[CONTRIBUTION FROM JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

A Further Study of the Dissociation and Association of Furoic and Thenoic Acids and of the Rates of Saponification of Their Ethyl Esters

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Additional data on the pK_a's for furoic and thenoic acids and on the rates of saponification of their ethyl esters indicate that the latter are not accurately predicted from the former by the Hammett equation. The difference is not due to differing degrees of association of the acids and, unlike the case of α-naphthoic acid, does not appear to be steric.

We have reported[1] that the saponification of ethyl 2-furoate proceeded at a rate considerably slower than predicted from the pK_a for 2-furoic acid.

In seeking additional evidence for the nature of this alleged effect, we have discovered a regrettable error of a factor of ten in the calculation of the rate constant for ethyl 2-furoate, which largely eliminates the discrepancy. We do, however, wish to report additional data on the pK_a's for furoic and thenoic acids, on the rates of saponification of their ethyl esters over a wider range in temperature and on the degree of their association.

Experimental

2-Furoic, benzoic, 1- and 2-naphthoic acids were commercial products (Eastman Kodak Co.), while the preparation and properties of 2-thenoic acid were described in the previous paper.[2] 3-Thenoic acid was kindly supplied by Dr. E. E. Campaigne of Indiana University. All these acids were recrystallized at least twice. The preparations of ethyl thenoates were also described elsewhere,[2] while the ethyl 2-furoate was obtained from Norwich Pharmacal Co. The esters were redistilled just before use. Dioxane was purified as before.[2] Benzene was purified by repeated crystallization after fractional distillation through an efficient column.

The saponification rate constants were determined as previously.[2] All the volumetric apparatus used was calibrated at each temperature under which kinetic measurements were made, while the thermostat used was maintained within the range of ±0.02°. Typical data are shown in Table I and all of the data are summarized in Table II.

TABLE I

ALKALINE SAPONIFICATION OF ETHYL 2-THENOATE IN 70% DIOXANE AT 45.00 ± 0.02°

(Ethyl 2-thenoate) = (NaOH) = 0.02500N = a

t, sec.	x	$a(a-x)t$	k_2, mole^{-1}, sec.$^{-1}$, l.
191	0.001850	0.110541	0.01673
505	.004325	.261022	.01656
853	.006550	.393446	.01664
1170	.008355	.489791	.01685
1549	.009758	.590246	.01653
1881	.011003	.658209	.01671
2255	.012050	.730056	.01650
2698	.013175	.797596	.01651
		Mean	0.0166 ± 0.0001

TABLE II

RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ETHYL ESTERS OF AROMATIC AND HETEROCYCLIC ACIDS IN 70% DIOXANE

	$10^3 \times k_2$, mole^{-1}, sec.$^{-1}$, l.									
Compound	7.5°	20.0°	25.0°	32.5°	40.0°	45.0°	E[d]	log PZ	$\Delta H\ddagger$[d, e]	$\Delta S,\ddagger$[e] e.u.
2-Thenoate		2.36 ± 0.03	3.51[a] (3.00[b])	6.51 ± 0.05	8.38[b]	16.6 ± 0.1	14.69	8.31	14.11	−22.45
3-Thenoate		2.20 ± .04	3.33[a] (3.17[b])	6.21 ± .06	11.2[b]	15.3 ± .1	14.42	8.09	13.84	−23.46
2-Furoate	4.17 ± 0.05	11.2 ± .1	15.9[a] (22.7[b])	31.1 ± .4			13.74	8.29	13.16	−22.54
Benzoate[c]			3.42		10.7		14.0	7.82		
1-Naphthoate[c]			1.28		3.77		13.4	6.9		
2-Naphthoate[c]			3.46		11.3		14.7	8.38		

[a] These kinetic values were calculated by interpolating from the values of E and log PZ. [b] Taken from the data in ref. 2. [c] Taken from the data by C. C. Price and R. H. Michel, THIS JOURNAL, **74**, 3652 (1952). [d] Kcal./mole. [e] Calculated from the equation, $k = \frac{kT}{h} e^{-\Delta H\ddagger/RT} e^{\Delta S\ddagger/R}$ and $\Delta H\ddagger = E - RT$, see Glasstone, Laidler and Eyring "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

