

cate that the fluorinated phenethylamines are slightly more toxic than the unsubstituted compounds. Toward dogs and guinea pigs the

amines showed pressor activity while with rabbits the effect was depressor.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Acid Catalyzed Esterification of Normal Fatty Acids

BY HILTON A. SMITH AND C. H. REICHARDT

In a recent article¹ the study of the effect of the length of the carbon chain on the rate of the catalyzed esterification of normal aliphatic acids in dry methanol was reported. It was demonstrated that an increase in the hydrocarbon chain length of the acid from one to three carbon atoms caused a lowering of the value of the specific reaction rate constant, while further increase in the number of carbon atoms had no effect. It was further demonstrated that the activation energy is, within experimental error, the same (about 10,000 cal./mole) for all normal acids.

In a subsequent publication, Fairclough and Hinshelwood² also reported a study of the esterification of normal fatty acids, including the catalyzed reaction in dry methanol. Their findings differ from those already published. Their activation energies are consistently higher by some 15–20%, and E for the esterification of acetic acid is also considerably greater than for acids of larger molecular weight. Also, their results indicate that, instead of remaining the same with increasing chain length, the reaction velocity constants for esterification of butyric and higher acids go through a minimum at a chain length of approximately ten carbon atoms.

The high activation energies in general and also the low k 's for pelargonic acid as reported by Fairclough and Hinshelwood, are a direct result of their choice of the values of r in Goldschmidt's equation

$$(1) \quad k = \frac{(a+r) \ln[a/(a-x)] - x}{rt \text{ (catalyst)}}$$

where a is the original concentration of organic acid, x is the concentration of ester formed after time t , and the catalyst is hydrogen chloride. The constant r , although determined experimentally by choosing that figure which gives the most consistent reaction rate constants, is defined theoretically by the equation

$$(2) \quad r = (\text{CH}_3\text{OH}_2^+)(\text{H}_2\text{O})/(\text{H}_3\text{O}^+)$$

(1) Smith, *THIS JOURNAL*, **61**, 254 (1939).

(2) Fairclough and Hinshelwood, *J. Chem. Soc.*, 593 (1939).

and hence should be essentially independent of the particular organic acid present or of its concentration. Nevertheless, these authors have used different r values for each acid studied. The low reaction velocity constant for pelargonic acid is due to their choice for this acid of an r which is approximately twice as great as that chosen for either hexoic or palmitic acids. (No intervening acids were studied.) Their high activation energies are caused by the fact that their values of r decrease with temperature. The non-constancy of r for different acids and its decrease with temperature are quite the opposite from the results not only of Smith¹ but also of Goldschmidt,³ Williamson and Hinshelwood,⁴ Hinshelwood and Legard,⁵ Hartman and co-workers⁶ and others. Fairclough and Hinshelwood explain the difference in their values of r for acetic acid esterification from those found by Williamson and Hinshelwood as being due to the change from 0.5 to 0.1 N solution. Considering the theoretical significance of r , it seems questionable that this dilution could decrease the value of this constant from 0.345 to 0.11 at 45°, and at the same time cause it to increase from 0.125 to 0.27 at 0°.

Because of these discrepancies, the study of the catalyzed esterification of normal fatty acids in dry methanol under the conditions described by Fairclough and Hinshelwood has been repeated.

Experimental

As in previous work,¹ dry methanol was prepared by distillation in a 5-ft. (1.5-meter) spiral column. All organic acids, with the exception of lauric acid, were purified by fractionation in efficient fractionating columns. Eastman Kodak Co. lauric acid was used without purification.

(3) Goldschmidt and co-workers, *Z. physik. Chem.*, **60**, 728 (1907); **81**, 30 (1912); **143**, 139, 278 (1929).

(4) Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

(5) Hinshelwood and Legard, *J. Chem. Soc.*, 587 (1935).

(6) Hartman and Borders, *THIS JOURNAL*, **59**, 2107 (1937); Hartman and Gassmann, *ibid.*, **62**, 1559 (1940).

All acids were analyzed before use by titration with standard base, and all analyzed better than 99.5% pure.

Runs were made in the manner previously described.¹ The expansion of the various reaction mixtures (without added catalyst) was measured experimentally over the complete temperature range of the esterification studies, and all measurements were corrected for solvent expansion.

