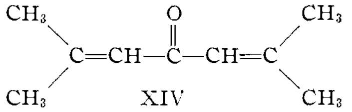
been confirmed by Mohler.[43] Both authors reported an absorption intensity of only 800. It is remarkable that the maximum for acetone shifts to *shorter* wave lengths in water, although Goodman[44] has suggested that a 2-center $\pi \rightarrow \pi^*$-transition might show this behavior.

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.

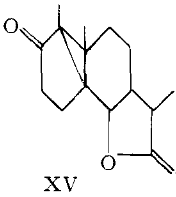


$(CH_3)_2C{=}CH{-}C({=}O){-}CH{=}C(CH_3)_2$

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).

about details of mechanism. Certain other conclusions of interest are made possible by the use of **Z**-values.

Iodide Exchange.—Swart and Le Roux[6] have made a careful study of the rate at which radioactive iodide ion exchanges with methyl iodide in water, ethylene glycol, methanol, ethanol and acetone. The Arrhenius activation energy for the exchange reaction is linear in **Z** (Fig. 1) within the experimental error. The free energy of activation (log *k*) is linear in **Z** for four hydroxylic solvents (Fig. 2); the maximum deviation from the line was found in ethylene glycol, in which the measured rate was 1.4 times that predicted by the correlation. In acetone, the actual rate was 7.54 times as fast as predicted.

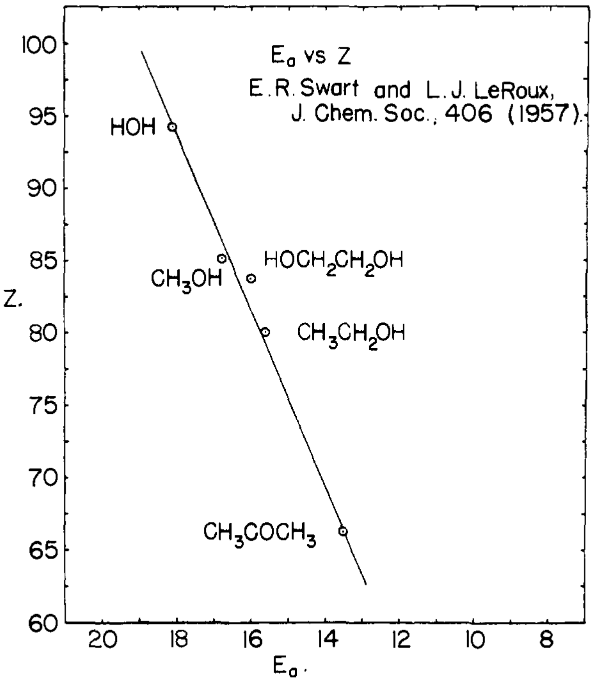


Fig. 1.—Arrhenius activation energy *versus* **Z** for the exchange reaction $I^{-*} + CH_3I \rightarrow I^*CH_3 + I^-$.

The deviation of the rate in acetone may be rationalized as an entropy effect. It has been suggested that acetone complexes with iodide ion,[5b] and it would be expected, on this basis, that the transition state I for the exchange reaction would involve less solvent reorganization in its formation than expected from the **Z**-value.[7]

