a Unicam SP800 spectrophotometer. The spectra were recorded within 2 min after preparation of the solution. The absorbance was obtained by comparison with a blank containing the particular buffer and 10% ethanol alone.

Polarography. Polarographic *i-E* curves were recorded in solutions placed in a Kalousek-type cell with separated reference calomel electrode, using a dropping mercury electrode with $t_1 = 3.4$ sec (at 0.0 V) and $m = 2.1$ mg/sec, by means of a Sargent-Welch Mark XVI polarograph.

Nine milliliters of a simple borate or carbonate buffer was transferred into the cell and deaerated by a stream of nitrogen for 2 min; then 1 ml of a 2×10^{-3} *M* stock solution of the corresponding ethyl benzoylacetate in ethanol was added. After deaeration for another 45 sec the polarographic curve was recorded. All buffer solutions were checked for impurities.

Keto-Enol Titrations. In the modified Meyer titration,[16] 50 ml of 2×10^{-3} *M* benzoylacetate in 10% ethanol was chilled and treated with 10 ml of a solution of bromine in 10% ethanol, followed immediately by 10 ml of a 10% solution of β-naphthol. After 2 min, 50 ml of 0.1 *N* potassium iodide solution was added, and the mixture was warmed up to room temperature and titrated with standard thiosulfate solution. End points tended to fade after a few minutes.

References and Notes

(1) (a) L. Meites, "Polarographic Techniques," 2nd ed, Wiley, New York, N. Y., 1965, p 132; (b) J. Heyrovský and P. Zuman, "Practical Polarography," Academic Press, London, 1968, p 32.
(2) G. Nisli, D. Barnes, and P. Zuman, *J. Chem. Soc. B*, 764 (1970).
(3) D. Barnes and P. Zuman, *Talanta*, **16**, 975 (1969).
(4) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1701 (1944).
(5) P. Zuman in "Progress in Polarography," Vol. 3, P. Zuman, L. Meites, and I. M. Kolthoff, Ed., Wiley, New York, N. Y., 1972, p 73.
(6) G. Nisli, D. Barnes, and P. Zuman, *J. Chem. Soc. B*, 778 (1970).
(7) S. G. Majranovskij, "Catalytic and Kinetic Waves in Polarography," Plenum Press, New York, N. Y., 1968, p 194.
(8) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967.
(9) (a) K. H. Meyer, *Ber.*, **45**, 2843 (1912); (b) *ibid.*, **47**, 826 (1914).
(10) P. Zuman, unpublished.
(11) R. Gelin, S. Gelin, and C. H. Zambartas, *C. R. Acad. Sci., Ser. C*, **270**, 832 (1970).
(12) M. Bergon and J. P. Calmon, *C. R. Acad. Sci., Ser. C*, **273**, 181 (1971).
(13) M. W. Rathke and J. Deitch, *Tetrahedron Lett.*, 2953 (1971).
(14) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).
(15) V. H. Wallingford, A. H. Homeyer, and D. M. Jones, *J. Amer. Chem. Soc.*, **63**, 2252 (1941).
(16) C. H. Ward, *J. Chem. Educ.*, **39**, 95 (1962).

Notes

Medium Effects in the Acid-Catalyzed Hydrolysis of Phenylacetohydroxamic Acid in Aqueous Sulfolane

D. C. Berndt

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001

Received July 23, 1973

Tetramethylene sulfone (sulfolane) is a typical dipolar aprotic solvent. Inspection of the data of Tommila and coworkers[1] on aqueous sulfolane mixtures reveals a rather special relationship, namely, that these mixtures approximate regular solutions[2] in which the entropy of mixing is nearly that of ideal mixtures. This result is unexpected for mixtures of polar substances such as sulfolane and water and might lead to interesting solvent effects upon reactivity. In addition there appear to be no studies of acid-catalyzed hydrolyses in these media. Consequently, a study of the effect of aqueous sulfolane mixtures on an acid-catalyzed hydrolysis reaction has been carried out.

The kinetics of acid-catalyzed hydrolysis of phenylacetohydroxamic acid in various aqueous sulfolane mixtures has been studied and the results are listed in Table I.

