

loss of the volatile olefin). The organic layer was extracted with dilute hydrochloric acid, followed by water and dried over Drierite. It was distilled to give 4.7 g. (26%) of 2-ethylbutene-1, b.p. 62–64°, n_D^{25} 1.3960, and 2.7 g. (7.6%) of recovered 2-ethylbutyl bromide-2*d*₁, b.p. 70–75° at 59 mm., n_D^{25} 1.4495. The olefin contained 0.03 D per molecule, and the recovered halide, 0.97 D per molecule.

In a preliminary experiment with the undeuterated bromide (stopped after 15 minutes), there were obtained 12 g. (55%) of 2-ethylbutene-1, b.p. 65–70° (reported 66.2–

66.7°²²), n_D^{25} 1.3950, and 1.7 g. (4.2%) of recovered halide, b.p. 144–145°, n_D^{25} 1.4495. The yield of olefin calculated on the basis of the reacted halide was 61%. On making the acid extract alkaline and adding benzenesulfonyl chloride, there was isolated in approximately 15% yield N-2-ethylbutylbenzenesulfonamide, m.p. 151–152°.

(22) S. Goldwasser and H. S. Taylor, *THIS JOURNAL*, **61**, 1751 (1939).

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Acid Dissociation Constants and Saponification Rate Constants for Some 1-Naphthoic and Thenoic Acid Derivatives

BY CHARLES C. PRICE,¹ EDWIN C. MERTZ² AND JOHN WILSON

RECEIVED MAY 13, 1954

Dissociation constants in 78% ethanol for several 1-naphthoic and thenoic acids are reported. The rates of saponification of the corresponding esters in 70% dioxane are also reported. These data are interpreted satisfactorily in terms of the Hammett equation only by referring the data to the unsubstituted 1-naphthoic or 2-thenoic acid, respectively, apparently due to important steric factors in the saponification reaction arising from the *peri*-hydrogen or the adjacent sulfur atom, respectively.

The work reported herein is part of a general program to evaluate the influence of substituents on reactivity in the naphthalene and thiophene nuclei.³

The data on acid dissociation constants in 78% ethanol and on ethyl ester saponification in 70% dioxane are summarized in Table II.

Experimental

The properties of the acids used for pK_a determination are summarized in Table I. The methods of preparation are described in the references cited.

taken as the pH of a 0.005 *N* solution in 78.1% ethanol, exactly half-neutralized with sodium hydroxide. The value of the Hammett reaction constant⁴ for dissociation in this solvent (σ 2.07) was determined from the pK_a for benzoic (6.37), *p*-toluic (6.74) and *p*-chlorobenzoic (5.94) acids, using as σ -constants Hammett's values (for *p*-methyl, σ -0.170; for *p*-chloro, σ 0.227). Results are summarized in Table II.

The saponification rate constants were determined as previously³ and are also summarized in Table II.

The values in Table I labeled σ_a and σ_s are the values of Hammett's substituent constant σ , calculated from acid dissociation and saponification rate, respectively, referred

TABLE I
PROPERTIES OF ACIDS AND ETHYL ESTERS

Acid	Acid		Ester			Lit. b.p. (mm.) or m.p., °C.
	M.p., °C.	Liter.	°C.	B.p. Mm.	n_D^{20} or m.p., °C.	
1-Naphthoic	161.5	161 ^a	127–128	0.9	1.5940	
4-Cl-1-Naphthoic ^b	223.5–224	224 ^b	156–157	1.3	m. 25.5–27
7-Cl-1-Naphthoic ^c	238–240	233.6, ^c 242 ^d			m. 44.5
4-NO ₂ -1-Naphthoic ^e	223.5–224	227 ^e			m. 57.5	58 ^e
5-NO ₂ -1-Naphthoic ^f	237–238	239 ^f			m. 92	92 ^m
2-Thenoic	126–127	127 ^g	71	1.0	1.5262	96 (18) ⁿ
5-CH ₃ -2-Thenoic	138–139.5	138.5 ^h	87	1.0	1.5247	89 (5) ^o
5-NO ₂ -2-Thenoic	158	158 ⁱ			m. 64	64 ⁱ
5-Cl-2-Thenoic	145–146	147 ^j	75	0.3	1.5376
3-Thenoic ^k	136	138 ^l	82	2.3	1.5219	208 (73) ^l