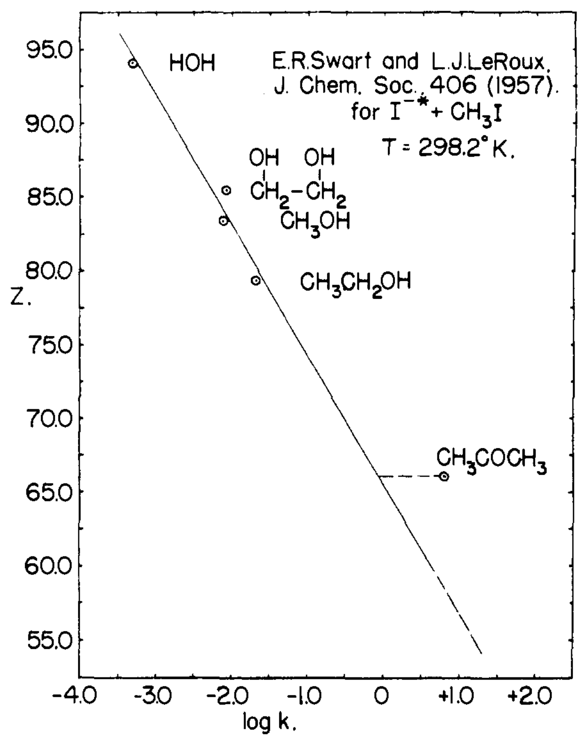
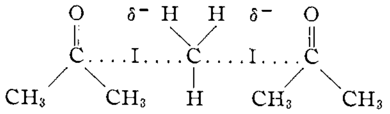


Fig. 2.—Log *k* *versus* **Z**.

Menschutkin Reaction.—The rate of reaction of amines with alkyl halides has been studied in a number of solvents. Caldin[9] and Fuoss[10] have concluded that simple electrostatic theory (*i.e.*, dependence on a function of *D*) cannot account for the variation in rate with solvent change. The rate of reaction of pyridine with ethyl iodide in a series of *alcohols* gives a fairly good straight line when plotted against **Z**.[11] The rate in acetone is faster than predicted by a factor of 22 (Fig. 3). As in the iodide exchange reaction, the high rate may result from the specific interaction of the iodide ion and an acetone molecule in the transition state; preliminary weaker interaction between ethyl iodide and acetone may also occur. A number of the other apparently anomalous rates listed by Caldin[9] may result from specific halide ion–solvent interaction; benzonitrile, for example, should resemble acetonitrile,[5b] and nitrobenzene seems to complex in a similar way.[12]



I

Enol–Keto Equilibrium.—Ordinarily, an equilibrium involving two or more species would not respond in a simple way to solvent change. The tautomerism between the keto and enol form of ethyl acetoacetate is an exception because the position of equilibrium is largely determined by the

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[6] E. R. Swart and L. J. Le Roux, *J. Chem. Soc.*, 2110 (1956); 406 (1957).

[7] Correction of the rate constants given by Swart and Le Roux to the mole fraction scale by the equation of Davis and LaMer,[8] which yields a set of "rate constants" proportional to the mole fraction rate constants, actually improves the fit of the *hydroxylic solvent* points to a straight line, mainly by "correcting" the position of the rate in ethylene glycol. The deviation of acetone from the line is *greater* using the mole fraction scale and in the same direction as with the volume molar scale. In presenting the data shown in Fig. 2, the usual units (moles/liter) are the basis for the rate constants. Although use of the mole fraction scale does simplify certain relationships, Davis and LaMer have pointed out that interpretation may entail rather complete knowledge of interactions occurring among the molecules in the reaction medium.

[8] H. G. Davis and V. K. LaMer, *J. Chem. Phys.*, **10**, 585 (1942).

[9] E. F. Caldin and J. Peacock, *Trans. Farad. Soc.*, **51**, 1217 (1955).

[10] M. Watanabe and R. M. Fuoss, THIS JOURNAL, **78**, 527 (1956).

[11] Data from Table 652.477 of Homogeneous Reaction Kinetics, Circular 510, National Bureau of Standards, Washington, 1951.

[12] R. W. Shellman, *J. Org. Chem.*, **22**, 818 (1957); E. M. Kosower, *Chemistry & Industry*, 1352 (1957).

