was removed by evaporation under reduced pressure and dry hydrogen chloride passed into the residue. The solid hydrochloride was removed by filtration and after crystallization from ethyl acetate–alcohol melted at 221–222°.

Anal. Calcd. for $C_{17}H_{34}N_2S_2 \cdot 2HCl$: C, 50.60; H, 8.99; N, 6.94. Found: C, 50.46; H, 8.77; N, 6.57.

Thiophenol-*d*.—Sodium hydride (1.3 g.) was suspended in pure dioxane (50 cc.) and thiophenol (5.5 g.) added. When the hydrogen evolution ceased, heavy water (4 cc.) was added and the mixture set aside at room temperature overnight. Carbon dioxide was then passed into the mixture and the precipitate removed by centrifugation. The dioxane extract was dried over anhydrous sodium sulfate and the dioxane was removed by evaporation under reduced pressure. The residue was distilled twice in a short path still, b.p. 75° (13 mm.), (block temperature), n^{20}_{D} 1.5468.

Hexanethiol-*d*.—Hexanethiol (5 g.) was dissolved in anhydrous ether (50 cc.) and sodium hydride (1.02 g.) added. When the hydrogen evolution ceased, heavy water (3 cc.) was added. After 30 min. the ethereal layer was decanted, dried over anhydrous sodium sulfate and the ether removed by evaporation under reduced pressure. The residue was distilled at 40 mm., b.p. 56–58°.

Measurements of Infrared Spectra.—The spectra were measured with a Perkin-Elmer Spectrophotometer, Model 12 AB, equipped with a calcium fluoride prism (synthetic crystal, apex angle 67.5°, polished faces 78 × 66 mm. high). Background absorption was reduced to a minimum by passing slowly through the optical path water-pumped nitrogen, dried in Drierite towers. Permanent cells with rocksalt plates were used. Spectra for the benzene solutions were taken in cells of 0.251 mm. thickness. Spectra for the pure compounds were taken in cells of 0.025 mm. thickness; the slit width in the 3.7–4.0 μ region was 0.072 mm.

The spectra of the pure deuterated compounds and their hydrogen analogs were obtained using the standard rock salt prism in the Perkin–Elmer instrument with slit widths of 0.023 mm. in the 3.9 μ region and of 0.033 mm. in the 5.4 μ region.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY]

Ester Cleavage in 100% Sulfuric Acid[1]

BY ARTHUR BRADLEY AND MARION E. HILL

RECEIVED AUGUST 11, 1954

It has been found that protonation (i = 2.0) of organic esters in concentrated sulfuric acid is ordinarily followed by cleavage into three particles (i = 3.0). The cleavage rate is strongly retarded by negative groups in the acid and accelerated by such groups in the alcohol portion of the ester. The results are discussed in connection with possible mechanisms for the reaction.

Both Treffers and Hammett[2] and Newman[3] have reported the complete hydrolysis of methyl mesitoate on pouring a freshly prepared sulfuric acid solution of this ester onto ice and water. Kuhn and Corwin[4] and Kuhn[5] applied this procedure to various aliphatic and aromatic esters and reported recoveries of acid ranging from 0% with ethyl acetate and ethyl benzoate to 76% with chloroethyl anisate and isopropyl anisate. They also found that cellosolve benzoate kept at 53° in sulfuric acid for five minutes gave 2.5 times the yield of benzoic acid obtained after two minutes at room temperature. Newman, Craig and Garrett[6] converted methyl benzoate to benzoic acid in 81% yield by heating at 90° for 15 minutes.

We have extended this work by investigating the effects of time and elevated temperature on a number of suitable esters, and in many cases have achieved considerable hydrolysis of compounds that previously were considered to be stable in this medium. Whereas methyl[2] and ethyl[5] benzoates were recovered unchanged after being dissolved in sulfuric acid at room temperature and poured onto ice after two minutes, they were completely cleaved by warming their sulfuric acid solutions to 50° for one and two hours, respectively. The yields of acid from these and other esters after varying intervals at 25, 50 and 75° are shown in Tables I and II.

