noted that these are extremely large molecules and hence a small percentage error leads to a large absolute error. Consequently any small differences in energy content due to structural modifications could easily be masked by the experimental uncertainties.

Summary

1. The isothermal heats of combustion at 25° of 3-phenyleicosane, 9-phenyleicosane, 3-cyclohexyleicosane, 9-cyclohexyleicosane, 11-cyclopentylheneicosane, 11-phenylheneicosane, 11-cyclohexylheneicosane, 5-*n*-butyldocosane, 11-*n*-butyldocosane, and 11-*n*-decylheneicosane have been determined.

2. From the above data the heats of formation have been calculated.

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[CONTRIBUTION NO. 40 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Kinetics of the Acid-catalyzed Esterification of Phenyl- and Cyclohexyl-substituted Aliphatic Acids in Methanol

BY HILTON A. SMITH AND JAMES BURN

In a series of papers[1] a study of the effect of position and nature of certain substituents on the velocity of esterification of aliphatic acids and of acid and base catalyzed hydrolysis of their ethyl esters has been reported. The purpose of the present paper is to report the results of further experiments dealing with the effect of phenyl and cyclohexyl substituents on the rate of acid-catalyzed esterification.

Experimental

Cyclohexylacetic acid was prepared from cyclohexyl bromide by a malonic ester synthesis carried out in the usual manner. The crude acid was fractionated under reduced pressure in a 5-ft. (1.5 meter) Vigreux column. The samples used distilled at 135° under a pressure of 12 mm., melted at 29.7°, and analyzed 99.8% by titration with standard base.

β-Cyclohexylpropionic acid, γ-cyclohexylbutyric acid, and **dicyclohexylacetic acid** were prepared by hydrogenation of hydrocinnamic, γ-phenylbutyric, and diphenylacetic acids, respectively. The hydrogenations were carried out in acetic acid solution using Adams catalyst. When hydrogenation was complete, the acids were thrown out of solution by addition of water, or were separated from the solvent by distillation. The β-cyclohexylpropionic acid was fractionated in a 5-ft. (1.5-meter) Vigreux column under reduced pressure. The samples used distilled at 141° at 9 mm. pressure, froze at 17.8° (cor.), and analyzed 99.8%. The γ-cyclohexylbutyric acid was fractionated in a small 25-cm. Vigreux column. The samples used distilled at 169° at 20 mm. pressure, froze at 31° (cor.), and analyzed 100.0%. The dicyclohexylacetic acid was recrystallized from ether. It melted at 138.6°, and analyzed 99.9%.

Phenylethylacetic acid, obtained from the Eastman Kodak Company, was fractionated under reduced pressure in a 5-ft. (1.5-meter) Vigreux column. The best samples from the fractionation (m. p. 39.6–41.4°) were recrystallized from ligroin. The purified material melted at 41.6–42.0°, and analyzed 99.9%.

δ-Phenylvaleric acid was prepared from γ-phenylpropyl bromide by a malonic ester synthesis carried out in the usual manner. The product was fractionated under vacuum, and the best samples (m. p. 57.7–58.2°) were recrystallized from ligroin. The resulting crystals melted at 58.2–58.7° (cor.), and analyzed 99.8%.

Diphenylacetic and **triphenylacetic acids** were used directly as obtained from the Eastman Kodak Company. The diphenyl compound melted at 148.2–148.7° (cor.), and analyzed 99.5%. The triphenyl compound melted at 265.6°.

Methanol was obtained in a pure, dry state, as in previously reported work, by careful fractionation of methyl alcohol through a 5-ft. (1.5-meter) spiral column. The material used distilled at a constant head temperature. A check sample was prepared according to the directions of Lund and Bjerrum.[2] When used in esterification, this methanol gave results identical with those obtained using methanol which had been fractionated only.

The method used to obtain rate constants was essentially that previously described.[3] Corrections were made for solvent expansion.

Experimental Results and Calculations

The rate constants were calculated from Goldschmidt's equation

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

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 values of the constant, r, used were those obtained in earlier work with normal aliphatic acids.[1,4] All of the acids except dicyclohexylacetic and triphenylacetic acids esterified sufficiently fast to make correction for reaction of the catalyst with the solvent unnecessary. The results of a typical run are given in Table I.