The accepted mechanism[3-5] for acid-catalyzed hydrolysis of hydroxamic acids is represented by eq 1 and 2.

$$\text{RCONHOH} + \text{H}^+ \overset{K}{\rightleftharpoons} \text{R}\overset{+}{\text{C}}\text{(OH)NHOH} \qquad (1)$$

$$\text{R}\overset{+}{\text{C}}\text{(OH)NHOH} + \text{H}_2\text{O} \xrightarrow{k_2} \text{RCO}_2\text{H} + \text{H}_3\overset{+}{\text{N}}\text{OH} \qquad (2)$$

Under pseudo-first-order conditions (excess catalytic acid and water) the observed first-order rate constant, k, is given by eq 3 for the above mechanism where K is an

$$k = k_2K[\text{H}^+][\text{H}_2\text{O}]^n \qquad (3)$$

equilibrium constant and k_2 is a rate constant. The order of reaction with respect to catalytic acid has been established previously[3-5] for the conditions employed in this study. Since sulfolane is a very weak base,[6] the hydrated proton is the catalytic acid under the conditions employed. The order with respect to water, n, will be one for the above mechanism unless there is a *difference* between the number of water molecules hydrogen bonded in the transition state and in the initial state. As the concentration of water is varied (with pseudo-first-order conditions maintained) in the presence of a nonreactive cosolvent, the rate changes as a result of general solvent effects as well as a result of differing water concentrations, as shown in eq 3.

If the solvent effect is only a dielectric constant effect, then a graph of $\log k/[\text{H}_2\text{O}]^n$ *vs.* the reciprocal of the dielectric constant would yield a straight line. This relationship was tested for the data at 50.5 and 70.3° for $n = 0$, 1, and 2. Dielectric constants for 50 and 70° were obtained by interpolation of the extensive data of Tommila and coworkers.[1] Curves resulted in all cases with the same trends obtained for the data at 50.5° (ionic strength 0.240 *M*) and at 70.3° (ionic strength 0.0479 *M*). Two ionic strengths were investigated, since in principle the ionic strength as well as the dielectric effect influence the reaction rates, although in practice the ionic strength effect is very small for this type of reaction and rate constants need not be extrapolated to zero ionic strength to test for dielectric constant correlations.[7] Reynaud[8] has determined pK_a values for some carboxylic acids and pK (BH+) values for some amines in aqueous sulfolane. Graphs of his values *vs.* the reciprocal of the dielectric constant yield essentially straight-line relationships.

A possible relationship between the observed pseudo-first-order constant, k, and the mole fraction of sulfolane, N_s, in the solvent is given in eq 4 and 5 where n, a, and b are

$$\log \frac{k}{[\text{H}_2\text{O}]^n} = aN_s + b \qquad (4)$$

or

$$\log k = n \log[\text{H}_2\text{O}] + aN_s + b \qquad (5)$$

Table I
Kinetic Data for Hydrolysis of Phenylacetohydroxamic Acid in Aqueous Sulfolane

Wt % sulfolane	Mole fraction of sulfolane	[Water], *M*	[HCl], *N*	Temp, °C	$10^5 k$,[a] sec^{-1}
0	0	55.51	0.240	50.5	4.12
32.58	0.0675	39.98	0.240	50.5	4.58
52.50	0.142	29.55	0.240	50.5	5.63
70.20	0.261	19.33	0.240	50.5	8.13
95.80	0.774	2.90	0.240	50.5	23.2
0	0	55.51	0.0479	70.3	4.45
34.92	0.0744	38.46	0.0479	70.3	5.03
49.09	0.126	31.56	0.0479	70.3	5.83
67.89	0.241	20.80	0.0479	70.3	8.02
88.57	0.537	7.785	0.0479	70.3	19.8

[a] Average pseudo-first-order rate constant.

constants. A least-squares multiple regression analysis of the data at 70.3° in Table I yields a value of 0.82 for *n*, the order with respect to water. The coefficient of multiple regression for eq 5 is 1.000 to three significant figures. Figure 1 shows a graph of this data for log $k/[H_2O]$ *vs.* mole fraction sulfolane where *n* is taken to be 1. An excellent linear relationship results. This represents a range of 0–88.6 wt % sulfolane (0–0.54 mol fraction sulfolane). A graph of log $k/[H_2O]$ *vs.* mole fraction sulfolane for the data at 50.5° (0–95.8 wt %, 0–0.77 mol fraction sulfolane) is linear but not as exact as Figure 1.

