

ride than is the monomer mixture from which they are formed. The copolymers made by complete polymerization of a given starting mixture of monomer vary in composition from chain to chain.

2. The monomer units appear to be oriented in a 1,3-fashion in the polymer chain.

3. Some reactions of these copolymers have been described.

URBANA, ILLINOIS

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## The Acid Catalyzed Hydrolysis of Phenyl Substituted Aliphatic Esters<sup>1</sup>

BY HILTON A. SMITH AND R. R. MYERS

In a recent publication<sup>2</sup> a study of the effect of the character of an alkyl chain on the reaction velocity of acid hydrolysis was reported for a number of esters of aliphatic acids. It was demonstrated that the effects were similar to those produced in the processes of esterification<sup>3</sup> and of saponification of the same (ethyl) esters.<sup>4</sup>

The purpose of the present paper is to report the results of a study of the velocity of hydrolysis of a number of phenyl substituted aliphatic esters, and to compare these results with those previously reported for saponification of the same esters<sup>5</sup> and for the acid-catalyzed esterification of phenylacetic, hydrocinnamic and  $\gamma$ -phenylbutyric acids in absolute methanol.<sup>6</sup>

### Experimental

All of the esters were prepared by esterification of the corresponding organic acid with absolute ethanol using sulfuric acid as a catalyst. The esters were purified by fractionation in efficient distillation columns. Each sample used for rate measurements distilled at a constant head temperature and was also shown by analysis using the method already described<sup>4</sup> to be, within the precision of the method, 100% pure.

Phenylacetic, hydrocinnamic, phenylethylacetic and diphenylacetic acids were obtained from Eastman Kodak Co.;  $\gamma$ -phenylbutyric,  $\delta$ -phenylvaleric, cyclohexylacetic and hydratropic acids were all prepared by methods which have been previously described.<sup>5,6,7</sup>

The hydrolyses were all carried out in 70%

acetone solution, the concentration of both ester and catalyst (hydrochloric acid) being 0.1 *M*. The acetone used in making up the medium was carefully purified by fractionation from alkaline permanganate in a five-foot, one-inch diameter column packed with glass helices. The fraction retained distilled at constant head temperature. The method employed in making up the reaction mixtures was the same as that already described by Smith and Steele,<sup>2</sup> and the general experimental procedure was also the same. Corrections were made for the contraction in volume which occurs when acetone is mixed with water and also for thermal expansion of the solvent. The reactions were run in electrically heated water thermostats which gave temperatures constant to  $\pm 0.01^\circ$ .

### Experimental Calculations and Results

The rate constants were calculated using the expression for a first order reaction

$$k = \frac{2.303 \log a/(a-x)}{(\text{catalyst})t}$$

where *a* is the initial ester concentration, *x* is the concentration of organic acid formed after time *t*, and the (catalyst) is the concentration of added

TABLE I  
ACID CATALYZED HYDROLYSIS OF ETHYL  $\delta$ -PHENYLVALERATE IN 70% ACETONE AT 30°  
*a* = (ester) = (HCl) = 0.100 *M*

<i>t</i> , minutes	( <i>a</i> - <i>x</i> )	$\frac{10^3 k}{\text{liters moles}^{-1} \text{sec.}^{-1}}$
5	0.0999	....
2080	.1246	22.6
2690	.1304	22.6
2980	.1331	22.5
3500	.1379	22.7
4240	.1429	22.0
4360	.1449	22.8
5025	.1497	22.9
5440	.1539	23.8
Average, 20-50%		22.6

(1) Presented at the Memphis meeting of the American Chemical Society, April 22, 1942.

(2) Smith and Steele, *THIS JOURNAL*, **63**, 3466 (1941).

(3) Smith, *ibid.*, **62**, 1136 (1940).

(4) Levenson and Smith, *ibid.*, **62**, 1556 (1940).

(5) Levenson and Smith, *ibid.*, **62**, 2324 (1940).

(6) Smith, *ibid.*, **61**, 1176 (1939).

(7) The authors are indebted to Mr. H. S. Levenson and Mr. J. H. Steele for the preparation and analysis of some of the esters used in this research.

hydrochloric acid. Table I gives the results of a typical run.

For each run, the individual rate constants were averaged over the range of about 20–50% reaction. These limits were set in order to avoid any possible effects due to errors in making up the reaction mixture, due to loss of solvent as samples were withdrawn from the reaction flask, or caused by the reverse esterification reaction. The number of values averaged was usually six or seven, and the  $\pm$  errors were of the order of one per cent. The average rate constant for each run is listed in Table II.

