Addition of ether, decolorization of excess iodine with aqueous sodium thiosulfate, washing with 5 × 100 ml of 5 *M* potassium iodide or 3 *M* sodium thiosulfate (to remove mercuric iodide) and 2 × 100 ml of saturated sodium bicarbonate, decolorization with activated carbon, and drying over anhydrous sodium sulfate gave a solution which upon distillation yielded 9.82 g (84%) of *n*-butyl acetate.

All yields determined by glpc analysis were run in a similar fashion on a 10-mmol scale using a suitable hydrocarbon internal standard. The exact experimental procedures used for hydroboration–mercuration are those reported earlier.[3] THF is readily removed under vacuum and replaced by dry diglyme. In those reactions in which diglyme interferes with the distillation of the desired ester, THF is recommended as a reaction solvent, although slightly lower yields are generally obtained.

All organoboranes prepared from monosubstituted alkenes by hydroboration in THF possess 6% of *sec*-alkylboron groups which will not react.[3] Thus 10% less mercuric acetate and iodine were used and all yields were based on available primary alkylboron groups.

The Boron Triacetate Catalyzed Conversion of *n*-Butyl Iodide to Acetate. Ten milliliters of 0.1 *M* boron triacetate was prepared by addition of 0.42 ml (1 mmol) of 2.4 *M* "borane" in THF to 9.4 ml of THF containing 0.18 g (3.0 mmol) of acetic acid at −78°. After removal of the cold bath, this solution was stirred for 3 hr at room temperature. To this solution was added 1.84 g (10 mmol) of *n*-butyl iodide, the appropriate amount of mercuric acetate (5 or 10 mmol) and/or mercuric iodide (5 mmol), and 0.8 ml of nonane as an internal standard. Glpc analysis indicated the extent of reaction.

Acknowledgment. The author gratefully acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research. The capable assistance of Mr. Gary Molander and Mr. Stephan McLain is also deeply appreciated.

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Polarographic and Spectrophohotometric Evaluation of Acid Dissociation Constants of Some Substituted Ethyl Benzoylacetates

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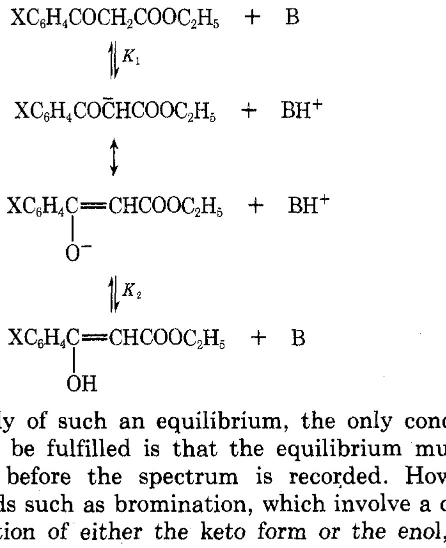
Received June 25, 1973

The overall dissociation constants K_Σ of ethyl benzoylacetate and *p*-methoxy, -methyl, -chloro, and -cyano derivatives were evaluated spectrophotometrically and polarographically, and [enol]/[keto] ratios were measured by titration with bromine. Values of the dissociation constants of the keto (K_1) and enol (K_2) forms were isolated; like polarographic half-wave potentials, they were shown to be linear functions of Hammett substituent constants $\sigma_{p\text{-X}}$.

In alkaline solutions of β-keto esters, the keto and enol forms dissociate to give a common conjugate base, the carbanion enolate (eq 1). When spectrophotometry is used for the study of such an equilibrium, the only condition which must be fulfilled is that the equilibrium must be established before the spectrum is recorded. However, with methods such as bromination, which involve a chemical interaction of either the keto form or the enol, it is essential that the establishment of the keto–enol equilibrium be slow in comparison with the competing reaction. Information on the rate of establishment of this equilibrium, which is of interest with respect to the general reactivity of the carbonyl compound, can be obtained by polarography. Using accepted criteria,[1] it is possible to show whether the limiting current is governed by diffusion or by the rate of chemical reaction. If, for a system at equilibrium, the limiting current of one species is diffusion controlled, the rate of establishment of the equilibrium must be much lower than the rate of the mass transport by diffusion. This has been found to be true for unsubstituted ethyl benzoylacetate.[2]



$$\begin{array}{ll} XC_6H_4COCH_2COOC_2H_5 + B & \\ \quad\upharpoonleft\!\downharpoonright K_1 & \\ XC_6H_4CO\bar{C}HCOOC_2H_5 + BH^+ & (1a) \\ \quad\updownarrow & \\ XC_6H_4\underset{O^-}{\underset{|}{C}}{=}CHCOOC_2H_5 + BH^+ & (1b) \\ \quad\upharpoonleft\!\downharpoonright K_2 & \\ XC_6H_4\underset{OH}{\underset{|}{C}}{=}CHCOOC_2H_5 + B & \end{array}$$

