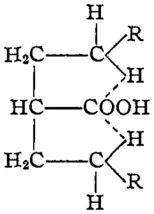
[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Kinetics of the Esterification of Cyclohexanoic Acid and of the Saponification of its Ethyl Ester

BY HILTON A. SMITH AND H. S. LEVENSON

In two recent articles[1,2] the effect of the aliphatic radical upon the velocity of the catalyzed esterification of an acid with methanol and upon the rate of saponification of its ethyl ester was discussed. In order to explain the results obtained, it was assumed that, when certain structural conditions are fulfilled, ring formation occurs, the ring involving an oxygen atom of the carboxyl group and four carbon atoms, and being held together by a hydrogen bond. One of the features which was most readily explained by this theory was the slow rates found when di-ethylacetic and higher di-substituted acids or their esters were employed. The structure postulated for these acids was



The formation of the rings would render the carboxyl group less susceptible to attack, and so explain the slower rates. Isobutyric acid is also a di-substituted acetic acid but, since no ring formation is possible, it reacts much more readily.

If this explanation is correct, any structural change which can be made in diethylacetic acid so as to prevent the formation of the postulated rings should produce a compound much like isobutyric acid as far as reaction velocities are concerned. This could easily be detected as the difference between isobutyric and di-ethylacetic and higher acids is so marked.

Such a structural change is found when the two terminal carbon atoms of diethylacetic acid are linked together by a methylene group. The resulting cyclohexyl ring is of the strainless type and there seems to be no reason to believe that any significant changes other than that of relative position of the groups with reference to the carboxyl would be caused by this change.

The present paper reports the results of a study of the kinetics of the esterification of cyclohexanoic acid and of the saponification of its ethyl ester.

Experimental

Eastman cyclohexanoic acid was fractionated in a 5 ft. (1.5 m.) Vigreux type column, the distillation being carried out under reduced pressure. The sample used for esterification studies distilled at constant head temperature. It analyzed 99.9% by titration with standard base, and melted at 31.2°.

For saponification studies, a portion of the purified cyclohexanoic acid was esterified with ethanol using sulfuric acid as a catalyst. The ester was fractionated under reduced pressure in the Vigreux column. The sample used distilled at a constant head temperature, and analysis by complete saponification of weighed samples with excess alkali and back titration with standard acid indicated a purity of 100% within the precision of the method.[3] The reaction media, dry methanol and 85% aqueous ethanol, were prepared and the velocity determinations carried out in the manner previously described.[3,4]

Experimental Calculations and Results

The esterification 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 were those used for normal aliphatic acids.[4] Table I gives the results for a typical run, and Table II the reaction rate constants at the temperatures used.

TABLE I

ESTERIFICATION OF CYCLOHEXANOIC ACID AND METHANOL AT 20°

$a = 0.500$, (HCl) $= 0.00500$

t, min.	$(a - x)$	10^3k (liters moles^{-1} sec.$^{-1}$)
40	0.453	9.25
78	.420	9.02
151	.369	9.03
252	.320	8.77
394	.266	8.80
577	.213	8.95
816	.168	8.82
1437	.096	8.71
	Average, 20–80%	8.87

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(1) Smith, THIS JOURNAL, **62**, 1136 (1940).

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

(3) *Cf.* Smith and Levenson, *ibid.*, **61**, 1172 (1939).

(4) Smith, *ibid.*, **61**, 254 (1939).

TABLE II

REACTION RATE CONSTANTS FOR ESTERIFICATION OF CYCLOHEXANOIC ACID IN METHANOL CATALYZED BY H^+ IONS

In all cases a = 0.500, (HCl) = 0.00500

	k (liters moles^{-1} sec.$^{-1}$) t = 20°	t = 30°	t = 40°	t = 50°	E (cal./mole)
	0.00885	0.0158	0.0264	0.0439	
	.00887	.0161	.0269	.0437	
Av.	.00886	.0160	.0267	.0438	10,000

The rate constants for the saponification reactions were calculated using the equation

$$k = x/at\ (a - x)$$

where a represents the initial concentration of each reactant, and x represents the concentration of each reactant at time t. Table III gives the results of a typical run, and Table IV the reaction rate constants at the temperatures used. The values in both Table II and Table IV result from averaging individual k's from 20 to 80% reaction. The ± deviations are of the order of 2% or less.