For several of the runs, the value of the rate constant fell off toward the end of the reaction somewhat more than in previous work. For this reason, only constants obtained in the interval represented by 20–60% reaction were averaged.

The calculated reaction rate constants are given in Table II. For these runs, the initial concentration of organic acid was 0.500 mole per liter, and the concentration of the catalyst, HCl, was 0.005 *M*. The plot of log k *versus* $1/T$ for the esterification of these acids is shown in Fig. 1. The activation energies in Table II are calculated from the slopes of these lines, and were checked

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[1] For the latest, see Smith and Myers, THIS JOURNAL, **64**, 2362 (1942).

(2) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

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

(4) Smith and Reichardt, *ibid.*, **63**, 605 (1941).

TABLE I

ESTERIFICATION OF δ-PHENYLVALERIC ACID AND METHANOL AT 40°

$a = 0.500$; (HCl) = 0.00500

t, min.	$(a - x)$	10^3k, liters moles^{-1} sec.$^{-1}$
2.17	0.4872	3.99
8.00	.4417	5.65
13.00	.4060	6.18
25.08	.3427	6.33
35.63	.3009	6.36
58.20	.2395	6.14
79.58	.1908	6.30
107.83	.1499	6.16
157.65	.1050	6.27
255.93	.0531	5.75

by the method of least squares. Activation energies are reported to the nearest 100 calories.

TABLE II

REACTION RATE CONSTANTS FOR ESTERIFICATION OF ALIPHATIC ACIDS IN METHANOL CATALYZED BY HCl

$a = 0.500$; (HCl) = 0.005

Acid	k(liters × mole^{-1} × sec.$^{-1}$)				E
	$t = 20°$	$t = 30°$	$t = 40°$	$t = 50°$	
Cyclohexylacetic	0.00529	0.00970	0.0173	0.0279	10,500
	.00521	.00988	.0166	.0279	
			.0168		
			.0172		
Av.	.00525	.00979	.0170	.0279	
β-Cyclohexylpropionic	.0211	.0348	.0595	.105	10,100
	.0209	.0362	.0605	.106	
		.0351	.0595	.106	
Av.	.0210	.0354	.0598	.106	
γ-Cyclohexylbutyric	.0196	.0323	.0584	.0972	10,100
	.0191	.0333	.0563	.0955	
	.0195			.0941	
	.0194				
Av.	.0194	.0328	.0574	.0956	
Phenylethylacetic	.00180	.00333	.00626	.0105	11,100
	.00181	.00332	.00627	.0105	
Av.	.00181	.00333	.00626	.0105	
Diphenylacetic	.00134	.00245	.00447	.00777	11,100
	.00133	.00245	.00445	.00779	
Av.	.00133	.00245	.00446	.00778	
δ-Phenylvaleric	.0212	.0356	.0625	.103	9,900
	.0208	.0363	.0612	.102	
				.102	
Av.	.0210	.0360	.0618	.102	

Values of the rate constants for dicyclohexylacetic and triphenylacetic acids are not included in Table II. This is due to the fact that these acids do not esterify under the conditions of this work, nor under other easily obtainable experimental conditions. It has already been shown by Braun and Fischer[5] that diisopropyl- and dicyclopentylacetic acids do not esterify. It is not surprising, therefore, to find that dicyclohexylacetic acid resists esterification. In considering triphenylacetic acid, however, one finds that Gyr[6] lists rate constants at 25° for the esterification in methanol of phenylacetic, diphenylacetic, and triphenylacetic acids. His catalyst was hydrogen chloride. These constants were calculated on the basis of the equation

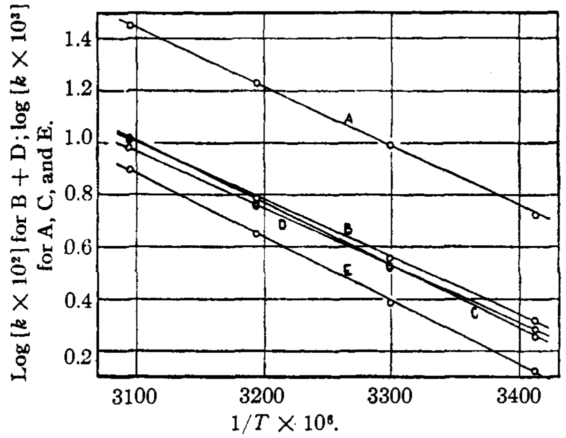

Fig. 1.—Temperature coefficients of acid-catalyzed esterification in methanol: A, cyclohexylacetic acid; B, β-cyclohexylpropionic or δ-phenylvaleric acid; C, phenylethylacetic acid; D, γ-cyclohexylbutyric acid; E, diphenylacetic acid.