TABLE II  
REACTION RATE CONSTANTS FOR ACID HYDROLYSIS OF ETHYL ESTERS OF PHENYL-SUBSTITUTED ACIDS IN 70% ACETONE

Ethyl ester	$a = (\text{ester}) = (\text{HCl}) = 0.100 M$			
	$t = 20^\circ$	$t = 30^\circ$	$t = 40^\circ$	$t = 50^\circ$
Phenylacetate	9.35	23.8	55.0	120
	9.32	23.6	54.9	120
Av.	9.34	23.7	54.9	120
Hydrocinnamate	8.03	20.7	47.5	110
	8.07	20.3	47.7	109
Av.	8.05	20.5	47.6	110
$\gamma$ -Phenylbutyrate	8.08	20.8	48.6	114
	7.99	19.7	48.6	111
	7.95	19.6		
		21.1		
Av.	8.00	20.4	48.6	112
$\delta$ -Phenylvalerate	8.56	22.0	53.2	123
	8.65	22.6	53.7	119
		22.6		
Av.	8.61	22.4	53.5	121
Hydratropate	0.169	0.443	1.11	2.46
	.172	.451	1.11	2.55
Av.	.171	.447	1.11	2.51
Phenylethylacetate	.0669	.177	0.435	0.99
	.0669	.179	.430	1.07
Av.	.0669	.178	.433	1.03
Diphenylacetate	.0296	.0839	.210	0.506
	.0296	.0833	.207	
Av.	.0296	.0836	.209	.506
Cyclohexylacetate	3.01	7.80	19.0	44.7
	2.99		19.0	43.9
Av.	3.00	7.80	19.0	44.1

Figure 1 gives a plot of  $\log k$  against  $1/T$  for the hydrolysis of these esters. The activation energies were calculated from the slopes of these lines,

and were checked by the method of least squares. These activation energies together with reaction rate constants at  $25^\circ$  are found in Table III. Included in this table are also  $k_{25}$  and activation energies for the processes of esterification and saponification. Figures for several unsubstituted esters are given for comparison purposes.

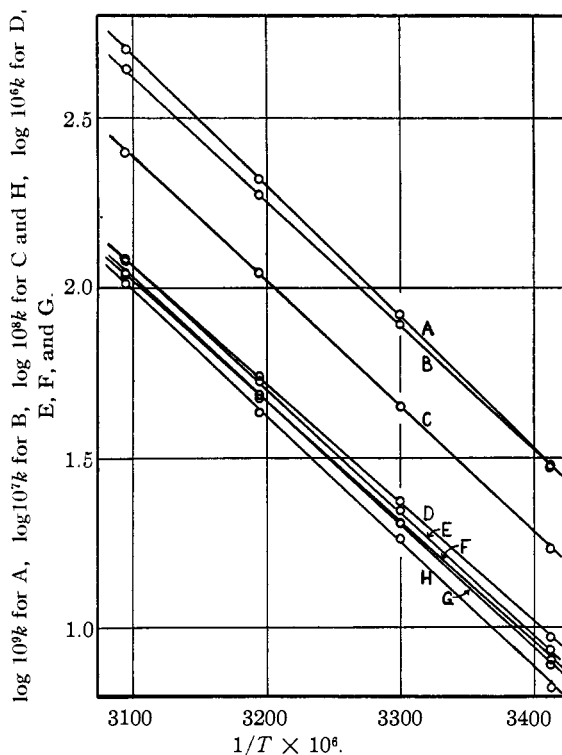


Fig. 1.—Temperature coefficients for acid hydrolysis of phenyl substituted aliphatic esters: A, ethyl diphenylacetate; B, ethyl cyclohexylacetate; C, ethyl hydratropate; D, ethyl phenylacetate; E, ethyl  $\delta$ -phenylvalerate; F, ethyl hydrocinnamate; G, ethyl  $\gamma$ -phenylbutyrate; H, ethyl phenylethylacetate.

The relative entropies of activation of these acids and esters have been calculated for the processes of esterification, acid hydrolysis and saponification, and are given in Table III. These values were calculated from the equation

$$\Delta S^* - \Delta S_0^* = R \ln A/A_0$$

where  $\Delta S^* - \Delta S_0^*$  is the relative entropy of activation and  $A$  is the "temperature independent" factor in the Arrhenius equation

$$k = Ae^{-E/RT}$$

The subscript zero refers to ethyl acetate for acid hydrolysis and saponification and to acetic acid for the process of esterification.

