

Esterification Rates of Some Saturated and Unsaturated Fatty Acids with Glycerol

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Abstract

Esterification rates of eight commonly occurring fatty acids were studied at 180C using equivalent and equimolar amounts of glycerol with and without a cosolvent. The esterification with equivalent amounts of glycerol without cosolvent followed second order kinetics and proceeded at a similar rate for all acids examined. Esterifications with equimolar amounts of glycerol were kinetically complex and their speed depended on the solubility of glycerol in individual fatty acids.

Introduction

THE ESTERIFICATION RATES of fatty acids with monohydric alcohols such as methanol and ethanol have been the subject of a number of investigations (1-6) which have revealed certain complexities. The early but accurate work of Sudborough and co-workers (1,2) has established that with the exception of the three lowest members, i.e., formic, acetic and propionic acids, saturated straight chain fatty acids are esterified with methanol at an essentially similar rate. In olefinic acids the double bond reduces the reaction rate considerably if it is adjacent to the carboxylic group, which is in agreement with the electronic theory of organic chemistry. However, if the double bond is in remote position as in oleic, elaidic or erucic acid its influence disappears altogether. Data to the contrary published in the International Critical Tables (7) and occasionally quoted in the literature have been recently shown to be due to an error in calculations (8). Subsequent work of Hinshelwood and co-workers (3,4) has confirmed earlier data on esterification in methanol. However, esterification with ethanol (4) has been shown to proceed differently the velocity constants showing a minimum for butyric acid and then rising with increasing molecular weight. Esterification in cyclohexanol was slightly different again. It thus would appear that the velocity of esterification depends on the compatibility of packing patterns of solvent and solute. Smith (5) obtained results similar to those of Sudborough and co-workers on esterification with methanol but he and Reichardt (6) disagreed with Hinshelwood on certain aspects connected with the determination of the activation energy and of the constant r appearing in the Goldschmidt equation (9) $k = \frac{(a+r) \ln(a/(a-x)) - x}{r t (\text{catalyst})}$.

The above differences seem to have remained unresolved.

The esterification of fatty acids with glycerol is still more complex owing to the polyhydric function of this alcohol, to its low miscibility with fatty acids and to the elevated temperatures required for obtaining reasonable reaction rates. Feuge et al. (10) investigated the kinetics of catalyzed and uncatalyzed esterification of peanut oil fatty acids at temperatures from 166C to 241C and found that the

reaction was essentially bimolecular the velocity constants in the initial stage of the uncatalyzed reaction being appreciably greater than in the final stage. Wocasek and Koch (11) using various metallic fluorides as catalysts found the esterification velocity of stearic, oleic and linoleic acids to be about similar. On the other hand Biswas and Ganguly (12) reported more recently that the alkali catalyzed esterification of several fatty acids with equimolar amounts of glycerol at 180C proceeded at considerably differing speeds. The percentage of fatty acids esterified after a given period for stearic, palmitic, myristic, oleic, lauric and linoleic acid increased in the above order, the percentage for linoleic acid after 1 hr reaction being nearly twice as great as for stearic acid. This was attributed by Biswas and Ganguly to the different miscibility of individual fatty acids with glycerol. No such differences were obtained for the same fatty acids by Choudhury (13) when using 3 moles of glycerol for 1 mole of fatty acid. However, his results are questionable since the acid values of the reaction mixtures determined by him for stearic, oleic and linoleic acids after 1 hr reaction at 180C were 108.0, 106.8 and 107.0, respectively, and thus higher than the calculated acid values at the beginning of the experiment, i.e., 98.6-100.7. According to Choudhury the fatty acids were pure and the reactants were preheated to 180C before mixing and thus should have been water-free. An increase of acid values during the course of reaction is therefore difficult to explain.

In view of the conflicting results mentioned above the esterification rates of some commonly occurring fatty acids have been reinvestigated in this laboratory.

Experimental

Six saturated fatty acids (caprylic, capric, lauric, myristic, palmitic and stearic) and two unsaturated acids (oleic and linoleic) were used. Commercial saturated acids were purified by fractional distillation of their methyl esters and crystallization. Oleic acid was prepared from olive oil by low temperature crystallization and linoleic acid from safflower oil by the urea adduct method (14). All acids were of at least 99% purity. Analytical reagent grade glycerol was made anhydrous by heating it with stirring to 180C.

