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Kinetic Parameters of a Homogeneous Transmethylation of Soybean Oil

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Abstract The kinetic parameters of a truly homogeneous base-catalyzed transmethylation of soybean oil at four temperatures from 23 to 50 °C have been determined for the first time. The addition of oxolane, as well as a high methanol/oil molar ratio (27:1), was used to achieve and maintain a monophasic system throughout the reactions. Second order rate constants were determined in terms of the concentrations of the mechanistic reactants, which were the glycerides and methoxide ions (and not methanol). Doubling the methoxide concentration increased the reaction rate twofold. At 23 °C the rate constants for the conversion of triglycerides to diglycerides, diglycerides to monoglycerides, and monoglycerides to glycerol were 6.3, 15.3 and 13.0 L mol^{-1} min^{-1}, respectively. These increased to 54.2, 136 and 139 L mol^{-1} min^{-1} at 50°C. These latter values (adjusted to 60 °C) were 65, 770 and 190 times larger, respectively, than values cited previously (and adjusted to the methoxide basis) for a transmethylation of Pongamia oil, which was also claimed to be homogeneous. Activation energies for all three steps were the same (63 kJ mol^{-1}). Pre-exponential factors showed that in diglycerides and triglycerides the second and third ester chains sterically hindered the attack of methoxide ions on the ester carbonyl groups.

Keywords Homogeneous transmethylation · Soybean oil · Kinetics · Rate constants · Activation energies

Introduction

The base catalyzed reaction of methanol with triglyceride-based vegetable oils produces fatty acid methyl esters (ME) and glycerol (G) with the sequential formation of diglycerides (DG) and monoglycerides (MG) by the three following equations. A molar equivalent of methanol is consumed at each step.

$$\mathrm{TG} + \text{methanol} \rightleftarrows \mathrm{DG} + \mathrm{ME}$$

$$\mathrm{DG} + \text{methanol} \rightleftarrows \mathrm{MG} + \mathrm{ME}$$

$$\mathrm{MG} + \text{methanol} \rightleftarrows \mathrm{G} + \mathrm{ME}$$

In the past 25 years these methyl esters have become accepted as diesel fuels which can be used without engine modifications. They are potentially renewable and, along with other lower alkyl esters, have been designated as “biodiesel”. In 1984 Freedman et al. [1] conducted the first experiments to identify optimum reaction conditions for the base-catalyzed transmethylation reactions. They claimed that it was not beneficial to use methanol/triglyceride molar ratios greater than 6:1 and sodium hydroxide (as catalyst) concentrations greater than 1.0 wt% (based on the oil). In 1986 Freedman et al. [2] studied the kinetics of both the transmethylation and transbutylation of soybean oil. They found that transbutylation followed second order kinetics, whereas transmethylation did not. They did not recognize the importance of the phase behaviors of the reactions. Transbutylation of soybean oil is monophasic throughout; however, transmethylation commences as two immiscible phases, a methanol phase and an oil phase. The catalyst is polar and exclusively dissolved in the methanol. Stirring causes the transport of triglycerides into the methanol phase where they are rapidly converted via diglycerides and monoglycerides

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to methyl ester and glycerol. The diglycerides and monoglycerides contain non-polar chains and polar OH groups which gives them surfactant properties. If sufficient mixing occurs then enough of them are formed such that an emulsion is created. The improvement in mass transfer then allows the reaction to continue. If stirring or agitation is discontinued too early, such that insufficient diglycerides and monoglycerides are formed, then the methanol and oil phases separate into layers, and the reaction stops [3]. In those cases where the reaction continues, a glycerol-rich phase forms rapidly within the emulsion, and this dissolves up to 90% of the catalyst [4]. Mass transfer again becomes limited and the reaction slows drastically. One result of this sequence is that some triglyceride never accesses the methanolic phase before the glycerol-rich phase forms, and often, but not always, triglyceride is the prevalent residual glyceride [3].

Since 1986 other attempts have been made to model the transmethylation reaction [2, 5–7]. All of them used systems which were not monophasic throughout, although one of the studies [7] claimed otherwise. In 1998 we showed that certain low-molecular weight ethers functioned as solvents in the reaction, and when added in sufficient amounts, made the resulting mixture monophasic [8]. The most efficient ether, in terms of the volume required, was oxolane (tetrahydrofuran); however at the usual methanol/oil molar ratio of 6:1 a glycerol-rich phase still separated during the reaction. We showed that if the methanol/oil molar ratio was raised to at least 25:1 and sufficient oxolane was added to form one phase at the beginning, then the reaction remained monophasic throughout at ambient temperatures [9]. Conveniently, a mixture which contains equal volumes of methanol, oil and oxolane has a methanol/oil molar ratio of approximately 27:1. We also showed that transmethylation in such a system was very fast and essentially at equilibrium after approximately seven minutes at 23 °C when 1.0 wt% sodium hydroxide (based on the oil) was used as the catalyst. Approximately 1.0 wt% monoglyceride typically remained as the only glyceride [9]. We did not determine any rate constants, but it was obvious that the reaction was much faster than in Freedman's study [2] as well as other studies conducted since then. We have now made measurements to determine rate constants and activation energies for the three consecutive forward reactions. The purpose was to demonstrate the speed of the reactions as well as to draw attention to the non-homogeneity involved in previous studies.