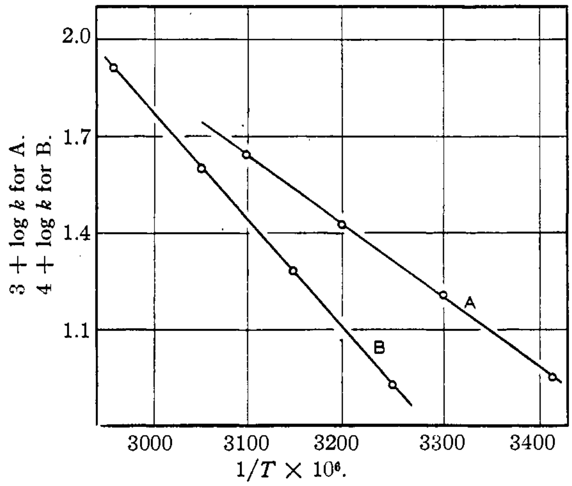

Fig. 1.—Temperature coefficients: A, esterification of cyclohexanoic acid with methanol; B, saponification of ethyl cyclohexanoate.

TABLE III

SAPONIFICATION OF ETHYL CYCLOHEXANOATE AT 55°

a = (NaOH) = (Ester) = 0.0500

t, min.	x	10^3k (liters moles^{-1} sec.$^{-1}$)
10	0.00569	4.28
25	.01174	4.09
40	.01648	4.10
64	.02187	4.05
92	.02649	4.08
126	.03023	4.05
181	.03415	3.97
265	.03814	4.05
370	.04094	4.07
	Average 20–80%	4.06

TABLE IV

REACTION RATE CONSTANTS FOR SAPONIFICATION OF ETHYL CYCLOHEXANOATE

In all cases, a = (NaOH) = (Ester) = 0.0500

t = 25°	10^3k (liters moles^{-1} sec.$^{-1}$) t = 35°	t = 45°	t = 55°	t = 65°	E (cal./mole)
	0.850	1.90	4.06	8.16	
	.845	1.92	4.00	8.22	
Av. 0.360[a]	.848	1.91	4.03	8.19	15,600

[a] Extrapolated.

Figure 1 represents the plot of log k against $1/T$ for both the esterification and saponification reactions. The activation energies calculated from the slopes of these lines are included in Tables II and IV. These were checked by the method of least squares, and are reported to the nearest 100 calories.

Discussion

A comparison of the reaction rate constants and activation energies for the compounds under consideration is given in Table V.

TABLE V

Acid	Esterification $k_{20°}$	E	Saponification of the ethyl ester $10^3k_{25°}$	E
Isobutyric	0.0147[5]	9,800	0.801[6]	15,000[7]
Cyclohexanoic	.00886	10,000	.360	15,600
Diethylacetic	.000351[1]	12,400	.0154[2]	17,200

From these values it is apparent that cyclohexanoic acid behaves much more like isobutyric acid than like diethylacetic acid. For both esterification of the acid and saponification of its ethyl ester, the cyclohexanoic compound reacts about one-half as fast as isobutyric acid or ethyl isobutyrate,[8] but more than twenty times as fast as the corresponding diethylacetic acid or ester. The activation energies also indicate much closer agreement with isobutyric acid or its ester.

The changes recorded in Table V might be attributed to alteration of inductive effect due to closing of the ring to form cyclohexanoic acid. This possibility seems to be excluded by the fact that ethyl cyclohexylacetate behaves similarly to ethyl isovalerate and ethyl β-methylvalerate, compounds to which it is structurally similar.[9] Furthermore, if any inductive effect may be attributed to the cyclohexyl group, it would un-

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

(6) Evans, Gordon and Watson, *J. Chem. Soc.*, 1439 (1938).

