The Equilibrium Distribution of Acyl Groups Between Primary and Secondary Hydroxyl Positions in Partial Esters

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Abstract

In a previous paper the authors discussed the concept of the "relative esterifiability" of primary and secondary hydroxyl groups and demonstrated its utility in predicting the composition of partial glycerides under ester-interchange equilibrium conditions. The concept is clarified and expanded in the present paper. The compositions of partial glycerides at ester-interchange equilibrium are calculated using the estimated reactivities of the primary and secondary hydroxyls at 100 and 220C, and are compared to the composition calculated assuming equal hydroxyl reactivity. Base catalyzed esterification of propylene glycol with fatty acids is shown to be accompanied by rapid ester-interchange. As with glycerol partial esters, the relative esterifiability of the primary hydroxyl of propylene glycol exceeds that of the secondary.

Introduction

IN A CLASSICAL PAPER a number of years ago, Feuge and Bailey (6) proposed that the composition of mono- and diglycerides made by glycerolysis or by esterification could be predicted, based on the assumption of random distribution of acyl groups on the hydroxyl groups of glycerol and that the probabilities of primary and secondary hydroxyls being esterified are equal. In a recent paper (3) the present authors pointed out an inconsistency in the treatment of Feuge and Bailey, in that they assumed equal chance of primary and secondary hydroxyls being esterified, but also assumed the absence of 2-monoglyceride in comparing their predicted total monoester content with experimental data obtained for 1-mono- content by periodate oxidation. The present authors proposed that since reaction conditions are favorable for the establishment of ester-interchange equilibrium, an equilibrium constant, K, could be determined for the exchange of the acyl group between a primary and secondary hydroxyl; thus

$$R_pOH + R_sOOCR' \rightleftarrows R_sOH + R_pOOCR'$$

where R_pOH and R_sOH denote a primary and a secondary hydroxyl group, respectively, and R'COO denotes the acyl group.

The previous data (3) show that K for glycerol varies with temp from ca. 2.3 at 200C, to ca. 4.5 at 100C, and to about 6–10 at ambient temp. These values of K are considerably different from unity, which is the value required if primary and secondary hydroxyls have equal probabilities of being esterified. The fact that the 2-monoglyceride is not negligible is also shown in a recent paper by Biswas and Ganguly (2) who reported that considerable quantities of 2-monoglyceride are formed during esterification.

Recent publications by Choudhury (5), Feuge (7) and Hartman (8) indicate that the unjustified assumption is still being made that K = 1. Furthermore, the term "relative esterifiability" has been misinterpreted by several authors to mean the rate of esterification. The present authors had attempted to make clear that relative esterifiability meant the relative probabilities of different kinds of hydroxyl groups being esterified under conditions resulting in ester-interchange equilibrium.

A recent report on the use of thin-layer chromatography to follow glycerolysis reactions (9) mentioned theoretical calculations of the composition of equilibrium mixtures of glycerides assuming different reactivities for the 1- and 2-hydroxyls of glycerol. This study by Brett and Faulkner (4), which had not previously been available, contains essentially the same theoretical treatment given by the present authors. Brett and Faulkner did not put their results in terms of an equilibrium constant, K, nor did they observe a temp dependence of hydroxyl reactivity or relative esterifiability. Another advantage of calculating an equilibrium constant is that it enables one to estimate any intramolecular and intermolecular acyl group migration.

Calculated Composition of Glycerol Esters

The method of calculating the composition of a glycerol partial fatty acid ester was described previously (3). Equilibrium constants of 1,2 and 4.5 were employed in making the calculations presented in Figures 1–4. K = 1 applies if all hydroxyls were equally reactive; K = 2 is the value estimated for equilibrium at ca. 220C; and K = 4.5 is the value at ca. 100C. The last is considered to give results representative of commercial mono- and diglycerides, presumably because equilibrium is not established readily at temp much below 100C.

Examination of Figures 1–4 reveals that for those species existing in only one form, such as free glycerol and triglyceride, there is only a small effect of the primary versus secondary hydroxyl reactivity, i.e. of variation of K, on the per cent of the component present at equilibrium. The above statement also applies to the total mono- and total di-content of the partial glycerides. However, the contents of isomeric 1- and 2- monoglycerides and of the 1,2- and 1,3-diglycerides are quite dependent on the relative esterifiability of the primary and secondary hydroxyl groups of glycerol. The available data indicate that the nature of the acyl group has litle or no effect on the value of the equilibrium constant, K (8,10).