It was of interest to investigate phenyl-substituted benzoylacetates to follow the substituent effects on the acid–base and keto–enol equilibria and to show whether the presence of substituents affects the relatively slow rate of establishment of equilibrium 1.

In view of the nature of system 1, it seemed preferable to attempt first separation of the two acid dissociation constants K_1 and K_2 from experimental data rather than to try to express the substituent effects on the [enol]/[keto] ratio.

Values of K_1 and K_2 are usually not directly accessible to measurement, but they can be calculated from two kinds of measurable quantities: The first of these is the value of the overall acid–base dissociation constant K_Σ, defined by the expression K_Σ = [carbanion enolate][H^+]/([keto form] + [enol form]). The value of K_Σ is re-

Table I
Spectral Properties of Substituted Benzoylacetates (10% Aqueous Ethanol)

	Keto form						Anion					
	$\pi \rightarrow \pi^*$		B		$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		B		$n \rightarrow \pi^*$	
Substituent	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	λ, nm
p-CH$_3$	<200	$>1.5 \times 10^4$	262	1.46×10^4	~290	$<2 \times 10^2$	<210	$>1 \times 10^4$	239	$\sim 6 \times 10^3$	304	1.4×10^4
H	<200	$>1.8 \times 10^4$	250	1.28×10^4	~286	$\sim 8 \times 10^2$	<210	$>8 \times 10^3$	232	$\sim 7 \times 10^3$	303	1.3×10^4
p-Cl	<190	$>1 \times 10^4$	260	1.45×10^4	~280	$<1 \times 10^2$	<200	$>1 \times 10^4$	237	$\sim 7 \times 10^3$	305	1.3×10^4
p-CN	<200	$>2 \times 10^4$	251	2×10^4	~320[a]	$\sim 6 \times 10^2$	<200	$>2 \times 10^4$	240	$>1.9 \times 10^4$	325	1×10^4
p-OCH$_3$	<200	$>1.3 \times 10^4$	283	1.5×10^4	~290	$<1 \times 10^2$	<200	$>1.3 \times 10^4$	248	$\sim 6 \times 10^3$	305	1.7×10^4

[a] Broad band, envelope of three or more peaks.

Table II
Acid Dissociation Constants and Half-Wave Potentials of Substituted Benzoylacetates

		Spectral data[a]			Polarographic data[b]		
						$-E_{1/2}$, V *vs.* sce	
Registry no.	Substituent	σ	pK_Σ	$\lambda_{\max}$ (nmr)	pK_Σ*	pH 8.45	pH 10.0
2888-83-6	p-OCH$_3$	−0.27	10.81	240	10.8	−1.46	−1.54
27835-00-3	p-CH$_3$	−0.17	10.51	305	10.5	−1.41	−1.47
94-02-0	H	0	10.35	305	10.35	−1.37	−1.43
2881-63-2	p-Cl	0.23	9.86	305	9.9	−1.31	−1.38
49744-93-6	p-CN	0.66	9.00	305	9.1		

[a] 1×10^{-4} M solutions containing 10% ethanol. [b] 2×10^{-4} M solutions containing 10% ethanol.

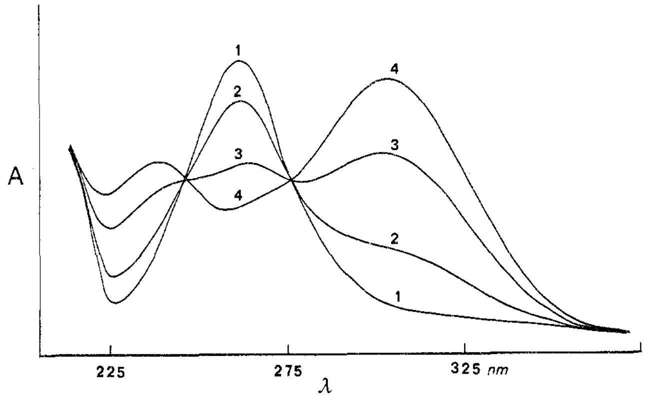


Figure 1. Dependence of absorption spectra of 1×10^{-4} M p-methylbenzoyl acetate on pH. Buffers used: (1) borate, pH 9.1; (2) borate, pH 10.1; (3) phosphate, pH 11.1; (4) phosphate, pH 11.4.

