change in over-all rate constant. In 75 to 100% acid $[BH^{\oplus}]/[B]_{stoich}$ is unity (*i.e.*, ionization to $BH^{\oplus}$ practically complete) and a gradual decrease in $\Sigma k_{-2}[A_i]/\Sigma k_3[A_i]$ apparently is such that the decreases in numerator and denominator of equation 18 approximately balance each other over a goodly part of this range, giving near agreement with the predictions of a unimolecular mechanism (dotted line, Fig. 2). Finally, in the highest sulfuric acid concentration (95–100%) the numerator will be decreasing more rapidly than the denominator (*i.e.*, the denominator is approaching the limiting value of unity as $\Sigma k_{-2}[A_i]$ becomes sufficiently smaller than $\Sigma k_3[A_i]$) and a decrease in over-all rate constant is observed.

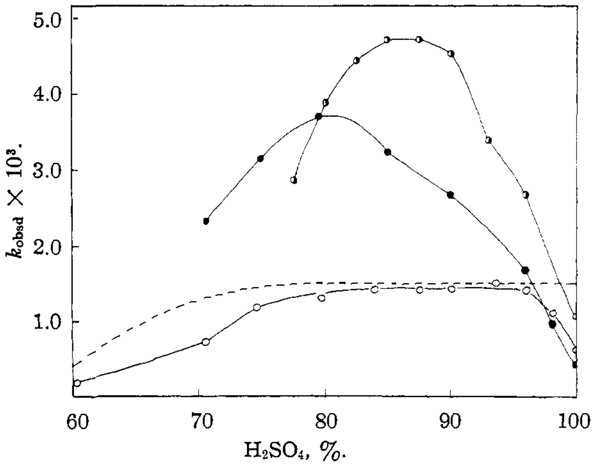


Fig. 2.—Change in k_{obsd} with % H_2SO_4: ○, mesitaldehyde at 100.0°; ◑, 2,4,6-triethylbenzaldehyde at 100.0°; ●, 2,4,6-triisopropylbenzaldehyde at 80.0°; ---, theoretical unimolecular k_{obsd} calculated for equation 4.

For triisopropylbenzaldehyde, ionization to $BH^{\oplus}$ is practically complete in 80% sulfuric acid (pK_a = −5.1, ref. 5) and k_{obsd} would reach a maximum at about this point. The quantity $\Sigma k_{-2}[A_i]/\Sigma k_3 \cdot [A_i]$ should be decreasing more rapidly with increasing acid percentage (*i.e.*, with decreasing water to bisulfate ion ratio) than for mesitaldehyde. This would be due to the greater increase in steric strain in the transition state for step 2 reverse (compared to step 3) with bisulfate ion as compared to water as the base. The result should be a sharper maximum in k_{obsd} and a more rapid decrease in k_{obsd} in higher acid percentages, as found. For triethylbenzaldehyde, the curve, Fig. 2, should be intermediate between that for mesitaldehyde and that for triisopropylbenzaldehyde, also as found.

Termolecular Mechanisms.—Conceivable termolecular mechanisms are given by equations 5 through 8. Mechanism 5 predicts $k_{H_2SO_4} > k_{D_2SO_4}$ for mesitaldehyde in all sulfuric acid concentrations and therefore does not account for the fact that $k_{H_2SO_4}$ is less than $k_{D_2SO_4}$ in 59–70% acid (Table IV). Mechanism 6 cannot account for the fact that $k_{H_2SO_4}/k_{D_2SO_4}$ is experimentally equal to $[BH^{\oplus}]/[BD^{\oplus}]$ in 59–70% acid (Table IV) since $k_{6(H_2SO_4)}$ should be greater than $k_{6(D_2SO_4)}$. Furthermore one would not expect k_{ArCHO} to be greater than k_{ArCDO} (Table III). Mechanism 7 can be rejected on the same grounds. Mechanism 8 is inconsistent with the observed isotope effects since it requires that $\Sigma k_{8(H_2SO_4)}[HA_i][A_i]$ be equal to $\Sigma k_{8(D_2SO_4)}[DA_i][A_{iD_2SO_4}]$ in 59 to 70% acid (although proton *vs.* deuteron transfer is involved) but not in higher per cent. acid.