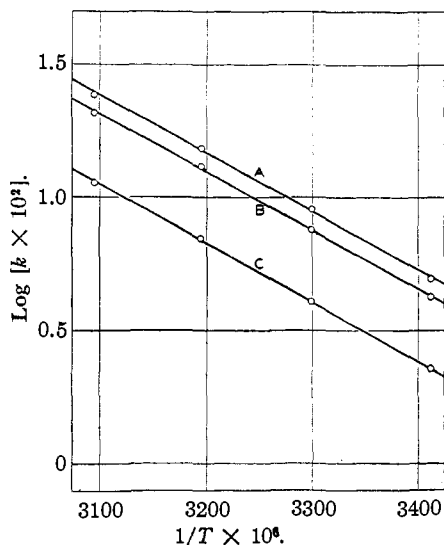


Fig. 1.—Temperature coefficients of hydrogen ion catalyzed esterification of normal fatty acids in methanol: A, acetic acid; B, propionic acid; C, higher normal acids.

Experimental Calculations and Results

The reaction rate constants were calculated from Goldschmidt's equation (Equation (1)).

Acid	Normality	r			
		20°	30°	40°	50°
Acetic	0.500	0.18	0.23	0.30	0.42
Acetic	.250	.19	.23	.30	.42
Acetic	.100	.20	.25	.34	.40
Propionic	.0993	.20	.23	.34	.48
Butyric	.100	.20	.28	.30	.44
Valeric	.100	.22	.27	.34	.40
Caproic	.0995	.20	.23	.28	.41
Lauric	.100	.20	.24	.32	.43
Average of above		.20	.25	.32	.42
Acetic ^a	.5	.17	.21	.28 ^a	.44 ^a
Acetic ^a	.1	.19	.16	.125 ^a	.09 ^a
Acetic ^b	.5, .1	.20 ^a	.26 ^a	.39 ^a	.58 ^a
Normal acids ^c	.5	.20	.25	.32	.42
Substituted benzoic acids ^d	.1	.20 ^a	.26 ^a	.36	.50

^a Fairclough and Hinshelwood, ref. 2. For values of r reported for other normal acids, see their paper. ^b Williamson and Hinshelwood, ref. 4. ^c Smith, ref. 1. ^d Hartman and co-workers, ref. 6. * Extrapolated.

The values of r used were those which gave the most constant k 's over the range 20–80% reaction. Table I gives the best values for r found for each acid. It also includes figures already in the literature.

The calculated reaction rate constants are given in Table II. For these runs the concentration of the catalyst, hydrochloric acid, was 0.005 N . The r 's used in calculating the reaction rate constants were the average figures listed in Table I. The plot of $\log k$ versus $1/T$ for the esterification of 0.1 N acids is shown in Fig. 1. The activation energies given in Table II are calculated from the slopes of these lines, and were checked by the method of least squares. Activation energies are reported to the nearest 100 calories.

TABLE II
REACTION RATE CONSTANTS FOR ESTERIFICATION OF NORMAL FATTY ACIDS IN METHANOL CATALYZED BY H^+ IONS

Normality	k (liter mole ⁻¹ sec. ⁻¹)				E
	$t = 20^\circ$	$t = 30^\circ$	$t = 40^\circ$	$t = 50^\circ$	
Acetic acid					
0.500	0.0443	0.0780	0.134	0.208	
	.0443	.0789	.132	.211	
Av.	.0443	.0785	.133	.209	9,800
.250	.0438	.0833	.137	.218	
	.0434	.0831	.135	.216	
Av.	.0436	.0832	.136	.217	10,000
.100	.0490	.0899	.151	.243	
	.0495	.0905	.155	.252	
Av.	.0493	.0902	.153	.248	10,000
Propionic acid					
.0993	.0422	.0754	.131	.207	
	.0423	.0762	.131	.208	
Av.	.0423	.0758	.131	.207	10,000
Butyric acid					
.100	.0217	.0387	.0667	.110	
	.0213	.0375	.0670	.107	
Av.	.0215	.0381	.0668	.108	10,000
Valeric acid					
.100	.0221	.0416	.0717	.115	
	.0229	.0414	.0708	.114	
Av.	.0225	.0415	.0712	.114	10,200
Caproic acid					
.0995	.0243	.0423	.0718	.119	
	.0241	.0429	.0719	.114	
Av.	.0242	.0426	.0719	.117	9,900
Lauric acid					
.100	.0226	.0403	.0694	.112	
	.0221	.0404	.0684	.114	
Av.	.0223	.0404	.0689	.113	10,200
Acetic acid ^a					
.500	.0440	.0814	.132	.219	10,000

^a Results previously published (ref. 1).