lated to the dissociation constants K_1 and K_2 by the equation $K_\Sigma = K_1K_2/(K_1 + K_2)$. The other accessible value is the ratio [enol form]/[keto form], which is equal to the ratio of K_1/K_2.

It may be pointed out that, contrary to some traditional belief, the [enol]/[keto] ratio is pH independent. As the pH increases,[3] the sum of concentrations [enol] + [keto] decreases. Simultaneously the concentration of the carbanion enolate increases, and the ratio of the sum of the [enol] + [keto] to the concentration of the anion changes. A plot of the concentration of any of these three forms (enol, keto, or carbanion enolate) against pH has the shape of a simple dissociation curve with an inflexion point at pH = pK_Σ.

The [enol]/[keto] ratio is most conveniently evaluated at a pH value low enough to render the concentration of the ambident anion negligible and maximize the concentrations of the keto and enol forms.

From the values of K_Σ and the ratio [enol]/[keto], it is possible[4] to calculate the value of K_1 by means of the expression $K_1 = K_\Sigma(1 + [\text{enol}]/[\text{keto}])$, then to calculate that of K_2 from K_1 and the expression $K_2 = K_1([\text{keto}]/\text{enol}])$. If in aqueous solutions the keto form strongly predominates, so that [enol] << [keto], then the measured value of K_Σ is practically equal to K_1.

To apply this treatment to substituted ethyl benzoylacetates, it was first necessary to determine corresponding values of K_Σ. Both spectrophotometric and polarographic measurements were used for this purpose. Titration with bromine was used to evaluate the ratio [enol]/[keto], taking advantage of the fact that the keto–enol equilibrium is slowly established.

Results and Discussion

At pH < 8 ethyl benzoylacetates show an intensive $\pi \rightarrow \pi^*$ absorption band at about 200 nm and a very weak n → π^* band at 290–320 nm. A third, intensive band corresponding to the benzenoid absorption of the C_6H_5CO grouping was observed at 250–280 nm. In alkaline media the carbanion enolate $XC_6H_4COCHCOOC_2H_5^- \leftrightarrow XC_6H_4C(O^-) = CHCOOC_2H_5$ shows an intensive $\pi \rightarrow \pi^*$ absorption band at short wavelengths, a medium-intensity benzenoid band at 230–250 nm, and an intensive band at 305–325 nm which is characteristic for carbanion enolates. Spectral data are summarized in Table I.

Spectra recorded at different pH values show an isosbestic point (Figure 1) provided that they are obtained within 5 min after mixing of the stock solution with the buffer. At higher pH values the spectra change during the

Table III
Separation of Dissociation Constants of the Keto (K_1) and Enol (K_2) Forms of Substituted Benzoylacetates

Substituent	σ	$K \times 10^{-11}$	% enol	[enol][a]/[keto]	K_2[b] $\times 10^{-9}$	K_1[c] $\times 10^{-10}$
p-OCH_3	−0.27	0.158	15.6	0.18	0.104	0.187
p-CH_3	−0.17	0.316	15.9	0.19	0.198	0.376
H	0	0.447	12.3	0.14	0.364	0.310
p-Cl	0.23	1.31	13.2	0.15	1.00	1.50
p-CN	0.66	8.90	14.3	0.17	6.12	10.4

[a] [Enol]/[keto] = K_1/K_2. [b] $K_2 = K_\Sigma(1 + [\text{enol}]/[\text{keto}])/([\text{enol}]/[\text{keto}])$. [c] $K_1 = K_2\,[\text{enol}]/[\text{keto}]$.