(7) Smith and McReynolds, THIS JOURNAL, **61**, 1963 (1939).

(8) Exact agreement is not expected here, but rather that the cyclohexanoic acid or ester will react somewhat the slower. In fact, if one ring is formed, as might possibly be the case, one would expect closer agreement with methylethylacetic acid[5,6] than with isobutyric acid. The values found for cyclohexanoic acid or its ester are intermediate between the two.

(9) Levenson and Smith, THIS JOURNAL, **62**, 2324 (1940).

doubtedly be $+I$; then one would expect ethyl cyclohexanoate to saponify considerably slower with a higher activation energy than ethyl cyclohexylacetate. Actually this is not found.

Thus the results of this investigation are in accord with expectations from the standpoint of the ring theory.

Summary

The kinetics of the acid catalyzed esterification of cyclohexanoic acid in dry methanol and of the saponification of ethyl cyclohexanoate in 85% aqueous ethanol have been studied at four temperatures. The effect of joining the terminal carbons of diethylacetic acid with a methylene group to make cyclohexanoic acid is to produce a compound kinetically much like isobutyric acid. This result is in accord with the conception of ring formation in diethylacetic and higher di-substituted acetic acids.

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The Relative Reducing Potential of Starch*

BY RALPH W. KERR

Many attempts have been made during the past decade to estimate the molecular magnitude of starch. Results have been variously reported which would indicate a chain length ranging from 20 to 30 glycopyranose units up to a thousand or more and from observations of the colloidal phenomena exhibited by starch pastes, possibly even higher. The following discussion is primarily concerned with the molecular magnitude of corn starch but it should not be interpreted as another attempt at this time to fix precisely the chain length and thus add one more confusing touch to an already confused picture. We intend that our observations be taken as a qualitative confirmation of work that has been done indicating that starch molecules are relatively simple and further to stimulate a more critical inspection of methods and theory that have led to almost incomprehensible magnitudes for molecular size.

Farrow[1] and his co-workers, Hixon[2] and others have attempted to arrive at the molecular magnitude of starch by taking the amount of copper reduced by dispersed starch solutions and comparing this value with amounts found for members of the aldehydic series dextrose, maltose, dextrins and starch. From this comparison, a surprisingly high molecular magnitude is obtained for starch, indicating that it contains possibly as high as one thousand glucopyranose units, or a molecular weight in excess of 150,000.

We suggest that there are considerable possibilities for error to enter the determination of the reducing capacity of a substance such as starch, when comparatively strenuous conditions must be imposed, *e. g.*, boiling for three hours in alkaline medium, to show that capacity. The capacity for reducing is very feeble for these carbohydrates at lower temperature. To induce them to exhibit a measurable one by imposing conditions which must simultaneously cause an extensive change in their constitution and molecular magnitude and to take the results obtained as indicative of original molecular weight, seems illogical.

Furthermore, in determinations such as those made by Farrow, the assumption is made that the power of a reducing group is quantitatively the same, whether it is on the end of maltose or on the end of a longer polysaccharide. Their data show that it is not quantitatively the same for dextrose as compared to the same reducing group on maltose. That the assumption is faulty may be explainable by the fact, as our data below show, that a potential may be estimated for this terminal, reducing group which varies in intensity with chain length and that there is some evidence that there is a relationship between potential and the tendency to react in a particular oxidation–reduction system.

Hence, we believe that there would be less error involved in measuring the comparative potentials of these products and using these values to estimate chain length, especially since we have found a potential for these carbohydrates to be measurable at ordinary temperatures in a few minutes of time.

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* This paper was presented at the 99th meeting of the American Chemical Society, Division of Sugar Chemistry, at Cincinnati, Ohio, April 11, 1940.

[1] Richardson, Higginbotham and Farrow, *J. Textile Inst., Transactions*, **27**, 130 (1936).

[2] C. G. Caldwell and R. M. Hixon, *J. Biol. Chem.*, **123**, 595 (1938).