Discussion

An examination of Table I shows that, within reasonable experimental error,⁷ the values of the constant r are the same for each acid. Furthermore, r is the same for different concentrations of organic acids. This is as would be expected from theoretical considerations. In all the data listed in Table I except those of Fairclough and Hinshelwood, r increases with increasing temperature.

The maximum difference in the r 's reported here from those of Fairclough and Hinshelwood occurs in the 50° values. Table III gives a comparison of the reaction rate constants calculated over the course of a single run, using the two different r 's for this temperature. The constants

TABLE III

t, min.	a - x	(HCl) = 0.00500	
		k (liters mole ⁻¹ sec. ⁻¹) $r = 0.42$	$r = 0.09$
1	0.09322	0.239	0.246
3	.08106	.242	.262
5	.07036	.246	.278
6.8	.06171	.251	.295
9	.05320	.251	.300
14	.03761	.256	.317
19	.02724	.255	.343
25	.01894	.252	.353
30	.01424	.249	.356
40	.00812	.244	.352

calculated with $r = 0.42$ are much better than those calculated with $r = 0.09$. Also, at the beginning of the run, the inhibition of the esterification by water formation is relatively unimportant since little water is present, and hence the value of r chosen makes little difference. After considerable esterification has taken place, however, inhibition by water formation becomes more important. If the correct value of r is chosen, the individual reaction velocity constants should be the same toward the latter part of the run as at the beginning. Table III shows plainly that the r at 50° of Fairclough and Hinshelwood is much too low.

It does not seem possible to state the cause of the low r values found by Fairclough and Hinshelwood at higher temperatures, particularly since they did not find this trend when 0.5 *N* acetic acid was studied. One explanation lies in the fact that different concentrations of catalyst were used for each run. Studies made with 0.1 *N* acetic acid

(7) The reaction rate constants are not very sensitive to changes in r , a variation of 10 or 15% in the latter producing little change in k . Conversely, a small error in k will produce a large error in r when the latter is calculated in the usual manner.

TABLE IV

ESTERIFICATION OF 0.1 *N* ACETIC ACID IN DRY METHANOL AT 30°

(HCl)	k (liter mole ⁻¹ sec. ⁻¹)
0.0100	0.0704
.0075	.0856
.0050	.0902
.0025	.0941

and concentrations of hydrochloric acid from 0.0025 to 0.1 *N* indicate some drift in k as shown in Table IV. This demonstrates the necessity of keeping the concentration of catalyst within fairly narrow limits when reaction rate constants for several acids are to be compared. However, there is no indication that the value of r varies sufficiently to account for the findings of Fairclough and Hinshelwood.

The data for 0.1 *N* acids given in Table II when compared with the data for 0.5 *N* acids (see ref. 1) indicate a slight drift in the reaction velocity constants with changing concentration of organic acid, the constants increasing with dilution. The same result was found for acetic acid by Williamson and Hinshelwood.⁴

The results of the work reported here confirm those reported earlier,¹ *i. e.*, that the activation energy for the catalyzed esterification reaction is, within experimental error, the same regardless of chain length of the organic acid. Fairclough and Hinshelwood found the same result for the uncatalyzed esterification of organic acids in ethanol. They conclude that "We should expect from the electronic theory of organic reactions that the first few members of the fatty acid series would show progressive changes in the energy of activation for esterification." This expectation is fulfilled for neither the catalyzed nor the uncatalyzed reactions. It is also interesting to note that for the uncatalyzed reaction in cyclohexanol, the data of Fairclough and Hinshelwood indicate a decrease in the reaction rate constants from acetic to butyric acids. The electronic theory of organic reactions would predict a corresponding increase in the activation energy with increasing chain length, while actually a decrease is reported.

Summary

The acid catalyzed esterification of normal fatty acids in dry methanol has been studied for 0.1 *N* solutions of six acids having from one to eleven carbon atoms in the hydrocarbon chain.

It is demonstrated that, contrary to the findings of Fairclough and Hinshelwood, the con-

stant r in Goldschmidt's equation is independent either of the nature of the organic acid or of its concentration. It is also demonstrated that, in agreement with esterification studies made with

0.5 N acid concentrations, the activation energy is constant throughout the normal series, having a value of 10,000 cal./mole.

BETHLEHEM, PENNA. RECEIVED SEPTEMBER 13, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. XIII. Sulfonation¹

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The use of hydrogen fluoride to promote a condensation between carboxylic acids and hydrocarbons² and also its use to rearrange *p*-cresyl benzenesulfonate to 2 hydroxy-5-methyl diphenyl sulfone³ indicate that this reagent would be useful in reactions for the preparation of sulfonic acids and sulfones.

