3 (acetonitrile). These ranges signify the great importance of hydrogen-bonding in solvation.

The Z-values for dimethylformamide, dimethyl sulfoxide and formamide may occasion some surprise, since it is commonly assumed that these solvents are "polar," on the basis that they have high dielectric constants and are good solvents for salts. Formamide, for example, has a Z-value about the same as that of methanol, and yet its dielectric constant (D 109.5, 25°[13]) is much higher than that of methanol (D 32.6, 25°[14]). The Z-values for these solvents correlate their effect on electronic transitions[10a] and on rate.[10b,15]

Winstein[1c] has already demonstrated that the dielectric constant, D, is not a quantitative measure of solvent polarity when the range of ionizing power is great. Inasmuch as Y is *not* linear in D, it is not astonishing that Z does not correlate well with the commonly used function of dielectric constant,

(13) G. R. Leader, This Journal, 73, 856 (1951).

(14) "Table of Dielectric Constants of Pure Liquids," A. A. Maryott and E. R. Smith, National Bureau of Standards Circular 514, August 10, 1951.

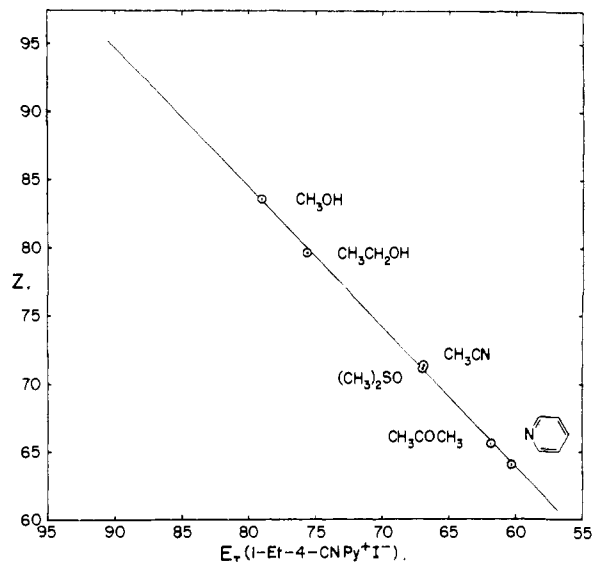(15) S. D. Ross and M. M. Labes, This Journal, 79, 4155 (1957).

Fig. 4.—E_T (1-ethyl-4-cyanopyridinium iodide) vs. Z; E_T = 0.97279Z − 2.0779.

(D − 1)/2D + 1 (Fig. 3). Both Z and Y are *microscopic* measures of solvent–solute interaction, while D is a *macroscopic* measure of the behavior of solvent in an electric field.

1-Ethyl-4-cyanopyridinium Iodide Complex.—In order to ascertain that Z-values were useful for correlating data in different solvents, a solvent-sensitive electronic transition similar to the one used in setting up the Z-values was measured. The c.-t. band for the 1-ethyl-4-cyanopyridinium iodide complex appears at wave lengths 200–300 Å. to the red from the corresponding 4-carbomethoxy complex, indicating that the electron-attracting power of the substituent is very important in determining the position of the c.-t. absorption. The steric and solvation requirements of a cyano group are sufficiently different from those of the carbomethoxy group to provide a test of whether these substituents affect the response of the pyridinium iodide complex to solvent in any way other than by modifying the electron-accepting properties of the pyridinium ring. In fact, an excellent correlation between the transition energies for the 1-ethyl-4-cyano complex and Z was obtained in six solvents, with Z 64.0 (pyridine) to Z 83.6 (methanol) (Fig. 4).

Theoretical Basis of the Solvent Effect.—The 1-alkylpyridinium iodide complexes are electrostatically equivalent to tight ion-pairs, *i.e.*, Ia is the major contributing form to the ground state of the complex I, and the charge-transferred
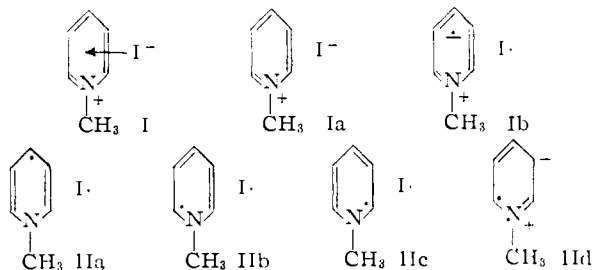
form Ib of minor importance. The excited state has Ib as the major contributing form: Ib may be considered as a combination of IIa, IIb and IIc. Forms like IId indicate the charge distribution. These structures are written in accordance with the interpretation of the complexes as *charge-transfer* complexes.[1,16] Since these complexes appear to be factors in some chemical reactions[17] and are similar to certain transition states in their energy of interaction with solvent, we do not appear to require the postulate of "contact charge-transfer"[18] as is necessary in other systems.