The main set of experiments consisted of determining the esterification rates of the above mentioned 8 fatty acids with glycerol at 180C using both equivalent and equimolar proportions of the reactants. As there were obvious differences in the miscibility of glycerol with the various fatty acids their miscibility at the above temperature was determined. To establish whether there were differences in the reactivities of individual fatty acids with glycerol unconnected with miscibility the esterification experiments were repeated using a suitable cosolvent. The esterification of fatty acids in methanol was carried out for comparison.

TABLE I
 Esterification of Various Fatty Acids with Glycerol at 180C

Fatty acid	Proportions of reactants	Percentage of fatty acid esterified after:						
		½ hr	1 hr	2 hr	3 hr	5 hr	7 hr	10 hr
Caprylic	equivalent	32.8	50.2	59.0	67.8	77.4	79.4	81.0
	equimolar	39.8	56.9	70.7	77.8	84.2	86.1	90.1
Capric	equivalent	32.7	48.4	59.7	68.1	76.3	79.8	81.3
	equimolar	38.9	56.1	71.1	76.8	83.8	85.9	92.5
Lauric	equivalent	30.5	45.3	61.0	67.8	73.9	79.7	80.4
	equimolar	36.5	52.8	69.8	78.1	84.1	87.8	94.0
Myristic	equivalent	26.3	41.0	57.4	65.2	71.3	78.3	80.2
	equimolar	31.0	50.4	64.7	76.2	83.0	87.1	93.9
Palmitic	equivalent	22.2	38.2	54.0	63.5	71.4	74.8	82.3
	equimolar	30.7	46.8	64.6	72.9	83.0	87.9	93.9
Stearic	equivalent	19.5	35.1	54.3	61.8	65.4	72.4	75.7
	equimolar	25.4	42.1	63.9	72.9	82.5	87.2	90.0
Oleic	equivalent	18.8	36.3	54.9	60.9	65.8	74.5	77.8
	equimolar	26.1	44.3	61.4	73.1	81.4	86.3	91.6
Linoleic	equivalent	19.2	36.8	53.3	59.4	65.8	73.2	76.5
	equimolar	27.1	44.7	63.4	73.2	81.8	86.7	91.1

The esterification experiments without cosolvent were conducted as follows:

The acids (0.002 mole) and appropriate amounts of glycerol (equivalent and equimolar, respectively) were weighed out into test tubes of 12 mm Ø. The test tubes were flushed with nitrogen, stoppered and shaken in a thermostatically controlled silicone oil bath for varying times (½ hr–10 hr) at 180C. The reaction mixtures were taken up in neutral ethanol and titrated with 0.1N aqueous NaOH in the presence of phenolphthalein. Results are shown in Table I.

The miscibility of glycerol with the fatty acids in question was determined in test tubes of 10 mm Ø at 180C. The mixture was stirred by bubbling nitrogen gas for 5 min. After 5 minutes' settling, samples of the upper fatty acid layer were drawn off with a preheated pipette and the amount of uncombined glycerol was estimated by the periodate method of Pole and Mehlenbacher (15) suitably modified. In addition to the eight fatty acids examined the miscibility of glycerol with some pure mono, di-, and triglycerides and with known mixtures thereof was determined. The results, some of which were taken from a previous communication (16) appear in Table II.

Esterifications in cosolvent were carried out using 0.1 molar solutions of fatty acids in Dowtherm A (a eutectic mixture of 73.5% diphenyl oxide and 26.5% diphenyl) the corresponding concentration of glycerol being 0.033 molar and 0.1 molar, respectively. At the above concentrations glycerol was found to dissolve in Dowtherm A at 180C. The ap-

 TABLE II
 Miscibility of Glycerol with Various Fatty Acids and Glycerides at 180C

Material	Per cent weight of dissolved glycerol on the fat basis
Caprylic acid ^a	Completely miscible
Capric acid	63.3
Lauric acid ^a	23.0
Myristic acid ^a	11.7
Palmitic acid ^a	7.6
Stearic acid ^a	5.1
Oleic acid ^a	5.9
Linoleic acid	6.0
1-monolaurin ^a	Completely miscible
1-monostearin ^a	32.7
Technical monostearin (30% monoester, 48% diester)	6.7
Technical monostearin (60% monoester, 35% diester)	11.1
1,3-Dipalmitin	2.4
1,3-Distearin	2.0
Tricaprylin ^a	3.6
Trilaurin ^a	1.2
Tristearin ^a	0.9
Triolein	0.9

^a Data taken from Reference 16.