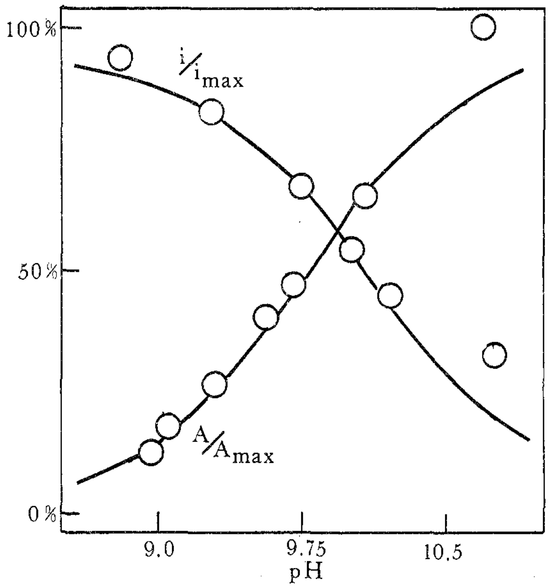


Figure 2. Dependence of absorbance at 320 nm ($100\,A/A_{max}$) and polarographic limiting currents ($100\,i/i_{max}$) of p-chlorobenzoyl acetate on pH. The value for i_{max} was measured at pH 8, that for A_{max} at pH 11. Experimental points, theoretical curves.

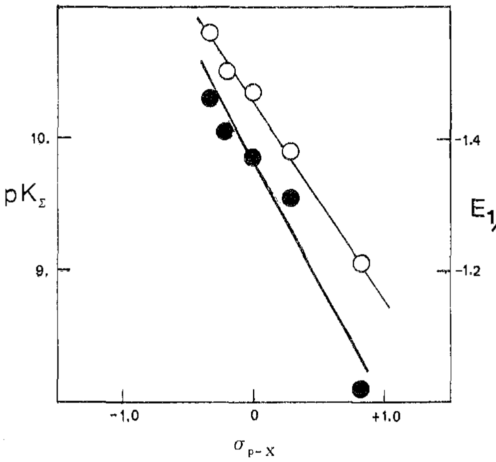


Figure 3. Dependences of the overall acid dissociation constant (pK_Σ) and half-wave potential ($E_{1/2}$) on Hammett substituent constants σ_X. pK_Σ values, circles; $E_{1/2}$ (*vs.* sce), full points.

first hour because of hydrolysis, which was particularly important in the case of the p-cyano derivative.

The absorbance of a freshly prepared solution measured at the wavelength of the absorption maximum of either the carbanion enolate or the benzenoid band of the keto form plotted against pH shows a dependence in the shape of a dissociation curve of a monobasic acid (in Figure 2 the deviation at pH 10.75 is due to hydrolysis). Values of pK_Σ determined from such curves are given in Table II.

Polarographic current–voltage curves, obtained with dropping mercury electrode, show one two-electron cathodic wave at pH ~ 8 which corresponds to the reduction of the unprotonated carbonyl group.[2] At pH > 8, a plot of the height of this wave against pH has shape of a dissociation curve decreasing with increasing pH, which corresponds to a monobasic acid (Figure 2). At pH 11, where the current i is less than 15% as large as at pH ~ 8, the wave height is directly proportional to the square root of the height of the mercury column, which indicates that the current is diffusion controlled. Hence the limiting currents are a linear function of the bulk concentration of the keto form over the entire pH range studied. Conditions are thus fulfilled for the use of the wave height measurement for determination of pK_Σ values.[5]

The values of pK_Σ obtained from the pH dependence of polarographic and spectrophotometric data were in very good agreement (Table II).

The facts that polarographic limiting currents were diffusion controlled and that the polarographic and spectrophotometric values coincide indicate that the keto form is comparatively slowly regenerated from the carbanion enolate when the equilibrium between them is perturbed by the electroreduction of the former. More specifically, it can be deduced[6] that the second-order rate constant for the protonation of the carbanion enolate on carbon must be smaller than about 4×10^9 l. mol^{-1} sec^{-1} for the p-cyanobenzoyl acetate or smaller than about 7×10^{10} l.mol^{-1} sec^{-1} for p-methoxybenzoyl acetate.

Polarographic curves of these compounds show an adsorption prewave, which is separated from the main wave only at pH < 5. At higher pH values, in the pH region where height of the main wave decreases, the adsorption process could be detected only through its effect on the shape of the instantaneous current–time curves recorded at potentials near the foot of the wave. The portion of the wave which is governed by adsorption is less dependent on pH than the diffusion-controlled portion at more negative potentials. This effect contributed to deviations of experimental points from the theoretical shape of the dissociation curve at higher pH values (*e.g.*, at pH 10.75, Figure 2).