TABLE III

REACTION RATE CONSTANTS, ACTIVATION ENERGIES AND RELATIVE ENTROPIES OF ACTIVATION (REFERENCE SUBSTANCE ACETIC ACID OR ETHYL ACETATE) FOR THE PROCESSES OF ACID HYDROLYSIS, ESTERIFICATION AND SAPONIFICATION

Acid or ethyl ester	Acid hydrolysis			Esterification <sup>9</sup>			Saponification <sup>10</sup>		
	$10^4k_{25}$	$E$	$\Delta S^* - \Delta S_0^*$	$10^4k_{25}$	$E$	$\Delta S^* - \Delta S_0^*$	$10^4k_{25}$	$E$	$\Delta S^* - \Delta S_0^*$
Phenylacetate	1.47	16,100	-2.58	2.62	9,900	-1.96	10.1	14,100	-1.26
Phenylacetate <sup>11</sup>	1.54	16,200							
Hydrocinnamate	1.28	16,300	-2.19	2.67	9,600	-2.93	5.04	14,500	-1.30
$\gamma$ -Phenylbutyrate	1.27	16,500	-1.53	2.67	10,100	-1.25	2.69	14,900	-1.21
$\delta$ -Phenylvalerate	1.39	16,600	-1.02				2.28	14,700	-2.21
Hydratropate	0.277	16,900	-3.22				0.802	15,400	-1.93
Phenylethylacetate	.110	17,100	-4.38				.264	15,900	-2.47
Di-phenylacetate	.0503	17,700	-3.92				.560	16,000	-0.63
Cyclohexylacetate	.481	16,900	-2.12				.509	15,600	-2.17
Acetate	4.55	16,200	0	5.93	10,000	0	6.92	14,700	0
Propionate	3.77	16,300	-0.03	5.73	10,000	-0.07	3.55	14,700	-1.33
Butyrate	1.86	16,400	-1.11	2.90	10,000	-1.42	1.83	15,100	-1.30
Valerate	1.82	16,500	-0.81	3.08	10,000	-1.30	1.92	14,700	-2.55

### Discussion

As seen from an inspection of Table III, the substitution of a phenyl group on the terminal carbon atom of an alkyl chain causes an increase in the reaction rate for the process of saponification, and this is accompanied by the expected decrease in the activation energy. These changes are apparently caused by the fact that the phenyl group, when not a part of a conjugated system, acts as an electron sink, thus drawing electrons away from the carboxyl group, and so facilitating the approach of the hydroxyl group. The magnitude of this effect decreases as the phenyl group is moved farther from the carboxyl group, as would be expected. When, however, substitution of the phenyl group takes place in the alpha position of an ester such as ethyl propionate or butyrate, the reaction rate is decreased, and the activation energy increased. This is evident from inspection of Table III.

This apparent discrepancy in the influence of the introduction of a phenyl group on the velocity of saponification has been explained as being due to the fact that this group not only acts as an electron sink, but also exhibits a rather large steric effect.<sup>5</sup> The former causes an increase in the rate of reaction and a lowering of  $E$ . The latter causes a decrease in the reaction rate, and apparently an increase in the activation energy.

(8) Interpolated from the data in Table II and from those of Smith and Steele, ref. 2.

(9) Calculated from the data of Smith, ref. 6, and of Smith and Reichardt, THIS JOURNAL, **63**, 605 (1941).

(10) From the data of Levenson and Smith, ref. 5.

(11) From the data of Davies and Evans, *J. Chem. Soc.*, 339 (1940). These values were determined using 0.05 *M* solutions of ester and catalyst. Under these conditions the reaction rate is greater by about 5% than when 0.10 *M* concentrations are employed (see Smith and Steele, ref. 2).

The data for acid hydrolysis as given in Table III offer no direct evidence that the phenyl group acts as an electron sink, since its introduction always decreases the reaction velocity. Other data, however, may lead one to expect the opposite result.<sup>12</sup> In fact, the postulated mechanisms for acid and alkaline hydrolysis involve the same intermediate,<sup>13</sup> although the influence of substituents is smaller for the acid catalyzed reaction.<sup>14</sup>

Some idea of the relative magnitude of the inductive effect may be gained from a comparison of the rates of ethyl cyclohexylacetate with those for ethyl phenylacetate. In saponification the activation energy is 15,600 calories per mole for cyclohexylacetate and 14,100 for the phenylacetate. For acid-catalyzed hydrolysis the corresponding values are 16,900 and 16,100. Assuming the steric influence of the phenyl and cyclohexyl groups to be the same, the inductive effect is represented by some 700 calories less influence in the activation energy for acid hydrolysis than for base catalyzed hydrolysis. Since the drop in activation energy caused by introduction of a phenyl group into ethyl acetate is only 600 calories for saponification, one would expect little change in the activation energy for the process of acid hydrolysis. This agrees with the experimental findings as shown in Table III.