A model for the ground state of the complex is shown in Fig. 5a, and is an iodide ion in contact with a 1-alkylpyridinium ion with the line joining the

(a)   **(b)**
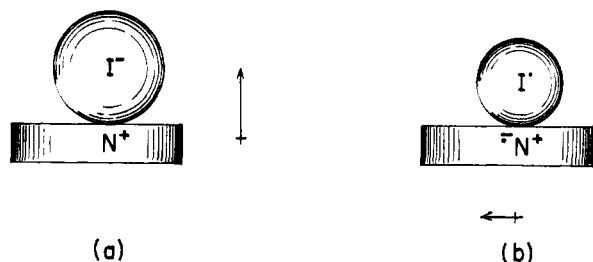
Fig. 5.—Models for electronic states of 1-alkylpyridinium iodide complex: (a) ground state, (b) excited state.

centers of charge perpendicular to the plane of the ring. The dipole moment of the ground state can be calculated as 13.9 Debyes, from the relation $\mu = eR$.[19] Although gas-phase measurements by the molecular beam method of the dipole moments of alkali metal halides show that mutual polarization reduces the moment below that calculated from the product of charge and distance, eR,[22a] the effect of polarization should be reduced in a polar solvent like water. The dipole moment values reported for glycine and alanine in water are very close to the values predicted from eR.[22b]

A model for the excited state is shown in Fig. 5b. By assuming that the negative charge is located on the average in the center of the pyridinium ring, and including the group moment for the carbomethoxy group,[19] the dipole moment for the excited state is estimated as 8.6 D.

The ground state of the complex will effect an organization of the solvent around itself. We suggest that such ill-defined "frozen" solvent regions be called *cybotactic regions*.[23] The net dipole moment of the cybotactic region will be parallel or

antiparallel to the moment of the complex. Upon excitation (*i.e.*, light absorption), the solute dipole vector is transformed into one smaller in size than the initial dipole, and *perpendicular in direction*. Since the dipole moment of the cybotactic region is a resultant of molecular moments, and cannot change during light absorption (the Franck–Condon principle), *no electrostatic solvent–solute interaction should exist in the excited state at the instant of formation*. The accuracy of this statement is dependent upon the validity of the models represented in Fig. 5, but, in any case, it is clear that a large decrease in solvent–solute interaction will result upon excitation, and that further remarks based on the model are, at the very least, qualitatively correct.

An approximate energy level diagram can be constructed on the basis of the consequences of the model proposed for the pyridinium iodide complexes. The gas-phase transition is shown as identical with the transition in isoöctane, although electronic polarization of the solvent by the solute dipole in both the ground and excited states would lower both with respect to the gas phase (Fig. 6).
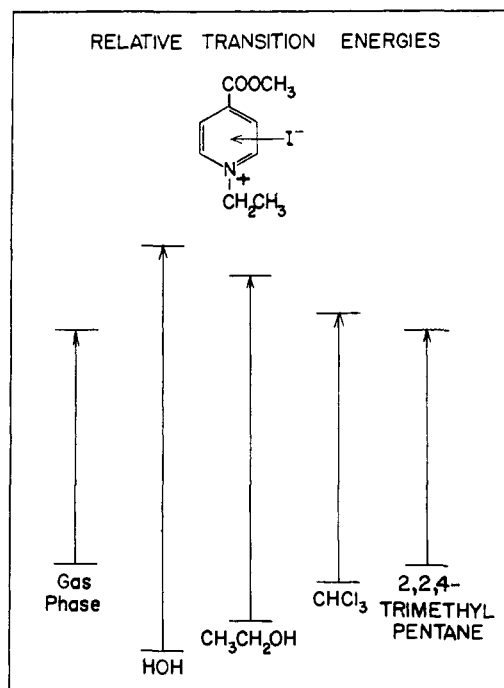

Fig. 6.—Relative transition energies for 1-ethyl-4-carbomethoxypyridinium iodide in different solvents. (*See text for comment on gas phase transition*).

Electronic polarization is not considered at this time for transfers of dipoles from one solvent to another, and the difference in refractive indices of water and isoöctane (1.3330 and 1.3915, respectively) is small enough to make this error unimportant. To obtain the other relationships shown in Fig. 6, one may proceed as follows: (a) Organize a cybotactic region in water (energy required, E_c) for the dipole of the pyridinium iodide complex (b) transfer the dipole from isoöctane to water, recovering through the interaction of the dipole

(16) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(17) E. M. Kosower, THIS JOURNAL, **78**, 3497 (1956).

(18) (a) R. S. Mulliken, *Rec. trav. chim. Pays-Bas*, **75**, 845 (1956); (b) L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

(19) Ionic radius, iodide ion, 2.16 Å.; covalent radius, nitrogen atom, 0.74 Å.[20] The moment of the carbomethoxy group is *ca.* 1.9 D,[21] and although its contribution would make a small change in the size and direction of the ground state dipole, it was not included in the estimate. The other moments would approximately cancel.

(20) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publishers, Inc., New York, N. Y., 1950.

(21) R. J. W. Le Fèvre, "Dipole Moments." John Wiley and Sons, Inc., New York, N. Y., 1953.