Whereas limiting currents of most of the waves were parallel with the potential axis even in the pH range where the wave height was observed to decrease, a deformation (a trough) was observed on the limiting current of ethyl p-cyanobenzoylacetate. This deformation has been attributed to adsorption. Since the wave remains diffusion controlled in its unaffected portion, the origin of this process must be different from the surface phenomena accompanying kinetic currents.[7]

The values of pK_Σ obtained either spectrophotometrically or polarographically for para-substituted ethyl benzoylacetates are a linear function of Hammett substituent constants $\sigma_{p\text{-}X}$ (Figure 3) and the reaction constant ρ is 1.84 (r = 0.992). Attempts to correlate the values of pK_Σ with $\sigma^+_{p\text{-}X}$ were much less satisfactory. Comparison of the values of the reaction constant for the bases $ArCOCH^-$ and $ArCOO^-$ for which ρ = 1.0 by definition indicates that the carbanion enolate is more susceptible to

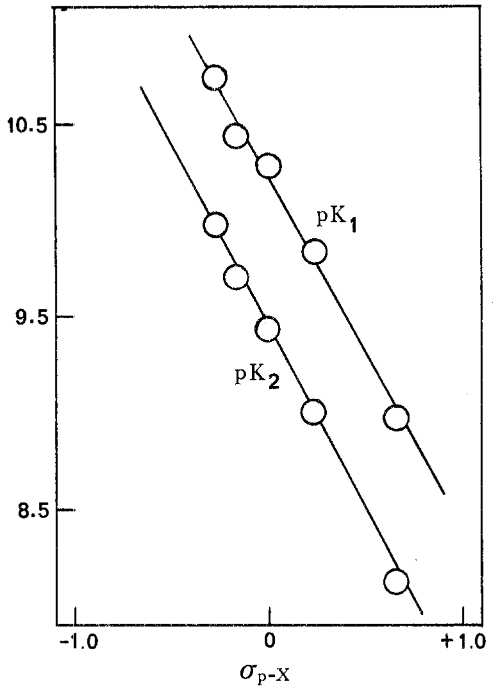


Figure 4. Dependence of the dissociation constant of the keto form (pK_1) and the enol form (pK_2) on Hammett substituent constants σ_X.

the transmission of substituent effects than the carboxylate ion by a factor of about 1.5.

Polarographic half-wave potentials of all benzoylacetates investigated in this study are shifted by about 45-50 mV/pH to more negative potentials with increasing pH. The linear plots were practically parallel at pH < pK_Σ, showing that the value of αn_a remains approximately constant within the reaction series. At higher pH values the half-wave potentials of the *p*-methoxy and *p*-methyl derivatives became pH independent. The intersection of the two linear portions, at pH 10.35 for *p*-OCH_3 and at pH 10.25 for *p*-CH_3, respectively, were observed at somewhat smaller pH values than corresponds to pK_Σ. For the other derivatives, the adsorption prewaves that were present at pH > p*K* made the measured values of half-wave potentials less accurate and reliable at higher pH values.

For a study of the substituent effects, the half-wave potentials measured at any pH value below 10 were suitable, because the plots of half-wave potentials against pH were parallel in this pH region. The half-wave potentials are a linear function[8] of Hammett substituent constants $\sigma_{p\text{-}X}$ (Figure 3). The susceptibility of the molecule to substituent effects (ρ_π = 0.29 V; *r* = 0.983) is of the order of magnitude which would be predicted[8] ($\rho_\pi \sim 0.3$ V) from the ρ_π–E_0 relationship for a system where the unsubstituted parent compound is reduced at about −1.4 V *vs.* sce.

Unlike the pK_Σ values and half-wave potentials, the ratio [enol]/[keto] does not seem to show any noticeable correlation with substituent constants $\sigma_{p\text{-}X}$ (Table III). This may be due to the small variations of these ratios with substituents. The enol concentrations found in solutions containing 10% ethanol are somewhat higher than the value reported[9] for aqueous solutions. This is in agreement with the prediction of the linear free energy relationship expressing solvent effects on such equilibria.[10] Nevertheless, when the dissociation constants (Figure 4) of the keto form (K_1) and enol form (K_2) are evaluated separately as described in the introduction, the values of pK_1 (*r* = 0.996) and pK_2 (*r* = 0.998) show an excellent correlation with substituent constants $\sigma_{p\text{-}X}$. Identical values of the reaction constant (ρ = 1.84) were determined for the two reaction series.