TABLE I

HYDROLYSIS OF ESTERS

PERCENTAGE RECOVERY OF BENZOIC ACID AT 25°

	2 min.	15 min.	1 hr.	3 hr.	24 hr.
Methyl benzoate			2	34	70
Ethyl benzoate			0	12	48[a]
Trichloroethyl benzoate	33[4]	50	74		
Isopropyl benzoate	36[5]	47	62	64	
Phenyl benzoate		57	71	75	
Tribromoethyl benzoate			44		

[a] After three days or seven days 75% benzoic acid was obtained.

TABLE II

PERCENTAGE RECOVERY OF ACID AT 50°

	5 min.	20 min.	1 hr.	5 hr.	24 hr.	3 days
Methyl benzoate	30	55	74	77		
Ethyl benzoate		29	57[a]	75	77	
Trichloroethyl benzoate	68	69	70			
Trichloroethyl 3,5-dinitrobenzoate						0 (87)[b]
Methyl *p*-nitrobenzoate				10	49	80
Methyl 3,5-dinitrobenzoate					9	26 (52)[b]
Methyl 3,5-dinitrobenzoate (4.0% SO_3)					77	

[a] After two hours 71% benzoic acid was obtained. [b] Recovered ester in parentheses.

At elevated temperatures, particularly at 75° with a slight excess of sulfur trioxide, sulfonation of benzoic acid appeared to take place. At room temperature, however, this side reaction was not significant, and yields over 75% are considered quantitative.[4]

These results amply justify the generalization in the literature[4,7] that negative substituents en-

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[1] Presented before the Organic Division at the 126th Meeting of the American Chemical Society, New York City, September, 1954.

[2] H. P. Treffers and L. P. Hammett, THIS JOURNAL, **59**, 1708 (1937).

[3] (a) M. S. Newman, *ibid.*, **63**, 2431 (1941); (b) M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

[4] L. P. Kuhn and A. H. Corwin, *ibid.*, **70**, 3370 (1948).

[5] L. P. Kuhn, *ibid.*, **71**, 1575 (1949).

[6] M. S. Newman, R. A. Craig and A. B. Garrett, *ibid.*, **71**, 869 (1949).

[7] L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 186.

TABLE III

PERCENTAGE RECOVERY OF ACID AT 75°

	5 min.	15 min.	4 hr.
Ethyl benzoate	73	67	60
Methyl benzoate (0.5% SO_3)	63[a]	47	
Trichloroethyl 3,5-dinitrobenzoate			0 (78)[b]
Methyl *p*-nitrobenzoate		16	75
Methyl 3,5-dinitrobenzoate			28
Methyl 3,5-dinitrobenzoate (14.0% SO_3)			74

[a] After ten minutes 54% acid was obtained; yield extrapolated to zero time about 70%. [b] Most of recovered ester never dissolved.

hance the reaction when in the alkyl part of the ester and retard it when in the acid part. The data may be summarized by the following order of decreasing rate: trichloroethyl benzoate, tribromoethyl benzoate, ethyl benzoate, methyl *p*-nitrobenzoate, methyl 3,5-dinitrobenzoate.

Cryoscopic measurements have frequently given evidence of the extent of ester ionization.[2–5] Esters which were thought not to be hydrolyzed appreciably by sulfuric acid, such as ethyl benzoate,[4,5] gave *i*-factors of 2.0, showing the existence of two particles in solution

$$\text{RO—CO—R}' + \text{H}_2\text{SO}_4 \rightleftarrows (\text{RO—CO—R}')\text{H}^{\oplus} + \text{HSO}_4^- \tag{1}$$

The first observation that an increase in the *i*-factor of an ester can be brought about by heating was made by Newman, Craig and Garrett.[6] These authors discovered that the value for methyl benzoate, starting at 2.0, had reached 3.0 after 15 minutes at 45°, and remained approximately constant despite further heating. They suggested that the particles obtained were methylsulfuric acid, the protonated benzoic acid and a bisulfate ion

$$\text{RCOOCH}_3 + 2\text{H}_2\text{SO}_4 \rightleftarrows (\text{RCOOH})\text{H}^{\oplus} + \text{CH}_3\text{OSO}_4 + \text{HSO}_4^- \tag{2}$$

In all cases where we observed ester hydrolysis after standing in sulfuric acid at 25° or 50°, there was a corresponding increase in the *i*-factor (Tables IV). Separation into three particles was found to be a general reaction of esters, regardless of the relative ease of cleavage.