The technique of calculating an equilibrium constant for the ester-interchange reaction is equally applicable to other polyols. Studies have been made in this laboratory on a number of other ester-interchange equilibria, one of which is reported below.

Fatty Acid Esters of Propylene Glycol

Theoretical

Since reaction conditions are favorable for ester-interchange, the base-catalyzed esterification of one mole propylene glycol with less than two moles fatty acid results in an equilibrium mixture of propylene glycol 1-monoester, propylene glycol 2-monoester, propylene glycol diester, and free propylene glycol.

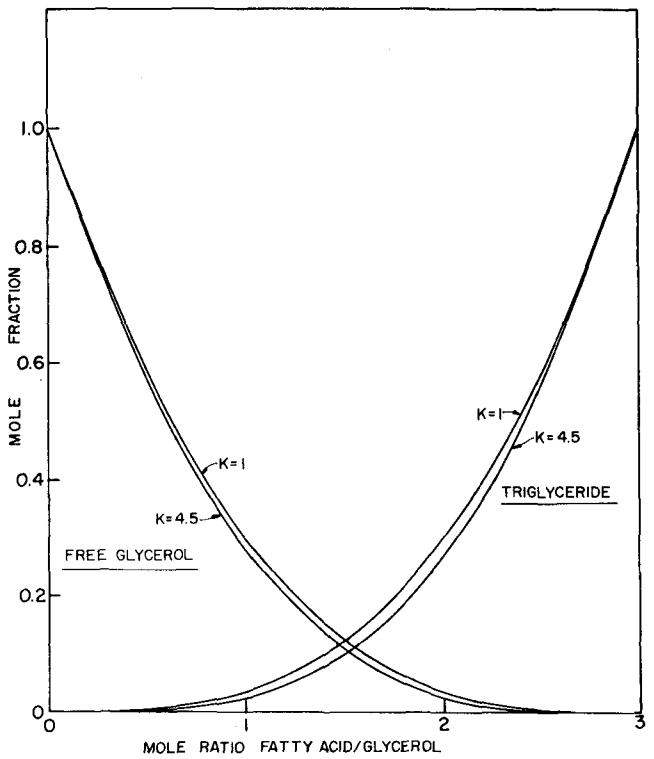

FIG. 1. Calculated mole fractions free glycerol and triglyceride as a function of fatty acid/glycerol ratio, for K = 1 and K = 4.5 (curves for K = 2 fall between K = 1 and K = 4.5 and are omitted for clarity).

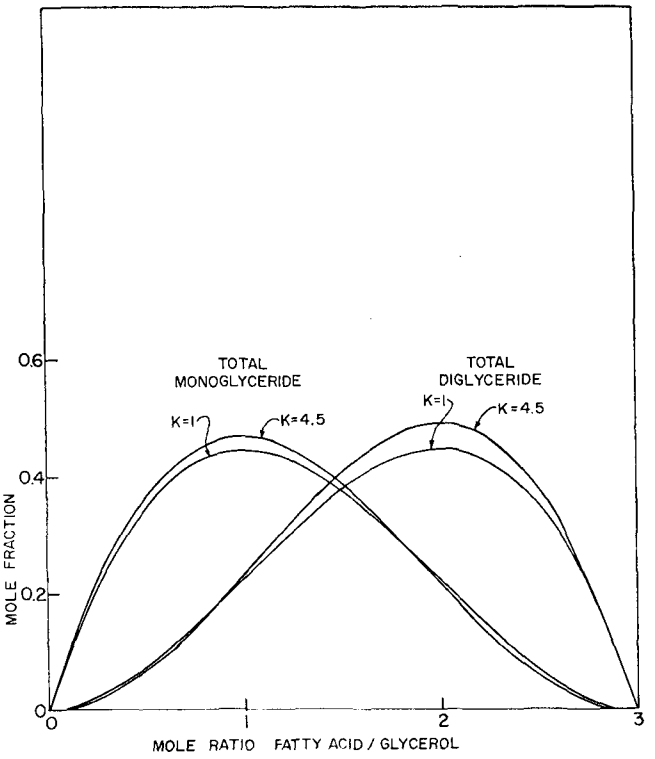

FIG. 2. Calculated mole fractions total monoglyceride and total diglyceride as a function of fatty acid/glycerol ratio, for K = 1 and K = 4.5 (curves for K = 2 fall between K = 1 and K = 4.5 and are omitted for clarity).