^a H. Gilman, N. B. St. John and F. Schulze, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 425. ^b T. L. Jacobs, S. Winstein, J. W. Ralls and J. H. Robson, *J. Org. Chem.*, **11**, 27 (1946). ^c T. L. Jacobs, S. Winstein, R. B. Henderson, J. Bond, J. W. Ralls, D. Seymour and W. H. Florsheim, *ibid.*, **11**, 229 (1946). ^d C. D. Hurd, O. E. Fancher and W. B. Bonner, *ibid.*, **12**, 369 (1947). ^e G. J. Leuck, R. P. Perkins and F. C. Whitmore, *THIS JOURNAL*, **51**, 1834 (1929). ^f A. G. Eckstrand, *J. prakt. Chem.*, [2] **33**, 159 (1888). ^g P. Schorigin, *Ber.*, **43**, 1942 (1910); H. D. Hartough and L. G. Conley, *THIS JOURNAL*, **69**, 3096 (1947), report m.p. 129–130°. ^h J. W. Schick and H. D. Hartough, *ibid.*, **70**, 1645 (1948). ⁱ O. Dann, *Ber.*, **76**, 419 (1943). ^j J. W. Schick and H. D. Hartough, *THIS JOURNAL*, **70**, 286 (1948). ^k We are indebted to Dr. E. E. Campaigne of Indiana University for a sample of this acid. ^l E. E. Campaigne and W. M. LeSuer, *THIS JOURNAL*, **70**, 1555 (1948). ^m A. G. Eckstrand, *Ber.*, **12**, 1395 (1879). ⁿ W. Schlenk and R. Ochs, *ibid.*, **48**, 679 (1915). ^o H. G. Gross and E. E. Campaigne, *THIS JOURNAL*, **71**, 3258 (1949).

The esters were prepared by Fisher esterification and their properties are also summarized in Table I.

The approximate dissociation constants for the acids were

(1) Department of Chemistry, University of Pennsylvania, Phila., 4, Pa.

(2) AEC Fellow 1948–1950; American Cyanamid Fellow 1950–1951. Abstracted from the Ph.D. dissertation of E. C. M., June, 1954.

(3) For the preceding paper, see C. C. Price and R. H. Michel, *THIS JOURNAL*, **74**, 3652 (1952).

back to benzene. The values labeled σ'_a and σ'_s are the same values referred back to the parent acid, 1-naphthoic or 2-thenoic, respectively.

Discussion

As might have been expected because it is to be considered an *ortho*-substituted ester, the ester of 1-

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 184–192.

TABLE II
 VALUES OF pK_a (78.1%) ETHANOL, RATES OF SAPONIFICATION (70% DIOXANE) AND HAMMETT σ -CONSTANTS

Acid	pK_a^a	$k_{sap}^b \times 10^{3b}$	σ_a^c	σ_s^d	$\sigma_a'^e$	$\sigma_s'^f$
Benzoic	6.37	3.422 ^g				
1-Naphthoic	6.13	1.28 ± 0.04^h	0.12	-0.18	(0)	(0)
4-Cl-Naphthoic	5.68	$4.42 \pm .005$.33	.05	0.21	0.23
7-Cl-Naphthoic	5.92	$2.38 \pm .01$.21	-.07	.09	.11
4-NO ₂ -Naphthoic	4.78	$46.5 \pm .05$.76	.49	.64	.67
5-NO ₂ -Naphthoic	5.22	$18.0 \pm .01$.55	.31	.43	.49
2-Thenoic	5.72	$3.00 \pm .02^i$.31	-.02	(0)	(0)
5-CH ₃ -Thenoic	5.99	$1.18 \pm .006$.18	-.20	-.13	-.18
5-NO ₂ -Thenoic	4.43	$(737.00 \pm 31.00)^j$.94	$(1.01)^k$.63	$(1.03)^k$
5-Cl-Thenoic	5.06	$15.4 \pm .01$.63	.28	.32	.30
3-Thenoic	6.23	$3.17 \pm .001^l$.07	-.01	(0)	(0)