(22) J. W. Smith, "Electric Dipole Moments," Butterworth's Scientific Publications, London, 1955. (a) p. 100. (b) p. 168.

(23) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. 2, p. 2, Longmans, Green and Co., London, 1951.
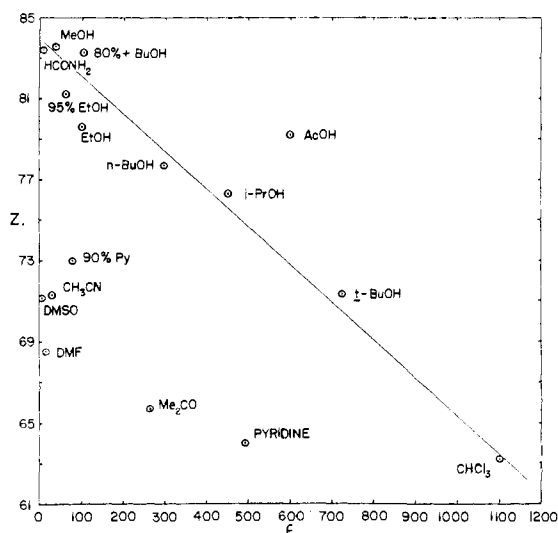
Fig. 7.—ϵ, apparent absorption coefficient, *vs.* Z for $c_0 = 2.0 \times 10^{-3}$ M; solute, 1-ethyl-4-carbomethoxypyridinium iodide.

with the cybotactic region $2E_c$,[23a] (c) excite the complex with a light quantum, thus producing a solute dipole perpendicular to the solvent dipole, and destroying the electrostatic interaction between the solute and solvent. The cybotactic region around the excited state is unstable with respect to unorganized solvent to the extent of E_c. The difference in transition energies between isooctane and water is thus $2E_c$, and E_c thus represents the decrease in free energy upon transfer of the complex dipole from isooctane to water. Although E_c is only a crude estimate, it appears to have some use in calculating the dipole moments of certain excited states[10a] and transition states.

The transition energy variation (*i.e.*, the change in Z) resulting from solvent change is, to the best of our knowledge, the largest ever observed for a single electronic transition.[24]

Z and ϵ.—Association of charged species increases as the ionizing power of the medium falls. We have taken the apparent absorption coefficient of the c.-t. band at a constant concentration (2.0 $\times$ 10⁻³ M) of 1-ethyl-4-carbomethoxypyridinium iodide in a series of solvents as an empirical measure of the association constants in these solvents. The measured (or estimated) ϵ is plotted against Z in Fig. 7. The point for chloroform is considered reliable because there is reason to believe that as-

sociation is complete in this solvent. A rough correlation for ϵ and Z can be seen for chloroform and the alcohols.

One group of solvents has *far lower* association constants than would be expected from the Z-values. These are dimethylformamide, dimethyl sulfoxide, acetonitrile, 90% pyridine–water and acetone. In three of these cases, acetonitrile, dimethyl sulfoxide and acetone, it can be shown directly that iodide ion complexes with the solvent.[10a,26] Lowering the concentration of pyridine as a solvent by almost complete replacement with benzene has virtually no effect on Z, but raises ϵ by a considerable factor (see Experimental). Experiments with methylamine and 1-methylpyridinium ion, which do not react readily, show increased absorption in the ultraviolet indicative of very weak complex formation.[27]

Solvents with unusually low association constants might be termed *dissociating* solvents, and exert their effect through either (a) specific interaction with one or both of the dissociated species or (b) a general ability to interact well with ions, but not dipoles. The classification of dimethylformamide and dimethyl sulfoxide as dissociating solvents removes some of the disparity between their low Z-values and general opinion as to their ionizing power based on other behavior.

One solvent was found in which the association constant was *higher* than expected. That solvent was acetic acid, and its behavior as an *associating* solvent is precisely what one would have predicted from a knowledge of "internal return" phenomena in the same solvent.[28] It thus appears to be advisable on experimental grounds, to make a qualitative distinction between two "kinds" of ionizing power. The first operates upon dipoles in ground states and transition states; the second controls the dissociation of ion pairs into ions.

MADISON, WISCONSIN

(23a) The author is indebted to iProfessor Rudolph A. Marcus, Chemistry Department, Brooklyn Polytechnic Institute, and Professor S. Winstein, Department of Chemistry, UCLA, for valuable discussions concerning this point.

(24) The merocyanine M88[25] possesses an absorption maximum which varies from 4875 Å. in water to 7100 Å. in pyridine. However, the change in transition energy is only 18.4 kcal./mole, whereas the corresponding figure for the 1-ethyl-4-carbomethoxypyridinium iodide complex is 30.6 kcal./mole.

(25) L. G. S. Brooker, *et al.*, THIS JOURNAL, **73**, 5332 (1951).

(26) E. M. Kosower, R. Martin and V. W. Meloche, *J. Chem. Phys.*, **26**, 1353 (1957).

(27) E. M. Kosower, unpublished results.

(28) (a) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951); (b) H. L. Goering, N. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).