The equilibrium constant, K, may be expressed as follows:

$$K = \frac{[\text{free secondary OH}]\,[\text{esterified primary OH}]}{[\text{esterified secondary OH}]\,[\text{free primary OH}]}$$

As in the previous paper, the quantities a and b are defined as the ratio of esterified to free primary hydroxyl groups and the ratio of esterified to free secondary hydroxyl groups, respectively. Therefore, K = a/b.

The probability of a primary hydroxyl group being esterified is equal to the ratio of esterified primary hydroxyls to total primary hydroxyls, or $a/(a+1)$. Likewise, the probability of a secondary hydroxyl being esterified is $b/(b+1)$. The probabilities of primary or secondary hydroxyls being free are $1/(a+1)$ and $1/(b+1)$, respectively. At ester-interchange equilibrium, the mole fractions of the various species present are as follows:

$$\text{free glycol} = 1/(a+1)(b+1)$$
$$\text{1-monoester} = a/(a+1)(b+1)$$
$$\text{2-monoester} = b/(a+1)(b+1)$$
$$\text{total monoester} = (a+b)/(a+1)(b+1)$$
$$\text{diester} = ab/(a+1)(b+1)$$

The ratio of 1-monoester : 2-monoester gives K directly. Unfortunately, the relative amounts of the glycol monoester isomers in the reaction mixture cannot be readily measured. Instead, K is determined from the relative amounts of diester, total monoester, and free glycol, which are calculated from the analyses as described in the Experimental Section.

If we let M = the equilibrium mole ratio of total monoester to diester and F = the equilibrium mole ratio of free glycol to diester, then it is seen from the list of equilibrium mole fractions given above that

$$M = (a+b)/ab$$
$$\text{and } F = 1/ab$$

Solving for a and b in terms of M and F yields the expressions

$$a = \frac{M \pm (M^2 - 4F)^{1/2}}{2F}$$

$$\text{and } b = \frac{M \pm (M^2 - 4F)^{1/2}}{2F}$$

Note that, in order to satisfy the original equations, if the positive square root is used in the expression for a, then the negative root must be used in b, and vice-versa. Since the expression with the positive root will be the larger, the correct assignment of root signs requires information as to whether it is the primary or the secondary hydroxyl group of propylene glycol that is the more esterifiable. This information must be obtained by an independent method, since the method described is inherently incapable of determining which hydroxyl is the more esterifiable. The mole fractions of diester, total monoester, and free glycol are the same whether it is the primary or the secondary hydroxyl that is the more esterifiable. This is the source of the ambiguity in the signs of the square roots. Since primary hydroxyls are known to be more reactive generally than are secondary hydroxyls, and since the primary hydroxyl of glycerol has been shown to be more esterifiable than the secondary hydroxyl (3), it can safely be assumed that the primary hydroxyl of propylene glycol is more esterifiable than the secondary. If so, the positive root is taken in the expression for a and the negative root for b. Since K = a/b, and we have assumed that a is greater than b, then