^a pK_a = pH of half-neutralized 0.005 *N* solution in 78.1% ethanol at 25°. ^b k_{sap} = $-d(\text{ester})/dt(\text{ester})(\text{OH}^-)$ at 25° in 70% dioxane in 1./mole sec. ^c σ_a = $(6.37 - pK_a)/2.07$. ^d σ_s = $\log(k_{sap}/3.422)/2.31^g$. ^e σ_a' = $(pK_a^0 - pK_a)/2.07$; pK_a^0 = 1-naphthoic or 2-thenoic acid, resp. ^f σ_s' = $\log(k_{sap}^0/k_{sap}^p)/2.31$; k_{sap}^0 = 1-naphthoate or 2-thenoate, resp. ^g Previous value³ 3.425×10^{-3} . ^h $k_{sap}^0 = 3.77 \pm 0.04 \times 10^{-3}$. ⁱ $k_{sap}^{40} = 8.38 \times 10^{-3}$. ^j $k_{sap}^{40} = 11.2 \pm 0.05 \times 10^3$. ^k The probable explanation of the discrepancy in this value may be that some reaction other than saponification is a complication. The saponification mixture is intensely colored and fails to yield the nitro-acid on acidification (E. C. M. and E. A. Dudley).

naphthoic acid saponified at a rate much slower than otherwise would have been predicted from its acidity. This slower-than-expected rate of saponification is noted for all the 1-naphthoate esters. However, when the substituted naphthoates are compared to 1-naphthoate (σ' values) rather than to benzene (σ values), the steric factor⁵ cancels and the σ -values from acidity and saponification agree quite well.

It is somewhat more surprising to find the same kind of evidence for a steric factor in the 2-thenoate esters.⁶ In fact, the data indicate the steric factor is even slightly greater for the *ortho*-sulfur atom in a 2-thenoate than for the *peri*-CH group in 1-naphthoate (as judged by the slightly greater spread between σ_a and σ_s).

One also may consider the influence of the nitro group on the dissociation constants in *p*-nitrobenzoic, 4-nitro-1-naphthoic and 5-nitro-2-thenoic as further support for a more effective steric hindrance factor for the *ortho*-sulfur than the *peri*-CH. In all three of these acids, the position of the nitro-group relative to the carboxyl corresponds to the *para* relationship. In the *para* position, at least part of the electron-withdrawing influence of the nitro group is usually ascribed to resonance interaction. The

strong electron-withdrawing action of the *p*-nitro group in benzoic acid (σ 0.78) is diminished considerably in 1-naphthoic acid (σ' 0.64) and in 2-thenoic acid (σ' 0.63). This may well be due to steric factors involving interference between the *peri*-CH or *ortho*-sulfur and the nitro group, inhibiting resonance interaction by preventing the nitro group and the ring from becoming coplanar.

There is much better agreement between the corresponding σ -values for the methyl and chloro groups, where such steric inhibition of resonance is not a comparable factor. The comparable values of σ are for *p*-chlorobenzoic (0.23), 4-chloro-1-naphthoic (0.22), and 5-chloro-2-thenoic (0.31) and for *p*-toluic (-0.17) and 5-methyl-2-thenoic (-0.16).

The difference between the σ -values for the 4-chloro and 7-chloro and for the sterically hindered 4-nitro and 5-nitro groups in 1-naphthoic acid can be accounted for quite adequately on the basis of the difference in direct dipole interaction between these groups and the negative charge placed on the carboxylate function in dissociation or saponification.⁷

NOTRE DAME, INDIANA

(5) See R. W. Taft, THIS JOURNAL, **75**, 4538 (1953), and earlier papers.

(6) Except for the 5-nitro ester. In this case it seems likely that the reaction whose rate constant was measured was not simple saponification since no 5-nitro acid was recoverable on acidification (E. C. M. and E. A. Dudley).

(7) Calculated on the basis that the energy of interaction is of the form $e\mu \cos \theta/r^2$. Assigning $r = 6.3 \text{ \AA}$. and $\theta = 0^\circ$ for 4-chloro and $r = 5.5 \text{ \AA}$. and $\theta = 65^\circ$ for 7-chloro, the calculated rate ratio for 4-chloro to 7-chloro is 1.9, very close to the observed 2.0. Assigning $r = 7.85 \text{ \AA}$. and $\theta = 0^\circ$ for 4-nitro and $r = 8.33 \text{ \AA}$. and $\theta = 30^\circ$, for 5-nitro, the calculated rate ratio for 4-nitro to 7-nitro is 1.31, reasonably close to the observed 1.43.³