 TABLE III
 Esterification of Various Fatty Acids in ½ Molar Solution in Dowtherm A with Equivalent and Equimolar Proportions of Glycerol at 180C

Fatty acid	Proportion of reactants	Percentage of fatty acids esterified after			
		12 hr	24 hr	48 hr	72 hr
Caprylic	equivalent	3.9	8.6	13.1	13.0
	equimolar	12.1	21.1	30.3	32.8
Capric	equivalent	4.3	9.1	13.6	14.1
	equimolar	12.8	20.9	30.3	32.5
Lauric	equivalent	4.3	10.1	13.4	13.9
	equimolar	13.0	20.2	28.2	30.9
Myristic	equivalent	3.9	9.7	12.1	12.4
	equimolar	13.1	20.4	29.2	29.5
Palmitic	equivalent	4.4	9.9	12.5	12.5
	equimolar	12.9	21.3	28.7	29.0
Stearic	equivalent	4.6	8.8	12.4	12.4
	equimolar	13.0	20.4	29.4	29.5
Oleic	equivalent	4.0	8.2	13.0	13.2
	equimolar	12.9	20.9	29.4	29.4
Linoleic	equivalent	4.1	9.6	12.4	12.5
	equimolar	12.9	21.1	28.1	28.0

propriate amounts of reactants were weighed out in ground joint test tubes followed by addition of 10 ml of Dowtherm A previously deaerated with nitrogen. 100 mm long ground joint air condensers were attached to the test tubes to facilitate the condensation of water vapor resulting from the esterification. After deaeration with nitrogen the condensers were stoppered and the test tubes submerged up to the connecting joint in a silicone bath held at 180C. After heating for a period of 12–72 hr the reaction mixtures were dissolved in 25 ml of neutral ethanol and titrated. Results are shown on Table III.

Esterifications in methanol were conducted by preparing 0.1 molar solutions of the individual fatty acids in the above alcohol containing 0.005 mole HCl per liter and holding 10 ml samples at 20C for 1 hr and 3 hr, respectively. The samples were titrated as usual (cf Table IV).

Discussion

The results of HCl catalyzed esterification of fatty acids in methanol were in agreement with the early work of Sudborough and co-workers (1,2) inasmuch as there was no appreciable difference in the reactivities of the acids examined due to molecular weight or degree of unsaturation. These results are probably not strictly accurate, since no attempt was made to prepare an anhydrous methanol but the comparative values obtained are sufficient to establish the point.

Esterification with glycerol in a cosolvent proceeded also at a similar speed for all acids examined. Incidentally Dowtherm A was chosen as a cosolvent since it is known to be very inert and its high boiling point made it possible to dispense with sealed tubes and to avoid high pressures associated with the use of volatile cosolvents. It will be observed that the reaction slowed down considerably or came to a standstill after 48 hr which might have been

 TABLE IV
 Esterification of Various Fatty Acids, ½ Molar Solution in Methanol Containing 0.005 Mole HCl/Liter at 20C

Acid	Percentage of fatty acid esterified after	
	1 hr	3 hr
Caprylic	22.9	53.0
Capric	22.1	52.8
Lauric	22.1	52.5
Myristic	22.0	50.9
Palmitic	21.9	51.9
Stearic	22.7	52.1
Oleic	22.6	51.6
Linoleic	22.9	52.9

due to the influence of water produced in the reaction or more likely to the increasing incompatibility of the solvent-solute systems. Nevertheless the esterification—especially when using equimolar proportions of the reactants—proceeded far enough to discount the likelihood of appreciable differences between the reactivities of individual fatty acids. No catalyst was employed in these and in subsequently discussed experiments nor was the water of reaction removed from the system to ensure a better uniformity of operating conditions.

For the same reason in esterifications both with and without cosolvent each run was carried out with weighed amounts of reactants instead of withdrawing successive samples from a larger batch at suitable time intervals. It was thought that some of the questionable results obtained by previous investigators were possibly due to nonhomogeneous mixtures and the resulting inaccurate sampling. The weighing out of reactants in right proportions for each run was time-consuming but did away with the above errors and made possible a more accurate calculation of the degree of esterification on the basis of fatty acids originally taken. It may be seen from Table I that in esterifications carried out without cosolvent there are appreciable differences in the percentage of individual fatty acids esterified after a given time when using both equivalent and equimolar quantities of glycerol. However, these differences should not be confused with the actual reaction rates. To obtain a more reliable picture of the reaction progress velocity constants for the esterification of the individual acids with the equivalent amounts of glycerol were calculated assuming that the reaction was bimolecular and followed second order kinetics. The above reaction is represented by the well-known

$$\text{equation } K = \frac{1}{at} \frac{x}{(a-x)}$$

where K is the velocity constant, a molar concentration of the reactants and x denotes the change of a in time t expressed in hours. In view of the difficulty of establishing the concentration of fatty acids in moles per liter when dealing with fatty acids—glycerol mixtures at 180°C, the molar concentration of fatty acids in 1000 g of the fatty acid-glycerol mixture was calculated for each acid and substituted for a . Accordingly K is expressed as 1000 g moles⁻¹ hours⁻¹. In agreement with the results of Feuge et al. (10) it was found that the velocity constants were greater at the initial stage of the reaction than towards its end. Table V shows these constants calculated for reaction times