$$K = \frac{M + |(M^2 - 4F)^{1/2}|}{M - |(M^2 - 4F)^{1/2}|}$$

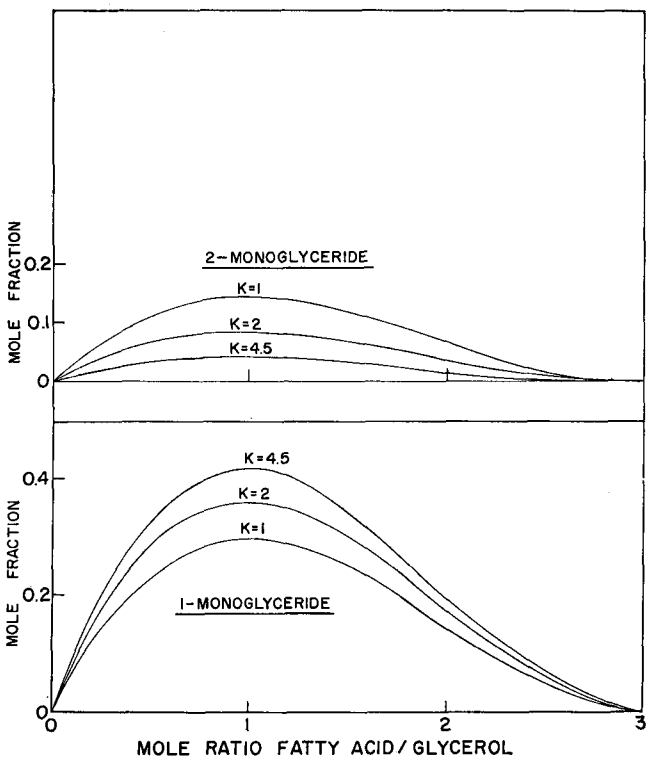

FIG. 3. Calculated mole fraction of 1- and 2-monoglyceride as a function of fatty acid/glycerol ratio, for K = 1, K = 2 and K = 4.5.

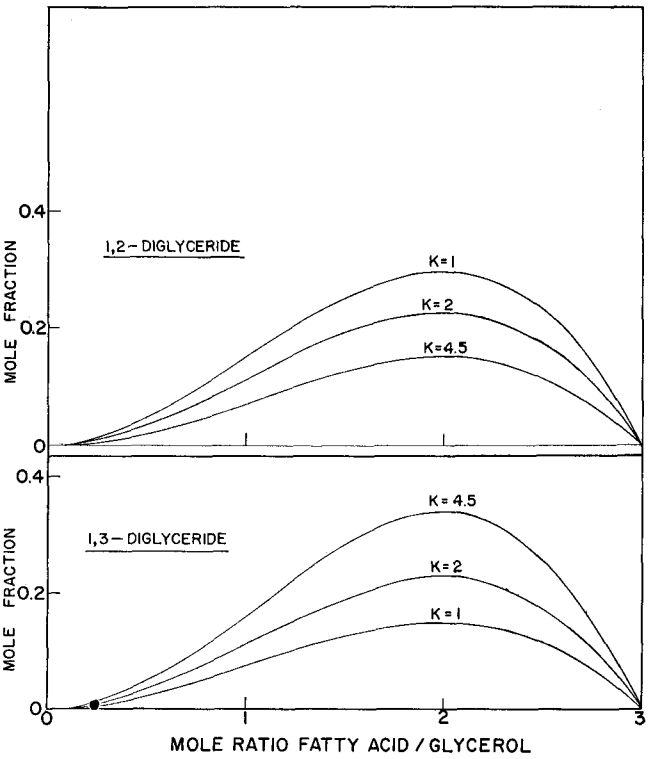

FIG. 4. Calculated mole fraction of 1,2-diglyceride and 1,3-diglyceride as a function of fatty acid/glycerol ratio, for K = 1, K = 2 and K = 4.5.

and the numerical values obtained for K will be greater than one.

Experimental

One mole propylene glycol was reacted in a stirred flask with 0.8 mole commercial oleic acid (average mol wt = 276 by acid number) at 175C under nitrogen, using 0.1% NaOH as catalyst. Samples were pipetted out of the reaction flask at 3,14,14.25 and 24 hr and analyzed in duplicate for acid number, saponification number and hydroxyl number and for free propylene glycol by periodate consumption. All samples were homogeneous both at reaction temp and at room temp. The mole ratio of total monoester to diester and of free glycol to diester, M and F respectively, are calculated from the analyses by the following series of steps:

1) The acid number of the sample is subtracted from the saponification number to give the ester number.

2) The wt fraction of free oleic acid in the sample, f, is found by dividing the acid number of the sample by 203, the acid number of the sample of oleic acid used.