$$k = 1/t \log a/(a - x)$$

which makes no allowance for the reaction

$$CH_3OH_2^+ + H_2O \rightleftarrows CH_3OH + H_3O^+$$

Taking this fact into consideration, Gyr's rate constants for phenylacetic and diphenylacetic acids are in reasonable agreement with those interpolated from the data of Table II. For triphenylacetic acid, the rate constants calculated from Gyr's data fall off very badly, as is shown in the following:

Time, hours	$k \times 10^3$
25	1.006
50	0.664
100	.376
200	.212
400	.152

Gyr notes that, during experiments covering a long period of time, methyl chloride is formed in amounts which affect the calculation of k. However, he feels that, for comparison with other acids which he studied, the measurements with triphenylacetic acid are sufficiently exact.

Hinshelwood[7] measured the initial rate (obtained by extrapolation to zero time) of the reaction of HCl with dry methanol, and found the following values for 0.1 M solutions:

Temp., °C.	Initial rate (%/minute)
100.0	2.77
84.2	0.80
80.0	.57
68.4	.146
56.3	.037
40.0	.00419

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[5] Braun and Fischer, *Ber.*, **66B**, 101 (1933).

[6] Gyr, *ibid.*, **41**, 4812 (1908).

[7] Hinshelwood, *J. Chem. Soc.*, 599 (1935).

A plot of the logarithm of the initial rate against the reciprocal of absolute temperature gives a straight line. The initial rate at 25°, obtained by extrapolation of this line, is 0.00049% per minute for a 0.1 M solution of HCl, while Gyr's data indicate for the reaction of 0.05 M HCl plus 0.05 M triphenylacetic acid with methanol a rate of 0.00040% per minute based on 200 hours and 0.00028% per minute based on 400 hours. These calculations demonstrate clearly that the interaction of HCl with methanol may well account for all of the reaction observed by Gyr.

To check this point, and also further to demonstrate the resistance of both triphenylacetic and dicyclohexylacetic acids to esterification, a strong solution (6.6 N) of HCl in methanol was prepared. Three portions of this solution were placed in stoppered Erlenmeyer flasks. One of these served as a blank, and triphenylacetic and dicyclohexylacetic acids were added to the other two. All three were allowed to stand in a water-bath held at 60 ± 1° for about twenty hours, after which time each showed the same concentration change. This indicates that the only reaction occurring in each of the three flasks was that between HCl and methanol, and that triphenylacetic and dicyclohexylacetic acids were not esterified.[8]

Discussion

It has already been demonstrated that substitution must take place in the α- or β-position of the acid in order to affect the rate of esterification.[9] Table III gives reaction rate constants, activation energies, and relative entropies of activation for the esterification of the acids which have been reported either in this paper or in previous ones. These acids have been listed in an order depending on the number of substituents in the positions which are α- or β- with reference to the carboxyl group.[10] In calculating these numbers, substitution of an ethyl group in the α-position is counted not as one substitution, but rather as two, *i. e.*, a methyl substitution in the α-position plus a subsequent methyl substitution in the β-position. Similarly, substitution of an isopropyl, cyclopentyl, cyclohexyl, or phenyl group in the α-position is counted as three substitutions. However, substitution of any of these groups in the β-position is only counted once.