The substrate concentrations convenient for freezing point depression measurements were usually about one-fifth those in which the cleavage product was isolated (Tables I, II, III). In the latter experiments the rates appear to be slightly less, possibly because of the decreased acidity of the medium.

The consistent, although approximate, correspondence between *i*-factor increase and experimentally determined cleavage in the aromatic series led us to believe that significant data on aliphatic esters could be obtained by *i*-factors alone. Some relative rates of cleavage (Table IV) were: ethyl acetate (≃ ethyl benzoate) > methyl chloroacetate > methyl acrylate.

Several of the organic acids from which these esters were derived had not been investigated previously in sulfuric acid solution. Their *i*-factor measurements are therefore included in Table IV, second section.

TABLE IV

i-FACTORS OBTAINED FROM FREEZING POINT DEPRESSIONS

		Duration of heating at 25°			
	Initial	1 hr.	7 hr.	1 day	2 days
Methyl benzoate	2.1	2.3	2.6	3.1	3.2
Ethyl benzoate	2.0		2.4	3.0	3.0
Trichloroethyl benzoate	2.8	3.0		3.2	
Isopropyl benzoate	2.8, 2.9, 3.1[a]				
Phenyl benzoate	5.1	5.2		5.5	
Tribromoethyl benzoate		3.0			
Ethyl acetate	1.9	1.9	2.7	2.9	2.8

		Duration of heating at 50°			
	Initial	1 hr.	3 hr.	1 day	2 days
Ethyl benzoate	2.0	2.9	3.0	3.0	
Methyl *p*-nitrobenzoate	2.0		2.3	3.0	
Methyl 3,5-dinitrobenzoate	1.4		1.4	1.8	2.1
Ethyl acetate	1.9	2.7	2.8		
Methyl chloroacetate	2.0		2.1	2.7	
Methyl acrylate	1.5		1.9	2.1	2.2
Acrylic acid	1.8				
Chloroacetic acid	1.8			1.8	
p-Nitrobenzoic acid	2.0				2.0
3,5-Dinitrobenzoic acid	1.5		1.6	1.7	

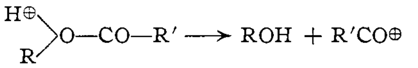
[a] Successive readings were taken as fast as possible (about 40 minutes apart) without the temperature rising above 12°.

Discussion

There has been frequent mention in the literature[3–5] that certain esters undergo "complex ionization" in sulfuric acid, giving five particles in solution including an acyl cation

$$\text{RO—CO—R}' + 3\text{H}_2\text{SO}_4 \rightleftarrows \text{ROSO}_3\text{H} + \text{H}_3\text{O}^{\oplus} + \text{R}'\text{CO}^{\oplus} + 2\text{HSO}_4^- \tag{3}$$

It was convenient to assume acyl–oxygen fission in these cases, since that would lead directly to the products. Some authors have specified that protonation at the alkyl oxygen precedes cleavage.[7,8]



$$\overset{\text{H}^{\oplus}}{\underset{\text{R}}{>}}\text{O—CO—R}' \longrightarrow \text{ROH} + \text{R}'\text{CO}^{\oplus} \tag{4}$$