3) The ester and hydroxyl numbers of the sample and the wt fraction free propylene glycol in the sample are corrected for the presence of free oleic acid by dividing each in turn by the factor $(1 - f)$, to give, respectively, the corrected ester number, e; the corrected hydroxyl number, h; and the corrected wt fraction free glycol, p.

4) The values obtained for e and h are corrected for the presence of the free propylene glycol to give the ester number of the mixed esters, E, and the hydroxyl number of the mixed esters, H. These mixed esters consist of propylene glycol 1- and 2-monooleate and propylene glycol dioleate. The corrections are made as follows:

$$E = e/(1 - p)$$
$$H = (h - 1475p)/(1 - p)$$

where 1475 = the hydroxyl number of propylene glycol.

5) The mole ratio of total monoester to diester, M, is calculated from the following expression, derived elsewhere (1):

$$M = 2H/(E - H)$$

6) The mole ratio of free glycol to diester, F, is calculated from the expression

$$F = (p)(334M + 592)/(76.1)(1 - p)$$

where 76.1 = the mol wt of the glycol
334 = the mol wt of the monoester
and 592 = the mol wt of the diester

7) The equilibrium constant, K, is calculated from M and F as shown in the Theoretical Section.

Discussion

Data and calculations for the propylene glycol oleate equilibrium run at 175C show in Table I.

TABLE I

Propylene Glycol Oleate Equilibrium at 175C, Base-Catalyzed Data and Calculations

	Sample No.			
	1	2	3	4
Equilibration time, hr	3.	14.	14.25	24.
Acid no.	26.25	3.05	3.10	0.83
Saponification no.	159.5	161.0	160.5	159.0
Hydroxyl no.	243.0	228.0	225.0	222.5
Wt % free glycol	10.40	8.45	8.50	8.50
e = corr.[a] ester no.	153.0	160.4	159.8	158.8
h = corr.[a] hydroxyl no.	279.1	231.5	228.5	223.4
100 p = corr.[a] wt% free glycol	11.94	8.58	8.63	8.54
E = ester no. of esters	173.7	175.5	174.9	173.6
H = hydroxyl no. of esters	116.8	114.9	110.8	106.6
M = moles monoester/diester	4.11	3.79	3.46	3.18
F = moles free glycol/diester	3.50	2.29	2.17	2.03
K = equilibrium constant	2.4	4.0	3.2	2.6

[a] Corrected for free oleic acid.

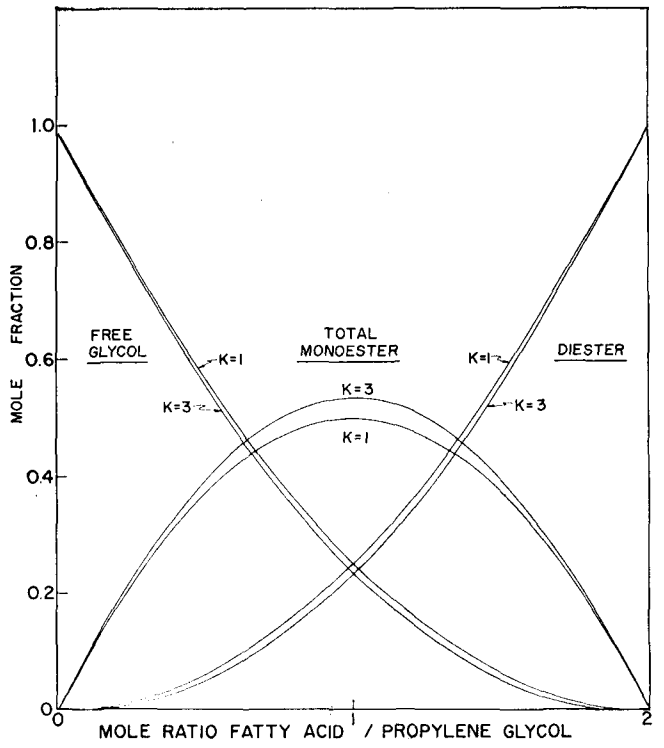

FIG. 5. Calculated mole fractions of free glycol, total monoester, and diester as a function of fatty acid/propylene glycol ratio, for K = 1 and K = 3.