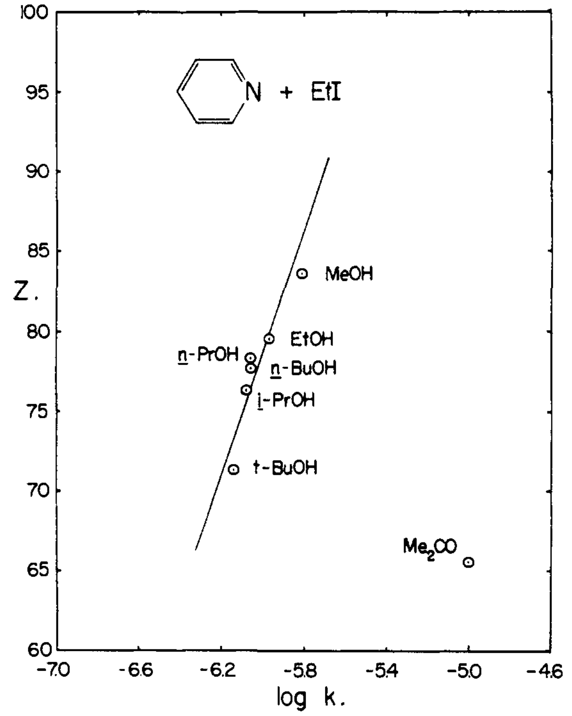


Fig. 3.—Log *k* *versus* **Z** for a typical Menschutkin reaction.

interaction of the keto form with the solvent. The enol form is internally hydrogen bonded (II). A relatively smooth curve is obtained for most solvents, if log K_{eq} is plotted against **Z** (Fig. 4).

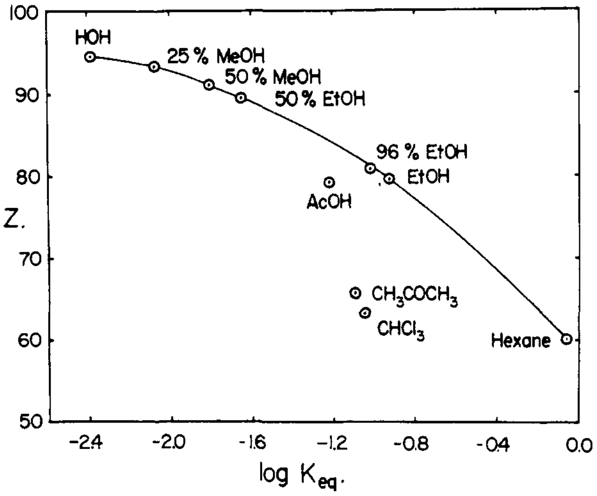
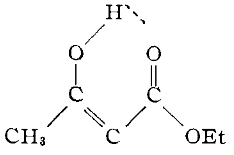


Fig. 4.—Log K_{eq}. *versus* **Z** for the equilibrium between keto and enol forms of ethyl acetoacetate.

Chloroform and acetic acid deviate in the expected direction by virtue of their ability to hydrogen bond. Acetone is also more "polar" than expected, and favors the keto form.



II

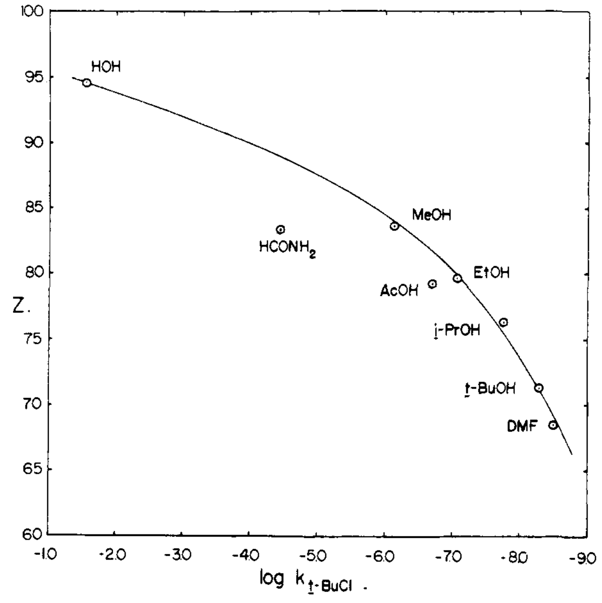


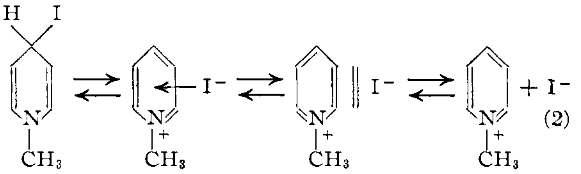
Fig. 5.—Log $k_{t\text{-BuCl}}$ *versus* **Z**.