However, since it now has been demonstrated that ester hydrolysis usually can be achieved without exceeding three particles in sulfuric acid, the necessity for the above formulations must be re-evaluated. For example, it is possible that all esters cleave first to three particles, with "complex ionization" a subsequent step reflecting the behavior of the organic acid

$$\text{RO—CO—R}' + 2\text{H}_2\text{SO}_4 \rightleftarrows \text{ROSO}_3\text{H} + (\text{R}'\text{COOH})\text{H}^{\oplus} + \text{HSO}_4^- \tag{5a}$$

$$(\text{R}'\text{COOH})\text{H}^{\oplus} + \text{H}_2\text{SO}_4 \rightleftarrows \text{R}'\text{CO}^{\oplus} + \text{H}_3\text{O}^{\oplus} + \text{HSO}_4^- \tag{5b}$$

Equation 5b represents an equilibrium that is shifted to the right when the formation of the acyl cation is favored, as in di-*o*-substituted benzoic acids.[2] The equilibrium of equation 5a appears to lie to the right for most esters. Apparent variations in cleavage rates reflect the relative ease with which different esters approach this equilibrium. Sulfur

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[8] J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 696 (1941).

trioxide is observed to be a powerful catalyst in this regard.

Separation into three particles may be expressed as acyl–oxygen cleavage, but extra steps then are required to "hydrate" the acyl cation: essentially the reverse of equation 5b. On the other hand, alkyl–oxygen cleavage gives the products directly, and without the necessity of placing the proton on a particular oxygen. A displacement on the alkyl carbon by bisulfate ion was suggested by Newman, Craig and Garrett[6] to account for the formation of three particles from methyl benzoate. It is of interest, however, that bimolecular ester hydrolysis involving alkyl–oxygen fission otherwise has not been reported in acidic medium.[9]

TABLE V

FREEZING POINT DATA

Time at 25°	Solute/molality	F.p., °C.	$\Delta\theta$	*i*
	Methyl benzoate			
	None	9.879		
[a]	0.1018 (1.263 g.)	8.573	1.306	2.16
1 hr.		8.500	1.379	2.29
24 hr.		7.998	1.881	3.12
	None	9.777		
[a]	.0784 (0.972 g.)	8.804	0.973	2.09
3 hr.		8.648	1.129	2.43
24 hr.		8.386	1.391	3.00
	None	10.068		
[a]	.0739 (0.917 g.)	9.176	0.892	2.03
7 hr.		8.943	1.125	2.57
2 days		8.681	1.387	3.16
	Ethyl benzoate			
	None	9.936		
[a]	.0848 (1.162 g.)	8.917	1.019	2.02
7 hr.		8.721	1.215	2.41
24 hr.		8.441	1.495	2.97
2 days		8.426	1.510	3.01
	Trichloroethyl benzoate			
	None	9.825		
[a]	.0764 (1.770 g.)	8.535	1.290	2.84
1 hr.		8.468	1.357	3.00
24 hr.		8.397	1.428	3.16
	Isopropyl benzoate			
	None	9.923		
[a]	.0732 (1.094 g.)	8.718	1.205	2.77
[b]		8.665	1.258	2.90
[c]		8.555	1.368	3.14
	Phenyl benzoate			
	None	9.869		
[a]	.0607 (1.095 g.)	8.046	1.823	5.08
1 hr.		8.000	1.869	5.20
24 hr.		7.893	1.976	5.49
	Tribromoethyl benzoate			
	None	9.755		
1 hr.	.0300 (1.059 g.)	9.222	0.533	2.98
	Ethyl acetate			
	None	9.921		
[a]	.1001 (0.803 g.)	8.824	1.097	1.85
1 hr.		8.813	1.108	1.87
7 hr.		8.311	1.610	2.71
24 hr.		8.161	1.750	2.94
2 days		8.264	1.657	2.80
	None	10.111		
[a]	.0820 (0.658 g.)	9.231	0.880	1.80
3 hr.		8.919	1.192	2.45
24 hr.		8.640	1.471	3.02
Time, 50°	Ethyl benzoate			
	None	9.827		
[a]	.0642 (0.879 g.)	9.071	0.756	1.98
1 hr.		8.710	1.117	2.93
4 hr.		8.700	1.127	2.96
1 day		8.698	1.129	2.97
	Methyl *p*-nitrobenzoate			
	None	9.827		
[a]	.0766 (1.265 g.)	8.931	0.896	1.97
3 hr.		8.787	1.040	2.29
24 hr.		8.464	1.363	3.00
	Methyl 3,5-dinitrobenzoate			
	None	10.061		
[a]	.1210 (2.494 g.)	9.043	1.018	1.42
3 hr.		9.048	1.013	1.41
1 day		8.795	1.266	1.76
2 days		8.581	1.480	2.06
	Ethyl acetate			
	None	9.820		
[a]	.0861 (0.691 g.)	8.840	0.980	1.91
1 hr.		8.435	1.385	2.72
3 hr.		8.404	1.416	2.78
	Methyl chloroacetate			
	None	9.573		
[a]	.0656 (0.646 g.)	8.800	0.773	1.98
3 hr.		8.756	0.817	2.10
24 hr.		8.526	1.047	2.69
	Methyl acrylate			
	None	9.875		
[a]	.1366 (1.071 g.)	8.624	1.251	1.54
3 hr.		8.300	1.575	1.94
24 hr.		8.176	1.699	2.10
2 days		8.082	1.793	2.22
	Acrylic acid			
	None	9.664		
[a]	.0956 (0.628 g.)	8.625	1.039	1.83
	Chloroacetic acid			
	None	9.644		
[a]	.1264 (1.083 g.)	8.284	1.360	1.81
24 hr.		8.264	1.380	1.84
	p-Nitrobenzoic acid			
	None	9.739		
[a]	.0882 (1.343 g.)	8.674	1.065	2.03
2 days		8.686	1.053	2.01
	3,5-Dinitrobenzoic acid			
	None	9.538		
[a]	.0866 (1.682 g.)	8.767	0.771	1.50
3 hr.		8.707	0.831	1.62
24 hr.		8.643	0.895	1.74