TABLE V
Velocity Constants of Reaction Between Equivalent Proportions of Fatty Acids and Glycerol at 180°C Expressed as 1000 g mole⁻¹ Hours⁻¹

Acids	Velocity constants after:	
	1 hr reaction	5 hr reaction
Caprylic	0.176	0.120
Capric	0.190	0.131
Lauric	0.191	0.130
Myristic	0.180	0.129
Palmitic	0.178	0.143
Stearic	0.171	0.120
Oleic	0.178	0.121
Linoleic	0.181	0.120

of 1 hr and 5 hr from the data in Table I and it will be seen that there are no great differences in the reaction rates of individual fatty acids. It may be therefore concluded that the esterification of the fatty acids examined proceeded at a similar rate if allowance is made for the differing molar concentrations of the various acids. (The molar concentration of caprylic acid in 1000 g of a mixture containing equivalent proportions of this acid and glycerol is 5.7 whereas that of stearic acid is 3.2.) It is of interest that the esterification rates of various acids in the absence of cosolvent were similar despite the fact that the solubility of glycerol in fatty acids for five out of the eight acids examined was lower on the percentage basis than the equivalent weight of glycerol. The formation of monoglycerides in the initial stage of the esterification with the concomitant increase of the solubility of glycerol (cf Table II) may explain to some extent this behavior.

The calculation of velocity constants for esterifications carried out with equimolar amounts of fatty acids and glycerol led to the conclusion that the reaction followed mixed order kinetics as could be expected from the interaction of fatty acids and glycerol with partial glycerides present in substantial quantities. If one considers the percentage of fatty acids esterified after a given time without taking into account the molar concentrations of fatty acids, the degree of esterification in the above mixtures is in line with the solubility of glycerol in the individual fatty acids (cf Table II), the sequence being caprylic > capric > lauric > myristic > palmitic > stearic \approx oleic \approx linoleic. It has been already mentioned that Biswas and Ganguly (12) attributed the different degree of esterification of the various acids to their different miscibilities with glycerol. However, their sequence linoleic > lauric > oleic > myristic > palmitic > stearic is incompatible with the actual miscibilities of fatty acids with glycerol and, generally speaking, hard to explain.

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REFERENCES

1. Sudborough, J. J., and J. M. Gittins, *J. Chem. Soc.* **93**, 210-217 (1908).
2. Sudborough, J. J., and J. M. Gittins, *J. Chem. Soc.* **95**, 315-321 (1909).
3. Hinshelwood, C. N., and A. R. Legard, *J. Chem. Soc.* 587-596 (1935).
4. Fairclough, R. A., and C. N. Hinshelwood, *J. Chem. Soc.* 593-600 (1939).
5. Smith, H. A., *J. Am. Chem. Soc.* **61**, 254-260 (1939).
6. Smith, H. A., and C. H. Reichardt, *J. Am. Chem. Soc.* **63**, 605-608 (1941).
7. Skrabal, A., "Chemical Kinetics," in "International Critical Tables," vol. 7, McGraw-Hill, New York, 1930, p 138.
8. Hartman, L., *JAOCS* **42**, 664 (1965).
9. Goldschmidt, H., and O. Udby, *Z. Physik. Chem.* **60**, 728-755 (1907).
10. Feuge, R. O., E. A. Kraemer and A. E. Bailey, *Oil & Soap*, **22**, 202-207 (1945).
11. Wocasek, J. J., and J. R. Koch, *JAOCS* **25**, 335-337 (1948).
12. Biswas, A. K., and D. Ganguly, *Nature* **188**, 56-67 (1960).
13. Choudhury, R. B. R., *JAOCS* **39**, 345-347 (1962).
14. Johnson, A. R., and G. M. Ali, *JAOCS* **38**, 453-454 (1961).
15. Pohle, W. D., and V. C. Mehlenbacher, *JAOCS* **27**, 54-56 (1950).
16. Hartman, L., *JAOCS* **40**, 142 (1963).

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