***Z versus* Y.**—A plot of **Y** against **Z** for a series of pure solvents gives a reasonably smooth curve, except for formamide (Fig. 5). Extrapolation of the curve to **Z** = 60.1, the value for isoöctane,[5a] leads to the conclusion that ionization in hydrocarbon solvents may not be impossibly slow The partial racemizations reported by Cram[13] for 3-phenyl-2-butyl *p*-toluenesulfonates in acetonitrile and chloroform are in accord with this idea. A similar conclusion regarding heterolysis in nonpolar media was expressed recently by Ingold[14] on the basis of Maccoll's work on gas-phase elimination of hydrogen halide from alkyl halides.

The Nature of the "Intimate Ion-pair."—Winstein[15] has proposed a detailed scheme for the solvolysis of alkyl halides, based on the interpretation of salt effects on the rate of solvolysis (eq. 1).

$$\underset{\substack{\text{alkyl}\\\text{halide}}}{\mathrm{RX}} \rightleftarrows \underset{\substack{\text{transition}\\\text{state}}}{\overset{\delta^+}{\mathrm{R}}\text{----}\overset{\delta^-}{\mathrm{X}}} \rightleftarrows \underset{\substack{\text{"intimate}\\\text{ion-pair"}}}{\mathrm{R^+X^-}} \rightleftarrows \underset{\substack{\text{solvent-separated}\\\text{ion-pair}}}{\mathrm{R^+//X^-}} \rightleftarrows \underset{\substack{\text{dissociated}\\\text{ions}}}{\mathrm{R^+ + X^-}} \quad (1)$$

An analogous scheme can be written for pyridinium salts, utilizing the knowledge that nucleophiles add to the pyridinium ring,[16] along with the probability of solvent-separated ion-pair formation[17] (eq. 2).



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(13) D. J. Cram, THIS JOURNAL, **74**, 2129 (1952).

(14) C. K. Ingold, *Proc. Chem. Soc.*, 287 (1957).

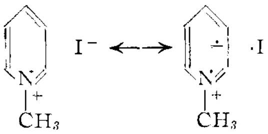
(15) (a) S. Winstein, *Experientia, Suppl.*, **II**, 152 (1955); (b) S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958).

(16) E. M. Kosower, *ibid.*, **78**, 3493 (1956).

(17) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).

Comparison of equations 1 and 2 shows that the charge-transfer complex of iodide ions and pyridinium ions occupies a position in the solvolysis scheme for 4-iodo-1-methyl-1,4-dihydropyridine identical to that of the "intimate ion-pair" in eq. 1. The question is thereby raised as to whether or not "charge-transfer" stabilization contributes significantly to the stability of the "intimate ion-pair." Charge-transfer of this type is equivalent to writing a contribution of covalent character to the stretched bond (*i.e.*, IIIa $\longleftrightarrow$ IIIb). Without doubt, IIIb is a minor resonance form of the ion-pair, just as the importance of the charge-transferred form IVb of the pyridinium iodide complex to the ground state is felt to be small.[5a] The relative importance of charge-transfer stabilization of the ion-pair would decrease as the anion was changed from iodide to chloride to *p*-toluenesulfonate, since the ionization potential of the anion increases in that order and charge-transfer is dependent on the ionization potential of the donor.[18,19] The opinion that there is a small contribution of covalent character to the structure of the first solvolysis intermediate also has been advanced by Doering, Zeiss and Streitwieser.[20]

$$\underset{\text{IIIa}}{R^+X^-} \longleftrightarrow \underset{\text{IIIb}}{R\cdot\ .X}$$