[a] After approximately 30 minutes at 10°. [b] After approximately 60 minutes at 10°. [c] After approximately 90 minutes at 10°.

A thorough investigation to establish the bond broken in this reaction must precede further consideration of the mechanism. Some evidence for al-

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[9] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 781.

kyl–oxygen cleavage of *t*-butyl benzoate was obtained by Kuhn,[5] who suggested a more general approach using an ester labeled with an oxygen isotope. It is hoped that such an experiment can be conducted in this Laboratory in the near future.

Experimental

Materials.—Trichloroethyl and tribromoethyl benzoates were prepared by the aluminum chloride catalytic method.[10] Methyl *p*-nitrobenzoate, m.p. 95–96°, and methyl 3,5-dinitrobenzoate, m.p. 107–108°, were prepared by dissolving the acid chlorides in methanol and recrystallizing *in situ*. The remaining esters and acids were commercial C.P. reagents used without further purification other than careful drying. The 100% sulfuric acid was prepared by the method previously described.[2b]

Hydrolysis of Esters.—In a typical experiment a solution of ethyl benzoate (1.982 g., 0.0132 mole) in 10.0 ml. of 100% sulfuric acid was kept at 50° for one hour and then poured onto ice and water. The precipitated benzoic acid, identified by mixed melting point, weighed 0.916 g. (0.0075 mole, 57%) after recrystallization from 10 ml. of 1:3 methylene chloride–petroleum ether.

Freezing Point Measurements.—The apparatus used was essentially the same as that described by Newman, Kuivila and Garrett.[2b] The vessel was constructed to fit a platinum resistance thermometer (Leeds and Northrup, No. 8163-S) which had a ground glass joint sealed to its shield. A reciprocating stirrer of nichrome wire was used, with a mercury seal to keep out moisture. The latter was replaced in a second apparatus with a self-lubricating Teflon stopper which was machined to fit a ground glass joint. This change greatly simplified construction, and avoided the danger of introducing mercury into the sulfuric acid solution. In each determination, the solvent was 50 ml. (91.2 g.) of approximately 99.9% sulfuric acid. For heating cycles the whole apparatus was partially immersed in a constant temperature bath kept at 50 ± 1°.