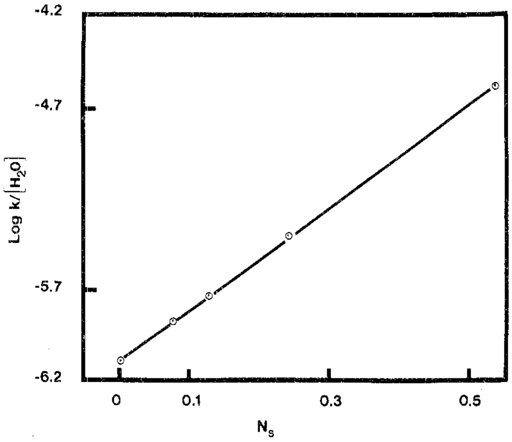

Figure 1. Log $k/[H_2O]$ as a function of mole fraction of sulfolane for hydrolysis of phenylacetohydroxamic acid in aqueous sulfolane mixtures 0.0479 *N* with respect to HCl at 70.3°.

Equation 4 is a linear free-energy relationship. Koppel and Palm[9] have discussed in detail linear free-energy relationships in solvent effects. A linear relationship between log *k* and the mole fraction of one component of a binary solvent system is predicted under certain conditions, namely, that the nonspecific and specific solvent–solute interactions of each solvent component are invariable (including the absence of shifts in solvation equilibria) throughout the range of solvent composition involved. Koppel and Palm[9] consider two types of nonspecific solvent effects, dielectric effects and polarizability interactions. Since a linear relationship between log $k/[H_2O]$ and the reciprocal of the dielectric constant does not exist for this system (see above) and since the reciprocal of the dielectric constant is not linear in mole fraction sulfolane, dielectric effects can be discounted in the system reported herein.

It is noteworthy that linear relationships between log *k* and mole fraction sulfolane are not evident in the alkaline hydrolysis of dimethylacetylacetone[10] or in the alkaline hydrolysis of benzoate esters[11] in aqueous sulfolane.

Experimental Section

Phenylacetohydroxamic acid has been described previously.[5] Sulfolane was distilled at low pressure from sodium hydroxide pellets, $n^{30}\text{D}$ 1.4816 (lit.[12] 1.4820). All solutions were prepared with double-distilled water with concentrations referred to ambient temperature. The kinetic measurements were made and the rate constants were calculated as described before.[5] Initial concentration of phenylacetohydroxamic acid for rate measurements at 50.5° was 0.0120 *M* and for those at 70.3° was 0.00600 *M*. Average deviation from the mean for average rate constants in Table I is less than 1.5%.

Registry No.—Phenylacetohydroxamic acid, 5330-97-2.

References and Notes

(1) E. Tommila, E. Lindell, M. Virtalaine, and R. Laakso, *Suom. Kemistilehti B*, **42**, 95 (1969).
(2) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.
(3) D. C. Berndt and R. L. Fuller, *J. Org. Chem.*, **31**, 3312 (1966).
(4) A. J. Buglass, K. Hudson, and J. G. Tillett, *J. Chem. Soc. B*, 123 (1971).
(5) D. C. Berndt and J. K. Sharp, *J. Org. Chem.*, **38**, 396 (1973).
(6) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).
(7) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York, N. Y., 1966, p 33.
(8) R. Reynaud, *Bull. Soc. Chim. Fr.*, 4597 (1967).
(9) I. A. Koppel and V. A. Palm, "Advances in Linear Free Energy Relationships," N. B. Chapman and J. Shorter, Ed., Plenum Press, New York, N. Y., 1972, Chapter 5.
(10) J. P. Calmon and J. L. Canavy, *J. Chem. Soc., Perkin Trans. 2*, 972 (1972).
(11) E. Tommila and J. Martinmaa, *Suom. Kemistilehti B*, **40**, 216 (1967).
(12) J. W. Vaughn and C. F. Hawkins, *J. Chem. Eng. Data*, **9**, 140 (1964).

Proximity Effects. Correlation of Ortho-Substituted Benzohydroxamic Acid Reactivities[1]

D. C. Berndt* and I. E. Ward

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001

Received October 2, 1973

The role of ortho substituents in chemical reactivity is complicated by several factors which may contribute to the reactivity effect of these substituents.[2,3] Empirical correlation schemes are useful for systematizing the data and for comparison of effects in related systems which will lead to further understanding of reactivity parameters and reaction mechanisms. The Pavelich–Taft equation (eq 1)

$$\log k/k_0 = \rho^*\sigma^* + \delta E_s \qquad (1)$$

is based upon reactions of esters and was developed for analysis of systems in which steric effects are expected to be present.[2,3]