This type of reasoning also explains the fact that ethyl diphenylacetate is hydrolyzed about twice as fast as ethyl phenylethylacetate in the

(12) Cf. Ingold and Nathan, *J. Chem. Soc.*, 222 (1936); Timm and Hinshelwood, *ibid.*, 862 (1938).

(13) Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, page 268.

(14) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 461.

TABLE IV  
EFFECT OF  $\alpha$ -PHENYL SUBSTITUTION ON SAPONIFICATION AND ACID HYDROLYSIS

	Saponification		Acid hydrolysis	
	$\Delta \log k$	$\Delta E$	$\Delta \log k$	$\Delta E$
Acetate $\rightarrow$ phenylacetate	+ .1642	- 600	- .4907	- 100
Propionate $\rightarrow$ hydratropate	- .6460	+ 700	-1.1338	+ 600
Butyrate $\rightarrow$ phenylethylacetate	- .8409	+1000	-1.2281	+ 700
Phenylacetate $\rightarrow$ diphenylacetate	-1.2561	+1900	-1.4657	+1600

base-catalyzed reaction, but only half as fast when the acid catalyst is employed. It is also substantiated by noting that in both processes the introduction of a phenyl group into the alpha position causes a much greater effect when another substituent is already present on the same carbon atom. This is shown in Table IV.

Unfortunately, the data for esterification are not sufficiently complete to allow many deductions, but apparently this process is similar to that of acid hydrolysis in that the steric effect due to phenyl substitution always outweighs the inductive influence, even when such substitution takes place on the terminal carbon atom. The fact that phenylacetic, hydrocinnamic and  $\gamma$ -phenylbutyric acids esterify with almost identical rates is perhaps better explained as a fortuitous balance between inductive and steric effects than as caused by ring formation.<sup>6</sup>

### Summary

The kinetics of acid catalyzed hydrolysis in 70% acetone has been studied for ethyl phenylacetate, ethyl hydrocinnamate, ethyl  $\gamma$ -phenylbutyrate, ethyl  $\delta$ -phenylvalerate, ethyl hydratropate, ethyl phenylethylacetate, ethyl diphenylacetate and ethyl cyclohexylacetate.

The introduction of a phenyl group into an aliphatic ester results in a decrease in the reaction rate for all esters studied, even though the phenyl group acts as an electron sink, and should cause an increase in the rate of hydrolysis. The results may be explained on the assumption that the steric effect of the phenyl group always outweighs its inductive effect for this process.

A comparison is made of the effect of phenyl substitution on the processes of acid hydrolysis, saponification and esterification.

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## The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. II. Aromatic Polynuclear Hydrocarbons<sup>1</sup>

BY S. WAWZONEK AND H. A. LAITINEN

Aromatic compounds possessing a high degree of resonance, such as benzene, do not undergo reduction at the dropping mercury electrode. On the other hand, aromatic polynuclear hydrocarbons showing a diminished degree of resonance are reducible. The polarographic reduction of such hydrocarbons is described in the present paper.

### Results

The behavior of various aromatic polynuclear hydrocarbons was studied in a 0.175 *M* tetrabutylammonium iodide, 75% dioxane solution.<sup>1</sup> A summary of the observed half-wave potentials and individual diffusion current constants is given in Table I.

(1) Paper I, Laitinen and Wawzonek, *THIS JOURNAL*, **64**, 1765 (1942). This paper was presented before the Division of Organic Chemistry of the American Chemical Society at the Buffalo meeting, September, 1942.

In general, all of the hydrocarbons gave well-defined reduction waves similar to that shown in Fig. 1 for 3-methylcholanthrene. Exceptions to this behavior were treated in the following manner. For compounds (phenanthrene and pyrene) showing two waves of equal height close together such as those shown in Fig. 2 for phenanthrene, the half-wave potentials were calculated by using one-fourth and three-fourths of the total diffusion current. In the table for such cases only the total diffusion current is reported even though two waves were obtained. For compounds (chrysene and 3,4-benzopyrene) which gave indefinite waves such as that shown in Fig. 3 for 3,4-benzopyrene, only the total diffusion current is given. For indene which gave a wave at a potential too negative to be measured, the starting point of the wave is given.