No termolecular mechanism accounts for the isotope effects in 59–70% acid. It is still conceivable, though not considered likely, that the bimolecular mechanism with step 3 rate-controlling, shown to prevail in 59–70% acid, changes to a termolecular mechanism (*i.e.*, equation 5) at higher acid percentages.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF NOTRE DAME AND UNIVERSITY OF PENNSYLVANIA]

Acid Dissociation Constants and Rates of Saponification for 2-Furoic and β-2-Furyl-, β-2-Thienyl- and β-1-Naphthylacrylic Acids

BY CHARLES C. PRICE[1] AND EDWARD A. DUDLEY

RECEIVED JULY 15, 1955

The rate of saponification of ethyl 2-furoate is considerably slower than predicted from the pK_a for the acid, similar to previous observations[2] for 2-thenoic and 1-naphthoic acids. This effect disappears in the three corresponding β-arylacrylic acids. The data indicate a stereospecific acid strengthening factor, for 2-thenoic and 2-furoic acids and it is suggested that this factor may be chelate hydrogen bonding.

In an earlier report,[2] it was pointed out that the esters of several 1-naphthoic and 2-thenoic acids all saponified at a rate slower than predicted from the Hammett expression relating the rate of saponification of various substituted[3] benzoic acids to the dissociation constants. Since the course of saponification, involving expansion of the carboxyl carbon from trigonal to tetrahedral, would impose considerable steric demands compared to the simple removal of a proton in dissociation, it was proposed that this effect was some sort of steric hindrance to the saponification process.

The source of such a steric hindrance for the case of ethyl 1-naphthoate is quite obvious since this ester is, in effect, an *ortho*-substituted benzoate. For ethyl 2-thenoate one would have to presume

---

[1] Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

[2] C. C. Price, E. C. Mertz and J. Wilson, THIS JOURNAL, **76**, 5131 (1954).

[3] The relationship fails frequently for *ortho*-substituted benzoic acids due to steric effects superimposed on the electrical effects normally involved in correlations following the Hammett equation.

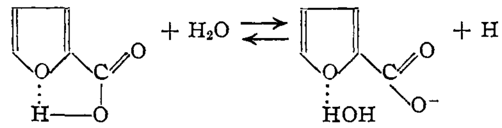
that the ring sulfur is about equal in bulk to the *peri*-CH group of the 1-naphthoate. To test further the possible steric nature of this effect we have studied 2-furoic acid and its ethyl ester and the three corresponding acrylic acids and esters, compounds in which electrical effects of the nuclei could be passed on to the reactive group but in which direct steric factors would be eliminated.

The experimental data, summarized in Table II, support the view that the saponification of ethyl 1-naphthoate proceeds slower than predicted from the pK_a of the acid because of steric hindrance, since the insertion of a vinylene group, which would eliminate the *ortho*-hindrance, produces an ester which saponifies slightly faster than predicted by the pK_a of the corresponding acid.

The data of Table II do not, however, support the previous suggestion that the discrepancy between the pK_a (σ_a) and saponification (σ_s) values for 2-thenoic acid was also due to a steric factor which decreased the rate of saponification. Thus the insertion of a vinylene group in either 2-thenoic or 2-furoic acid gave values for σ_a and σ_s for furyl and thienylacrylic acids in agreement with σ_s for the parent acids. The most reasonable interpretation of the data is therefore that there is a stereospecific factor in 2-thenoic acid, and more so in 2-furoic acid, which causes them to be stronger acids. This is not a normal electrical effect, for this would be exerted in the ester as well as the acid and would be transmitted by the vinylene group.

We therefore conclude that the stereospecific acid strengthening factor is one involving the proper relationship of the carboxylic hydrogen and the heteroatom of the ring. This view is further supported by the earlier data[2] indicating agreement between σ_a and σ_s for 3-thenoic acid.

The most likely representation we can offer for this acid-strengthening effect is chelate hydrogen bonding. Support for the importance of such a chelate bonded structure may be derived from the fact that no evidence for dimer could be obtained cryoscopically for solutions of 2-furoic acid in benzene.[3a] It is for this reason that we suggest the idea that dissociation may involve breaking only one, not *both*, of the bonds between the acidic hydrogen and oxygen.