TABLE III

HAMMETT σ-CONSTANTS FOR THE ACID DISSOCIATION CONSTANTS IN 78.1% ETHANOL AND THE RATES OF ALKALINE SAPONIFICATION OF THE ESTERS, IN 70% DIOXANE

Acid	pK_a	$k_2$sapn. × 10^3 at 25°	σa[a]	σs[b]	$\Delta\sigma$
Benzoic	6.70 (6.37[c])	(3.42[c])	(0.00)	(0.00)	(0.00)
2-Thenoic	5.95 (5.72[c])	3.51 (3.00[c])	0.36 (.31[c])	0.005 (−0.02)[c]	.35
3-Thenoic	(6.23[c])	3.33 (3.17[c])	(.07[c])	− .005 (− .01[c])	.08
2-Furoic	5.43 (5.37)[d]	15.9 (22.7[d])	0.61 (.47[d])	.29 (.36[d])	.32
1-Naphthoic	6.25 (6.13[c])	(1.28[c])	.22 (.12[c])	(− .18[c])	.40
2-Naphthoic	6.30	(3.46[e])	.03	(0.00[e])	.03

[a] $\sigma_a = (pK_a \text{ for benzoic } - pK_a)/2.07$. [b] $\sigma_s = \log (k_{sap.}/3.42)/2.31$. [c] Taken from the data in ref. 2. [d] Taken from the data in ref. 1. [e] C. C. Price and R. H. Michel, THIS JOURNAL, **74**, 3652 (1952).

New measurements of the acid strengths of benzoic, 2-thenoic, 2-furoic, 1- and 2-naphthoic acids at 25° in 78.1% ethanol by volume were made as before,[2] using a Beckman glass electrode pH meter model H2. The values obtained are listed in Table III.

Freezing point determinations were made for each acid using 43.60 g. (50.0 ml. at 25°) of pure benzene. Benzoic acid is quite soluble in benzene, but 2-thenoic acid is not very soluble (less than 2.3 g. in 100 ml. of benzene at 5°),

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[1] C. C. Price and E. A. Dudley, THIS JOURNAL, **78**, 68 (1956).

[2] C. C. Price, E. C. Mertz and J. Wilson, *ibid.*, **76**, 5131 (1956).

while 2-furoic acid is still much less soluble (less than 0.6 g. in 100 ml. of benzene at 5°). Therefore, the freezing point determination of 2-furoic acid was made only in a rather lower concentration. The determined values are listed in Table IV.

Discussion

The data on rates of saponification, outlined in Tables II and III, show clearly that the rates of saponification of ethyl benzoate, 2-naphthoate and 3-thenoate are in reasonable agreement with values predictable from pK_a (indicated by reasonable agreement between σ_a and σ_s in Table III). The earlier discrepancy[1,2] between σ_a and σ_s for 1-naphthoate, 2-furoate and 2-thenoate persists. However, as judged from energy and entropy of activation, the reasons for these discrepancies are dissimilar. For example, the 1-naphthoate has very much the lowest temperature independent factor (log $PZ = 6.9$), whereas the 2-furoate and 2-thenoate have the largest (log $PZ = 8.29$ and 8.31, respectively).

A redetermination of pK_a values for benzoic, 2-furoic, 2-thenoic, 1- and 2-naphthoic acids (Table

Table IV

The Values of Observed Molecular Weights and Degree of Association of 2-Furoic, 2-Thenoic and Benzoic Acids in Benzene Solution

Acid	Mol. wt.	Weight of sample, g.	ΔT, °C.	Mol. wt. (obsd.)	Degree of association, %
2-Furoic	112	0.2343	0.150	183	82
		.2011	.127	186	83
		.2128	.144	174	78
2-Thenoic	128	0.2131	.130	192	75
		.3268	.205	190	74
		.7018	.370	223	87
		.7551	.420	211	82
		1.0186	.520	230	90
		1.2553	.670	220	86
Benzoic	226	0.3268	.205	190	78
		.7551	.420	211	87
		.7393	.390	226	93
		1.2553	.670	220	90

Infrared spectra of benzoic, 2-thenoic, 2-furoic, 1- and 2-naphthoic acids were obtained in potassium bromide disks, using a Perkin–Elmer, model 21, autorecording spectrophotometer, as shown in Table V.