It was found that a mixture of hydrogen fluoride and sulfuric acid would react with an aromatic compound to form either the sulfonic acid or the symmetrical sulfone depending on the temperature. The sulfone was formed at higher temperatures. Unsymmetrical sulfones were formed by the treatment of either a sulfonic acid or sulfonyl chloride with an aromatic compound in the presence of hydrogen fluoride. It is believed that sulfuric acid reacts with hydrogen fluoride to form fluorosulfonic acid and water,⁴ and fluorosulfonic acid is an effective sulfonating agent.⁵ We have found it more reactive than chlorosulfonic acid. It reacts with chloroform but not carbon tetrachloride at room temperature and it also reacts with normal pentane at room temperature.

Experiments using hydrogen fluoride as an aid in nitration were also investigated. It was found that benzene in the presence of hydrogen fluoride was rapidly nitrated by nitric acid at 0° but that nitrobenzene did not nitrate at this temperature. Patents⁶ have indicated the use of potassium nitrate to nitrate benzene and phenol in the presence of hydrogen fluoride.

Experimental

Benzene and Sulfuric Acid.—A mixture of 75 g. of hydrogen fluoride, 25 g. of sulfuric acid, and 100 cc. of benzene

was heated for sixteen hours at 85 to 95° in a copper bomb. Less than 1 g. of diphenyl sulfone was formed but a yield of 75% of benzene sulfonic acid was obtained as the calcium salt. This was analyzed for calcium: found 11.2% calculated 11.3%.

A mixture of 9.8 g. of sulfuric acid, 118 g. of hydrogen fluoride, and 110 g. of benzene was heated in a bomb for eighteen hours at 140–150°. From the reaction products 8.9 g. of diphenyl sulfone melting at 127–128° was obtained. This represented a yield of 40%. A dinitro derivative⁷ was prepared which after one recrystallization melted at 196–197°.

Benzene and Fluorosulfonic Acid.—A mixture of 25 g. of fluorosulfonic acid and 88 g. of benzene was heated at 160° for sixteen hours. A yield of 14% of diphenyl sulfone, melting at 127–128°, was obtained. It was identified by the melting point, 195.5–196.5°, of its dinitro derivative.

At 60–70° a mixture of benzene and fluorosulfonic acid gave a 53% yield of benzene sulfonic acid.

***p*-Toluene Sulfonic Acid and Benzene.**—A mixture of 20 g. of the acid, 70 g. of hydrogen fluoride, and 250 cc. of benzene was heated at 85–95° for twenty-four hours. From the reaction mixture 2 g. of *p*-tolyl phenyl sulfone was obtained. It melted at 119–122°.

Benzenesulfonyl Chloride and Toluene.—A mixture of 17 g. benzenesulfonyl chloride, 200 cc. of toluene, and 200 g. of hydrogen fluoride was first allowed to stand for twenty-four hours at 0° and then heated for twenty-four hours at 85–95°. A small amount of *p*-tolyl phenyl sulfone, m. p. 120–122°, was obtained.

Benzene and Nitric Acid.—A mixture of 44 g. of benzene and 47 g. of hydrogen fluoride was placed in a copper vessel which was coated on the inside with a high melting wax. This was placed in a salt-ice mixture and one-eighth mole of nitric acid was added with stirring in a fifteen-minute period. An 83% yield of nitrobenzene was obtained. No dinitrobenzene nor fluorobenzene was detected. A portion of the nitrobenzene was further nitrated to give *m*-dinitrobenzene, m. p. 89–90°. A similar experiment using nitrobenzene instead of benzene failed to produce any detectable amount of dinitrobenzene.

Summary

Hydrogen fluoride has been shown to be effective in promoting sulfonation and nitration. Benzene sulfonic acid and diphenyl sulfone were

(7) Buehler and Masters, *J. Org. Chem.*, **4**, 262 (1939).

(1) For the previous paper of this series see Simons and Passino, *THIS JOURNAL*, **62**, 1624 (1940).

(2) Simons, Randall and Archer, *ibid.*, **61**, 1795 (1939).

(3) Simons, Archer and Randall, *ibid.*, **62**, 485 (1940).

(4) Simons, *Chem. Rev.*, **8**, 213 (1931).

(5) Meyer and Schramm, *Z. anorg. allgem. Chem.*, **206**, 24 (1932).

(6) Fredenhagen, German Patent 529,538, Aug. 2, 1930; Gleich, Russian Patent 39,775, Nov. 30, 1934.