IVa IVb

In one other important respect, the pyridinium iodide complex behaves like the "intimate ion-pair." The latter is less rapidly dissociated in acetic acid, resulting in a greater degree of "internal return"[21] in that solvent. We have already reported that acetic acid, with a **Z**-value close to that of ethanol, allows considerably more association of the pyridinium and iodide ions than does ethanol by a factor estimated at 6 at a salt concentration (1-ethyl-4-carbomethoxypyridinium iodide) of 2×10^{-3} *M*.[5a]

In agreement with Winstein,[15b] we would refer to the first intermediate in solvolysis as an "intimate ion-pair" unless the special light absorption attributable to charge-transfer could be observed. Nevertheless, consideration of certain ion-pairs from what might be called the "charge-transfer viewpoint" facilitates understanding of their reactions. The approach is illustrated in the next section.

Tri-(*p*-nitrophenyl)-methyl Derivatives.—It has been reported that tri-(*p*-nitrophenyl)-methyl bromide[22] and the corresponding nitrate[23] yield the free radical on treatment with sodium iodide in acetone. The free radical also is formed from the bromide in the presence of a number of reagents which increase the solvent ionizing power somewhat in acetone, benzene or dioxane.

The bromide yields the carbinol on refluxing with perchloric acid in aqueous acid[22] and the nitrate apparently forms the carbonium ion in concentrated sulfuric acid.[23]

A third pathway occurs with sodium iodide in 1:1 acetic acid–methylene chloride, which gives carbinol, radical and tri-(*p*-nitrophenyl)-methane from the nitrate and only the methane and carbinol from the bromide.[24]

These results are summarized in Table I.

TABLE I

PRODUCTS FROM TRI-(*p*-NITROPHENYL) DERIVATIVES

Solvent	Product R^+	$R\cdot$	R^-
Low **Z**[5a]		x	
Intermed. **Z**[a]	x	x[b]	x
High **Z**	x		

[a] With iodide ion. [b] Only formed from nitrate (see text).

A qualitative scheme to explain these results involves (a) "intimate ion-pair" (for R^+ and $R\cdot$) and (b) a displacement of the triaryl methide ion (R^-) as proposed by Hawthorne.[24] The "intimate ion-pair"[14,15] presumably is formed in all solvents (eq. 3). The lifetime and mode of dissociation of

$$Ar_3CX \longrightarrow Ar_3C^+X^- \qquad (3)$$

the "intimate ion-pair" would vary with the solvent. In low **Z**-value[5a] (non-polar) solvents, the species would probably possess a greater contribution of charge-transferred (or covalent) character and thus be more prone to form radical by simple electron transfer. Replacement of the bromide ion by another anion, *e.g.*, iodide ion, might facilitate radical formation, but such replacement is not a requirement for this pathway. Light of the appropriate wave lengths should promote radical formation and it would be of interest to see whether this could be correlated with ion-pair formation.

In high **Z**-value solvents, formation of carbonium ion is favored, while in intermediate **Z**-value solvents containing proton-donors (protons have low steric requirements and can therefore be involved in the transition state for formation of the triarylmethane), a good nucleophile (I^-) can form the equivalent of methide ion, probably by direct displacement on the un-ionized triaryl halide.

The multifold reactivity of these derivatives seems worth further investigation.

Acknowledgment.—It is a pleasure to note here that Professor E. L. King of this Department has provided valuable comments on this paper.

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[18] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

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

[20] *Cf.* A. Streitwieser, Jr., *Chem. Revs.*, **56**, 638–641 (1956).

[21] W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951).

[22] J. E. Leffler, *ibid.*, **75**, 3598 (1953).

[23] M. F. Hawthorne, *ibid.*, 5523 (1955).

[24] M. F. Hawthorne, *ibid.*, **77**, 5739 (1955).