Table V

Infrared Spectra of Benzoic, 2-Thenoic, 2-Furoic, 1- and 2-Naphthoic Acids (in Potassium Bromide)

Benzoic		2-Thenoic		2-Furoic		1-Naphthoic		2-Naphthoic	
ν	Rel. % abs.	ν	Rel. % abs.	ν	Rel. % abs.	ν	Rel. % abs.	ν	Rel. % abs.
3400	35	3400	42	3400	52	3450	59	3450	53
3100–2800*	57	3100–2800*	79	3150–2800*	77	3100–2800*	73	3080–2750*	64
2670*	55	2620*	78	2650*	78	2620*	68	2640*	63
2550*	55	2530*	78	2560*	78	2520*	65	2560*	64
						1950	48	1960	45
						1820	42	1810	43
1690*	83	1680*	95	1685*	93	1680*	90	1680*	83
1605	46					1625	72	1635	69
1585	47			1585	89	1595	77	1595	56
						1575	66	1575	57
1500	35	1525	92			1515	75	1510	52
				1476	91	1465	57	1475	61
1450	65					1450	63	1445	52
1425*	66	1433*	95	1428*	86	1420*	69	1425*	69
		1405	82	1387	73	1395	54		
1330	75	1355	89			1350	54	1360	66
1285*	79	1283*	97	1300*	91	1300*	83	1305*	82
								1265	62
		1230	82	1240	83	1250	74	1240	74
1180	55			1180	87	1205	72	1200	68
						1145	68	1155	57
1130	50			1125	88			1130	66
1100	37	1107	84					1100	50
1075	47	1078	66	1078	68	1082	58	1080	49
1028	50	1045	85	1020	88	1028	50	1015	43
1000	37					998	54	985	47
						945	48		
933*	63	930*	71	933*	86	928*	47	945–925*	64
		910	84	926–913	80	890–880	64	905	65
		866	72	887	86			864	69
		858	88	851	60	855	57	832	60
						808	61		
						794	49		
		761	76			772	89	778	84
707	84	748	87	770–755	90	755–745	66	755	80
683	56	735	92					732	56
665	64	722	95			720	56	728	56

* Bands so marked are characteristic for the associated form of the acid.

III) leads to values of σ_a in reasonable agreement with those from earlier data.[1,2]

Recently there have appeared two papers which are related to our study, the one dealing with the alkaline hydrolysis of ethyl 2-thenoate and 2-furoate[3] and the other of ethyl 1- and 2-naphthoate,[4] both in 85% ethanol. Using these data[3,4] together with the rates of saponification and ρ in the same solvent,[5] we can calculate the Hammett σ-constants for the saponification rates of ethyl benzoate, 2-furoate, 2-thenoate, 1- and 2-naphthoate, as shown in Table VI.

Although the temperature-independent factors in these two separate experiments[3,4] are quite far apart, the over-all picture thus calculated is in fairly reasonable agreement with our data.

To test the hypothesis that the heterocyclic acids might have intra- rather than intermolecular hydrogen bonding, the degree of association of benzoic, 2-thenoic and 2-furoic acids were determined cryoscopically in benzene. These data, summarized in Table IV, indicate that all three acids have almost the same degree of association, and our data do not support the earlier claim that 2-furoic acid is largely monomeric in benzene.[6] For the solid acids, infrared spectra in potassium bromide disks, as shown in Table V, reveal no significant changes in position or relative intensity of the bands associated with the carboxyl group, in support of the conclusion that all the acids are associated in the crystalline state, as was already pointed out previously by X-ray study,[7] in the case of 2-furoic acid.