The operational technique has been discussed by many authors.[3,11] A correction for supercooling (which was usually about 1°) was made according to the method of Gillespie, Hughes and Ingold.[11] The value for the cryoscopic constant determined by these authors[11] (5.98) was incorporated into the equation for "*i*" used by Hammett[2] and Newman.[3]

$$i = \frac{\Delta\theta}{m \times 5.98(1 - 0.0047\theta)}$$

The symbol m represents the molality of the solute, $\Delta\theta$ is the freezing point depression due to m, and θ is the total freezing point depression.

In a recent publication, Wyatt[12] questioned the invariance of the cryoscopic "constant," and thereby rendered all *i*-factor measurements suspect, at least in the second decimal. We have retained this third significant figure in Table V, although it might have been discarded on the basis of some experimental variations alone. For this report, all the *i*-values were checked by duplicate experiments.

WHITE OAK, SILVER SPRING, MD.

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[10] M. E. Hill, THIS JOURNAL, **76**, 2329 (1954).

[11] R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

[12] P. A. H. Wyatt, *ibid.*, 1175 (1953).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Boric Acid Dehydration of Alcohols

BY GEORGE L. O'CONNOR[1] AND HAROLD R. NACE

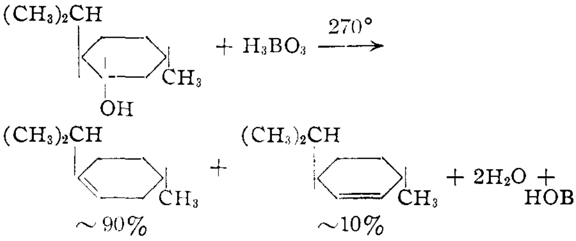
RECEIVED FEBRUARY 18, 1954

Evidence is presented that the dehydration of an alcohol by pyrolysis with boric acid takes place through a metaborate ester in which the eliminated groups have the *cis*-configuration. The preparation and properties of several metaborate esters are described and a mechanism for their pyrolysis is proposed.

Brandenberg and Galat[2] have recently recorded a new method for the preparation of olefins by the pyrolysis of equimolar amounts of boric acid and an alcohol. In the cases studied, excellent yields were obtained. The mechanism of the reaction was stated to involve two steps: (1) the formation of the orthoborate ester ($(RO)_3B$); and (2) the decomposition of this ester into olefin and boric acid. The authors pointed out that this reaction was analogous to the decomposition of acetate esters which also yields olefins.

A further study of this reaction has been carried out to extend its synthetic utility and to shed further light on its mechanism.

l-Menthol was studied first because of the elegant work of Hückel, *et al.*,[3] and Barton, *et al.*,[4] on the elimination reactions of this compound. When equimolar amounts of *l*-menthol and boric acid were heated at 150–180°, two moles of water were formed, and on raising the temperature to 270°, an 83–92% yield of a mixture of 9–13% of Δ^2-menthene and 91–87% of Δ^3-menthene was obtained.



Approximately 70% of the Δ^3-menthene formed by the boric acid elimination was racemized. In order to determine if this was characteristic of the reaction or if the Δ^3-menthene was racemized, following its formation, by metaboric acid, a sample of menthene obtained from *l*-menthyl S-methylxanthate by the Chugaev reaction, containing approximately 70% Δ^3-menthene and 30% Δ^2-menthene, was heated with metaboric acid at 270°. The Δ^3-menthene was partly racemized (10%) by this treatment and, therefore, it seems likely the racemization observed in this elimination is caused by the action of metaboric acid on the Δ^3-menthene after it has been formed. When a sample of pure Δ^2-menthene, obtained from *l*-menthyl chloride by elimination with sodium methoxide, was heated with metaboric acid at 270°, no racemization was observed.

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[1] Dow Chemical Company Fellow, 1952–1953.

[2] W. Brandenberg and A. Galat, THIS JOURNAL, **72**, 3275 (1950).

[3] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[4] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 453 (1952).