TABLE III

EFFECT OF ACID STRUCTURE ON ESTERIFICATION VELOCITY

Acid	Number of substitutions	10^2k_{25}	E	$\Delta S^* - \Delta S_0^*$	Ref.
Acetic	0	5.93	10,000	0 (ref. acid)	*a*
Propionic	1	5.73	10,000	−0.07	*a*
Butyric	2	2.90	10,000	−1.42	*a*
Valeric	2	3.08	10,000	−1.30	*a*
Caproic	2	2.92	10,000	−1.41	*a*
Pelargonic	2	2.80	9,800	−2.16	*b*
Lauric	2	3.05	10,200	−0.60	*a*
Isobutyric	2	1.95	9,800	−2.88	*c*
Isocaproic	2	2.95	9,600	−2.73	*c*
β-Phenylpropionic	2	2.67	9,600	−2.93	*c*
β-Cyclohexylpropionic	2	2.81	10,100	−1.15	*f*
γ-Phenylbutyric	2	2.67	10,100	−1.25	*c*
γ-Cyclohexylbutyric	2	2.60	10,100	−1.30	*f*
δ-Phenylvaleric	2	2.79	9,900	−1.83	*f*
Methylethylacetic	3	0.546	10,400	−3.35	*c*
Isovaleric	3	.651	10,000	−4.44	*c*
β-Methylvaleric	3	.627	10,400	−3.58	*d*
Trimethylacetic	3	.194	11,400	−2.10	*d*
Phenylacetic	3	2.62	9,900	−1.96	*c*
Cyclohexylacetic	3	0.622	10,500	−2.81	*f*
Diethylacetic	4	.0502	12,400	−1.89	*d*
Cyclohexanecarboxylic	4	1.18	10,000	−3.21	*e*
Benzoic	4	0.0194	15,500	+7.08	*g*
Dipropylacetic	4	.0425	12,400	−1.76	*d*
Dibutylacetic	4	.0387	12,900	−0.27	*d*
Diisobutylacetic	4	.0201	12,600	−2.58	*d*
Phenylethylacetic	5	.248	11,100	−2.62	*f*
Diisopropylacetic	6	0			*h*
Dicyclopentylacetic	6	0			*h*
Dicyclohexylacetic	6	0			*f*
Diphenylacetic	6	.185	11,100	−3.21	*f*
Triphenylacetic	9	0			*f*

[a] Smith and Reichardt, ref. 4. [b] Smith, ref. 3. [c] Smith, ref. 9. [d] Smith, ref. 10. [e] Smith and Levenson, ref. 12. [f] This research. [g] Hartman and Borders, THIS JOURNAL, 59, 2107 (1937); Hartman and Gassmann, *ibid.*, 62, 1559 (1940). [h] Braun and Fischer, ref. 5.

In general, the acids fall pretty well into definite classes depending on the number of α- and β-substitutions. For both zero and one substitution, there is only one possible acid. Of the 12 acids with two substitutions, all except isobutyric have rate constants between 0.026 and 0.031 liter per mole second. Of those with three substitutions, all except trimethylacetic and phenylacetic acids have rate constants between 0.0055 and 0.0065. Of those with four, all except benzoic and cyclohexanecarboxylic acids have rate constants between 0.0002 and 0.0005, while of those with more than four substitutions, only phenylethylacetic and diphenylacetic acids have measurable rates.

The reasons for these exceptions are probably the following:

1. For isobutyric and trimethylacetic acids, all substitutions are in the α-position. While a single substitution in the β-position evidently has at least as great a retarding effect as a single methyl substitution in the α-position,[9,11] multiple methyl substitution seems to be more effective when it takes place entirely in the α-position, rather than in both α- and β-positions.

2. Phenylacetic, phenylethylacetic, and diphenylacetic acids esterify faster than would be predicted on the basis of Table III. This may be attributed to the fact that an α-phenyl group acts as an electron sink, and thus facilitates esterification. The magnitude of this inductive effect can be estimated by comparison with the corresponding cyclohexyl-substituted acids.

3. Because of its high activation energy and relative entropy of activation, benzoic acid must

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(8) The authors are indebted to Mr. R. R. Myers, who performed this experiment.

(9) Smith, THIS JOURNAL, **61**, 1176 (1939).

(10) *Cf.* Smith, *ibid.*, **62**, 1136 (1940).

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

be considered an exception, even though its rate constant is not far from the expected value. For this acid, both the inductive effect of the phenyl group and the influence of substitution are outweighed by resonance between the carboxyl and phenyl groups. This causes the slow rate of esterification and high activation energy found with this acid.

4. The relatively fast rate for cyclohexanecarboxylic acid is apparently due to the lack of freedom of the β-carbon atoms to be oriented toward the carboxyl group. This has been previously discussed.[12]

In general, activation energies show an increase with decreasing rate constants, this effect being negligible until three or more substitutions are present.