We recognize the arguments which have been advanced by others to support the experimental evidence that chelation *decreases* acidity of the hydrogen atom in phenols and phosphonic acids so involved.[3b]

Experimental

The furoic acid and β-(2-furyl)-acrylic acid used were commercial products (Eastman Kodak Company) as was the ethyl furoate (Norwich Pharmacal Company). The acids were recrystallized once and the ester distilled before use. The three substituted acrylic acids were prepared by the method of King and Nord[4] for the synthesis of β-(2-thienyl)-acrylic acid. The acids were esterified with absolute ethanol using 15% fuming sulfuric acid as catalyst. The properties of the compounds are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES OF ACRYLIC ACIDS AND ETHYL ESTERS

Acrylic acid	Acid, m.p., °C. Found	Acid, m.p., °C. Lit.	Ester, b.p. (mm.), °C. Found	Ester, b.p. (mm.), °C. Lit.
β-(2-Furyl)-	142–143	141[a]	118–119 (11)	120–121 (17)[e]
β-(2-Thienyl)-	144–145	144–145[b]	138–139 (6)	118–120 (3)[f]
β-(1-Naphthyl)-	213–215	209–210[c] 212[d]	37–38 (m.p.)	37.5–38[c]

[a] S. Rajagopalan and P. V. A. Raman, *Org. Syntheses*, **25**, 51 (1945). [b] W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 405 (1949). [c] S. I. Sergievskaya and A. S. Alina, *J. Gen. Chem.* (*U.S.S.R.*), **13**, 864 (1943), *C. A.*, **39**, 926 (1945). [d] G. Lock and G. Gergely, *Monatsh.*, **79**, 521 (1948). [e] L. Claisen, *Ber.*, **24**, 143 (1891). [f] R. E. Miller and F. F. Nord, *J. Org. Chem.*, **15**, 89 (1950).

The approximate acid dissociation constants were determined at 25° in 78.1% ethanol, as previously.[2] The acid dissociation constants of 2-thenoic and 1-naphthoic acids, and the value of the Hammett equation rho for acid dissociation in this solvent are also taken from this reference. The rho value for the dissociation of the β-substituted acrylic acids (ρ = 0.80 ± 0.05) was determined from the pK_a of cinnamic (6.46), *p*-chlorocinnamic (6.32), *p*-nitrocinnamic (5.87), and *p*-methoxycinnamic (6.73) acids. The results are contained in Table II.

TABLE II

Acid	pKa	k^{25}sap × 10^3	σ_a	σ_s
Benzoic	6.37	3.42	0	0
2-Furoic	5.38	2.27	0.47 ± 0.06	−0.08 ± 0.07
2-Tbenoic	5.72	3.00	.31 ± .06	− .02 ± .04
1-Naphthoic	6.13	1.28	.12 ± .06	− .18 ± .07
Cinnamic	6.46	4.97	0	0
β-(2-Furyl)-acrylic	6.49	5.35	−0.03 ± .06	0.03 ± .06
β-(2-Thienyl)-acrylic	6.45	4.90	.01 ± .06	.00 ± .09
β-(1-Naphthyl)-acrylic	6.37	8.40	.10 ± .06	.26 ± .06

The saponification rate constants were also determined as previously,[2] and the rates for ethyl 2-thenoate and ethyl 1-naphthoate have been taken from the same source. The rho value (0.79 ± 0.05) for the saponification rates of the ethyl acrylates was determined from the saponification rates of the ethyl esters of cinnamic, *p*-chlorocinnamic, *p*-nitrocinnamic and *p*-methoxycinnamic acids ($k_{25} \times 10^3$ = 4.97, 6.94, 23.4 and 2.89 l./mole sec., respectively). The results are listed in Table II.

The values in Table II labeled σ_a and σ_s are the values of the Hammett equation constant, sigma, computed by referring the acid dissociation constants and saponification rates of furoic acid and ethyl furoate to benzoic acid and ethyl benzoate, and β-(2-furyl)-acrylic acid, β-(2-thienyl)-acrylic acid and β-(1-naphthyl)-acrylic acid and their ethyl esters to cinnamic acid and ethyl cinnamate, respectively. The σ values for 2-thenoic and 1-naphtholic acids and their ethyl esters are taken from the previous papers.[2]

PHILADELPHIA 4, PENNA.

(3a) L. M. Nazarova and Y. K. Syrkin, *Izvest. Akad. Nauk. S.S.S.R., Otdel, Khim, Nauk*, 35, 1949 (*C.A.*, **43**, 4913 (1949)).

(3b) R. T. Arnold and J. Sprung, THIS JOURNAL, **61**, 2475 (1939); H. H. Jaffe, L. D. Freedman and G. O. Doak, *ibid.*, **76**, 1548 (1954).

(4) W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 405 (1949).