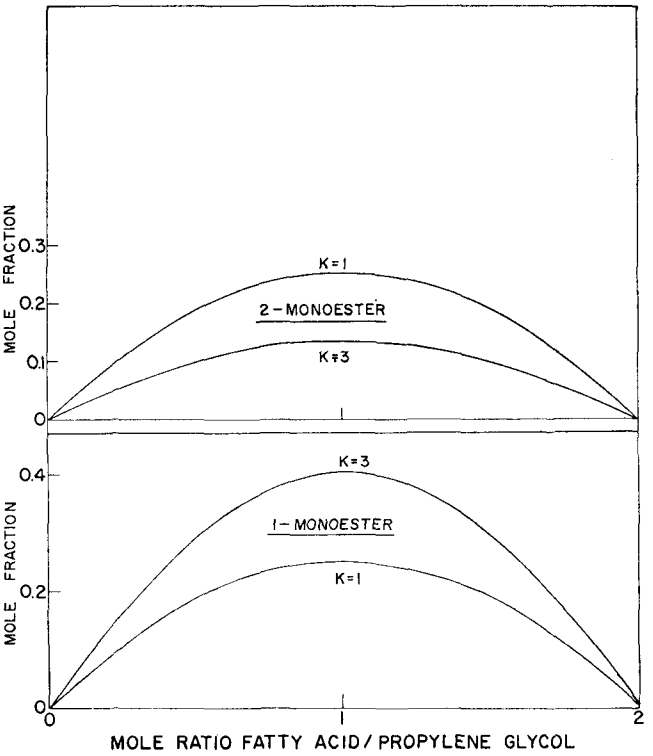

FIG. 6. Calculated mole fraction of 1- and 2-monoester as a function of fatty acid/propylene glycol ratio, for K = 1 and K = 3.

The average value found for the equilibrium constant, K, is 3.0 ± 0.6, indicating that at 175C, the primary hydroxyl of propylene glycol is about three times as esterifiable as the secondary hydroxyl.

Table I shows that sample No. 1, taken after three hr, was incompletely esterified, containing 13% free oleic acid. However, since the value for K found for sample No. 1 is in reasonable agreement with the other K values, ester-interchange is seen to proceed ca. as rapidly as esterification in the base-catalyzed reaction of propylene glycol with oleic acid. A similar observation was made previously concerning the esterification of oleic acid with ethylene glycol, also base-catalyzed at 175C (3).

It will be noted that the calculated K values show considerable scatter among the four samples. This is because a small error in determination of the mole fractions of diester, total monoester, or free glycol will result in a relatively large error in the value calculated for K. This is illustrated in Figure 5, in which the mole fractions at equilibrium are calculated for these three species for K = 1, which assumes equal esterifiability of the primary and secondary hydroxyls, and K = 3, which is the value actually observed at 175C. Figure 5 shows a relatively small change in composition for this large change in K. However, as with glycerol esters, the relative amounts of propylene glycol 1- and 2-monooleate change quite appreciably with this same change in K, as illustrated in Figure 6. The data presented in Figures 5, 6 were calculated by solving the simultaneous equations

$$K = a/b$$

$$\text{and } a/(a+1) + b/(b+1) = \text{moles fatty acid/mole glycol},$$

for a and b at K = 1 and K = 3, and at various ratios of acid to glycol, and then substituting in the expressions, in terms of a and b, for the mole fractions of the various species, as given in the Theoretical Section.

It will be noted that the equilibrium constant for the relative esterifiability of propylene glycol primary and secondary hydroxyl groups at 175C is ca. the same as that for glycerol primary and secondary hydroxyl groups at the same temperature. Very possibly this agreement may be coincidental.

It should be noted that none of the data reported here imply anything concerning the relative esterifiability of the propylene glycol primary hydroxyl vs. glycerol primary hydroxyl, nor concerning the relative esterifiability of the secondary hydroxyl of propylene glycol versus that of glycerol. To obtain this information would require analysis of the equilibrium mixture formed by reacting glycerol and propylene glycol simultaneously and competitively with fatty acid.

The propylene glycol results support earlier observations made on glycerol esters, namely that primary and secondary hydroxyls have different probabilities of being esterified under equilibrium conditions. The probability of esterification varies with temp. It is possible to predict accurately the composition of partial esters by means of the probability considerations.

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