TABLE VI

HAMMETT σ-CONSTANTS FOR THE ACID DISSOCIATION CONSTANTS AND THE RATES OF ALKALINE SAPONIFICATION OF THE ESTERS IN 85% ETHANOL

Acid	pKa^e	$k_2$sapn. × 10^4 at 25°	σa^e	σs^f	$\Delta\sigma$
Benzoic	6.70	6.07^a	0.00	0.00	0.00
2-Thenoic	5.95	5.63^b	.36	− .01	.37
2-Furoic	5.43	24.5^c	.61	.24	.37
1-Naphthoic	6.25	4.79^d	.22	− .04	.26
2-Naphthoic	6.30	10.0^d	.03	.08	.05

[a] Taken from ref. 5. [b] Extrapolated from the value of ΔE (18.9 kcal./mole) and log PZ (10.6) in ref. 3. [c] Directly taken from ref. 3. [d] Extrapolated from the values of ΔE (14.5 kcal./mole for 1-naphthoate and 16.1 kcal./mole for 2-naphthoate) and log PZ (7.3 for 1-naphthoate and 8.8 for 2-naphthoate, respectively) in ref. 4. [e] Taken from our measurement—see Table III. [f] $\sigma_s = \log (k_{sap}/6.07 \times 10^4)/2.54$.

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[3] E. Imoto, Y. Otsuji, T. Hirai and H. Inoue, *J. Chem. Soc. Japan* (Pure Chem. Section), **77**, 804, 809 (1956).

[4] P. Fitzgerald, J. Parker, J. Vaughan and A. F. Wilson, *J. Chem. Soc.*, 170 (1956).

[5] (a) D. P. Evans, J. J. Gordon and H. B. Watson, *ibid.*, 1430 (1937); (b) C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936); (c) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[6] L. M. Nazarova and Y. K. Syrkin, *Isvest. Akad. Nauk. S. S. R., Odtel. Khim. Nauk.*, **35** (1949) (*C. A.*, **43**, 4913 (1949)).

[7] T. Goodwin and C. M. Thomson, *Acta Cryst.*, **7**, 166 (1954) (*C. A.*, **48**, 7385 (1956)).

[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, PENNSYLVANIA SALT MANUFACTURING CO.]

Thermal Syntheses of Telomers of Fluorinated Olefins. I. Perfluoropropene[1]

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A novel method of producing addition-type polymers by a process which does not proceed by chain propagation is described. The formation of telomers of perfluoropropene of formula $R[CF_2CF(CF_3)]_nI$ where $R = CF_3, C_3F_7, C_4F_9CF(CF_3)$, $C_4F_9CF(CF_3)CF_2CF(CF_3)$ and $CF_2ClCFCl$ and $n = 1$ to 15 has been accomplished by purely thermal means. The unique advantages of this simple process as a method of producing telomers of certain types of relatively non-polymerizable olefins are expounded.

This is the first paper in a series dealing with the syntheses of telomers of fluorinated olefins by purely thermal means.

Considerable work from both academic and industrial laboratories has been described on photochemical and peroxide-induced telomerizations of fluoroölefins which are readily polymerized by free radical initiators. Little information has been reported, however, on (1) thermally induced telomerizations and (2) telomerizations of olefins which do not readily homopolymerize in the presence of free radical initiators.[2]

Although perfluoropropene has been copolymerized with fluorinated[3,4] and unfluorinated[3,5] olefins as well as with ethylene oxide,[6] there is no literature reference to the homopolymerization of perfluoropropene to $[-CF_2CF(CF_3)-]_n$, in spite of considerable study.[5] We have now found that polyperfluoropropenes of molecular weights to 2500 may be synthesized by reaction of perfluoropropene with perfluoroalkyl iodides at about 200°. Moreover, the reaction may be controlled to give products of any desired narrow molecular weight range from $n = 1$ to 15.

Replacement of the iodine atom by fluorine or

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[1] The work herein reported was carried out under contract between the Office of Naval Research and the Pennsylvania Salt Manufacturing Co. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] See R. N. Haszeldine, *J. Chem. Soc.*, 4291 (1955), for an excellent review of many of the factors affecting telomerization.

[3] J. C. Sauer, U. S. Patent 2,549,935 (1951).

[4] W. T. Miller, U. S. Patent 2,598,283 (1952).

[5] R. M. Adams and F. A. Bovey, *J. Polymer Sci.*, **9**, 481 (1952).

[6] M. Hauptschein and J. M. Lesser, THIS JOURNAL, **78**, 676 (1956).