Summary

The kinetics of the acid catalyzed esterification of the following organic acids have been studied: cyclohexylacetic, β-cyclohexylpropionic, γ-cyclohexylbutyric, dicyclohexylacetic, phenylethylacetic, δ-phenylvaleric, diphenylacetic, and triphenylacetic acids.

It is demonstrated that, in general, the rate of esterification of such organic acids is governed primarily by the total number of substitutions in the α- or β-positions. Exceptions may be caused by such complicating factors as multiple α-substitution, resonance, the inductive effect of an α-phenyl group, and joining of the β carbon atoms.

KNOXVILLE, TENNESSEE RECEIVED JUNE 9, 1944

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[12] Smith and Levenson, THIS JOURNAL, 62, 2733 (1940).

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Ultraviolet Absorption Spectra of Hydrocarbon–Trinitrobenzene Complexes

BY R. C. JONES AND M. B. NEUWORTH

The identification of aromatic hydrocarbons from their ultraviolet absorption spectra has been well established. Since the substitution of an alkyl group or an alicyclic ring does not alter significantly the spectrum of the aromatic ring system, ultraviolet absorption spectra have become a valuable identification tool.[1]

The ability of aromatic hydrocarbons to form crystalline complexes with polynitro compounds is a very useful property. These complexes permit purification, separation of mixtures, and serve as crystalline derivatives. This is particularly advantageous when the hydrocarbons are liquids or difficultly crystallizable oils.[2] The direct interpretation of the spectrum of a hydrocarbon–polynitro complex would, therefore, be a convenient technique.

The ultraviolet absorption spectra were determined for the symmetrical trinitrobenzene complexes of naphthalene, anthracene, phenanthrene, pyrene, chrysene, 1,2-benzopyrene, and 1,2,5,6-dibenzanthracene. At the concentration employed for the spectrum analysis (10^{-3} molar maximum concentration) in methanol, it was found that the complexes were completely dissociated.[3] The absorption curve was the sum of the absorption of the hydrocarbon and the trinitrobenzene. This was substantiated in all cases by adding the molar extinction coefficients of the hydrocarbon and the trinitrobenzene at a given wave length, and comparing the sum with the experimental molar extinction coefficient of the complex. Fortunately, for all ring systems except naphthalene, the hydrocarbon absorption is sufficiently higher than the trinitrobenzene for most of the spectrum so as to enable direct identification of the aromatic ring system without the necessity of calculating the trinitrobenzene absorption.

Preliminary experiments with picrates indicated undesirable complications existed. When pyrene picrate was studied in methanol, it became obvious on examination of the spectrum that the picric acid was almost completely ionized. The picrate ion has a very high absorption[4] and tends to mask a considerable portion of the fine structure of the hydrocarbon. Attempts to eliminate the ionization by an increase in acidity of the solvent were unsuccessful. This is not a serious drawback since symmetrical trinitrobenzene forms more stable complexes with aromatic hydrocarbons than picric acid.

In Fig. 1 the ultraviolet absorption spectra of naphthalene and trinitrobenzene are indicated. The spectrum of naphthalene–trinitrobenzene complex is included superimposed on the calculated curve obtained by adding the molar extinction coefficients for naphthalene and trinitrobenzene at each wave length and plotting the logarithm of the sum against the wave length of light. Deviations of the experimental curve from the calculated curve are indicated by a dotted line.

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[1] R. N. Jones, *Chem. Rev.*, **32**, 1 (1943).

[2] C. K. Bradsher and L. Rapoport, THIS JOURNAL, **65**, 1646 (1943); F. Bergmann and H. E. Eschinazi, *ibid.*, **66**, 183 (1944).

[3] This is in agreement with the dissociation constants of acenaphthene–trinitrobenzene and acenaphthene–picric acid which have been determined spectrographically (H. von Halban and E. Zinpelmann, *Z. physik. Chem.*, **117**, 461 (1925)). A spectroscopic analysis of the desoxycholic acid complexes of methylcholanthrene and 1,2,5,6-dibenzanthracene showed complete dissociation of the complex in dilute ethanol and ether solutions (L. F. Fieser and M. S. Newman, THIS JOURNAL, **57**, 1603 (1935)).

[4] P. Gross, A. Jamok and F. Batat, *Monatsh.*, **63**, 117 (1933).