This indicates that the introduction of a substituent exerts its predominant effect on the electron density distribution on the carbanion enolate rather than on that of either on the keto or the enol form. Comparison of the individual contributions indicates that changes in the value of the dissociation constant of the keto form are predominantly due to the changes in the value of K_Σ and are almost unaffected by the relatively small changes in the value of the [enol]/[keto] ratio.

On comparing the results presented here with the fractions of the keto form reported[11] in neat substituted ethyl benzoylacetates, it can be concluded that the larger variations observed in neat compounds than in solutions are probably chiefly due to the effect of the change in solvent rather than to the substituent effect in the solute. A neat compound should be regarded as a solution of the given compound in the same compound as solvent. The role of a strong solvent effect might explain why the correlation of the log ([enol]/[keto]) was reported[11] to be better with σ_X^+ than with σ_X. Our results for dilute solutions of β-keto esters can be compared with those for dilute solutions of β-diketones.[12] Although variations in the ratios [enol]/[keto] are relatively small also for substituted benzoylacetones, the differences, *e.g.*, between the unsubstituted parent compound (34% enol form) and the *p*-chloro derivative (35.5%), are comparable with those observed for benzoylacetates (Table III). As values of K_Σ are not available for benzoylacetones, it is difficult to distinguish the origin of the individual contributions as expressed by the values of dissociation constants K_1 and K_2. Nevertheless, from the reported linear dependence of log ([enol]/[keto]) on σ (even though *r* is only 0.952), it is possible to assume that the variation in [enol]/[keto] ratios of β-diketones is more affected by introducing a meta or para substituent than we have found it to be for β-keto esters.

Experimental Section

Synthesis. The procedure of Rathke[13,14] has been found to be superior to Claisen condensation[15] for preparation of ethyl benzoylacetates substituted on the phenyl ring.

General Procedure. In a dry 250-ml round-bottom flask equipped with a magnetic stirrer and a mercury bubbler, 14.1 g of *N*-isopropylcyclohexylamide was added dropwise under N_2 to 30 g of a 1 *M* solution of *n*-butyllithium in hexane. After 10 min, the hexane was removed by reduced pressure and 50 ml of tetrahydrofuran was added to the residue.

After cooling in a Dry Ice-acetone bath, 4.4 g (50 mmol) of ethyl acetate was added dropwise over 5 min, followed after 10 min by 50 mmol of the substituted benzoyl chloride. After another 10 min, 30 ml of 20% HCl was quickly added to quench the reaction.

After warming to room temperature and adding enough water to dissolve the LiCl formed, the tetrahydrofuran was separated and the remaining aqueous phase was washed with ether. The combined tetrahydrofuran-ether mixture was dried and evaporated off. The residue was dissolved in 50 ml of absolute ethanol, and a saturated solution of $Cu(OAc)_2$ was added until no more precipitate formed. After filtering and washing the solid with ethanol, enough 10% acetic acid to dissolve the precipitate was added along with 50 ml of ether. The organic layer was separated off, washed with H_2O and with saturated $NaHCO_3$, and then removed by evaporation.

The residue was recrystallized from petroleum ether (bp 30-60°)-ether if solid, or distilled under reduced pressure if liquid. All compounds gave physical and spectral properties in agreement with the reported values.

The yields follow: *p*-Cl (10%), *p*-CH_3 (40%), *p*-CN (90%), *p*-OCH_3 (50%). Ethyl *p*-cyanobenzoylacetate, previously unreported, formed yellow crystals, mp 63-64° (uncorrected).

Spectra. Electronic spectra of 1×10^{-4} *M* aqueous solutions of ethyl benzoylacetates, containing 10% ethanol and simple borate or phosphate buffers, were recorded in a 10-mm quartz cell using 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.

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Notes

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

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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.

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

$$\mathrm{R\overset{+}{C}(OH)NHOH} + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{RCO_2H} + \mathrm{H_3\overset{+}{N}OH} \qquad (2)$$

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

$$k = k_2K[\mathrm{H}^+][\mathrm{H_2O}]^n \qquad (3)$$

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 $k/[\mathrm{H_2O}]^n$ *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

$$\log \frac{k}{[\mathrm{H_2O}]^n} = aN_s + b \qquad (4)$$

or

$$\log k = n \log[\mathrm{H_2O}] + aN_s + b \qquad (5)$$