The mechanism of the transesterification involves the attack of methoxide ions, and not methanol molecules, on the glyceride bonds [10]. The resulting tetrahedral intermediate collapses to form methyl ester and an anion of a diglyceride, or a monoglyceride or glycerol. These anions rapidly abstract protons from the bulk methanol to regenerate methoxide ions. The consecutive reactions should be first order in both methoxide ion and the relevant glyceride. Previous investigations have failed to recognize the mechanistic implication and have assumed kinetic dependency on the methanol concentration. In addition, many previous studies have added an extra complication by using hydroxide catalysts, in which case the equilibrium between hydroxide ions and methanol must be relied on to form methoxide ions.

$$\mathrm{HO^- + CH_3OH \rightleftarrows CH_3O^- + H_2O}$$

This poses potential problems. For example, the reactions are usually initiated by adding a concentrated solution of catalyst in methanol to the bulk mixture of methanol and oil. If hydroxide catalysts are used then the equilibrium concentration of methoxide ions may not be established before reactions take place, leading to the excessive and irreversible attack of hydroxide ions on the glycerides to form soaps. For this reason we used sodium methoxide as the catalyst.

Two other comments are necessary. First, we had previously shown that at equilibrium in a truly monophasic transmethylation, approximately 99% of the ester bonds were cleaved [9]; therefore, the overall reverse reactions are approximately 100 times slower than the forward reactions, in which case for mathematical modeling purposes the rates of the reverse reactions could be ignored in determining the forward rate constants. Secondly, the monophasic reactions are so fast that low concentrations of catalyst must be used to slow them so that they may be studied over a suitable temperature range (23–50 °C). Previous studies typically used 1.0 wt% sodium hydroxide based on the oil as catalyst; in this study 0.05 wt% sodium methoxide was required to slow the reaction sufficiently. When the volumes of the reactants and solvent are taken into account, the catalyst concentration (in mol $\mathrm{L^{-1}}$) used in our study was approximately 50 times lower than normally used.

Experimental Procedures

Materials

The soybean oil was food grade obtained from Loblaws Inc. (Toronto, ON, Canada) and produced by Presidents Choice, Sunfresh Ltd., (Toronto, ON, Canada). It had a water content of 107 ppm [11]. The following chemicals were supplied by Sigma Aldrich (Milwaukee, WI, USA). Methanol (anhydrous, >99%), tetrahydrofuran (anhydrous, >99%), pyridine (anhydrous, >99%), heptane (anhydrous, >99%), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) (>99%), 2.3-bis(decanoyloxy)propyl decanoate (“tricaprin”, >99%), sodium methoxide in anhydrous methanol (25%w/w) and oxalic acid (>99%). Sodium chloride (analaR grade, >99%) and anhydrous sodium sulfate were obtained from Fisher Scientific (Nepean, ON, Canada). The methanol and tetrahydrofuran were stored over molecular sieves and had water contents of 30 and 38 ppm, respectively [11].

Procedure

Soybean oil (40.0 g), methanol (50.0 mL) and tetrahydrofuran (44.0 mL) were added to a 250 mL three-neck (ground glass) round-bottom flask. A water-cooled condenser, a thermometer and a drying tube (calcium chloride) were inserted into the three ground glass joints. The contents of the flask were gently swirled to achieve miscibility. The flask was then placed in a temperature controlled water bath at one of the four reaction temperatures (23, 30, 40 or 50 °C). Once the reactants achieved the required temperature, then, sodium methoxide methanolic solution (80 μL, 25 wt%) was added from an automatic micropipette. This represented “time zero” for each reaction. The reaction mixture was swirled manually for the first 20 s. Prior to starting the reaction, a methanolic solution of oxalic acid [0.037 g of oxalic acid in 15 mL of methanol (1.0 mL)] was added to each of twelve 20 mL scintillation vials. At reaction times of 1, 3, 5, 7, 10, 20, 30, 60, 120, 240, 360 and 480 min, a sample of the reaction mixture (10.0 mL) was pipetted into one of the labeled vials. Each vial was allowed to cool and then washed with a 10% brine solution (4 × 9 mL) effecting separation each time by gravity settling alone. After the fourth wash the brine wash was tested with wide range pH paper to check that it was neutral. The 12 vials were then sealed with “Parafilm” and centrifuged to separate any residual water.

Analysis

The liquid from each of the above vials (1.0 mL) was added to 2 mL vials followed by a few crystals of anhydrous sodium sulfate crystals. Each vial was agitated and left overnight to settle. Samples (100 mg) of each liquid layer were then added to 20 mL scintillation vials. To each of these vials tricaprin (100 μL) and MFSTFA (100 μL) were added. Each vial was agitated and allowed to stand for 20 min. Then anhydrous heptane (8.0 mL) was added to each vial. For some early samples, further dilution with heptane was necessary to bring the concentration of the analytes into the ranges valid for the GC method. The samples were analyzed for the glycerides and glycerol according to ASTM method D 6584 [12].

Kinetic Modeling

Standard series kinetic reaction equations were used to model the second order system [13].

The three forward rate equations in this study were:

$$\mathrm{d[TG]}/\mathrm{d}t = -k_1[\mathrm{CH_3O^-}][\mathrm{TG}]$$

$$\mathrm{d[DG]}/\mathrm{d}t = k_1[\mathrm{CH_3O^-}][\mathrm{TG}] - k_2[\mathrm{CH_3O^-}][\mathrm{DG}]$$

$$\mathrm{d[MG]}/\mathrm{d}t = k_2[\mathrm{CH_3O^-}][\mathrm{DG}] - k_3[\mathrm{CH_3O^-}][\mathrm{MG}]$$

where [TG], [DG], [MG] and [CH_3O^-] were the molar concentrations of the triglycerides, diglycerides, monoglycerides and methoxide ion, respectively. It was assumed that there were no significant volume changes during the reactions and that the polarities of the reaction mixtures did not change. These are valid assumptions because the methanol was present at relatively high concentration. In addition, during the reactions, the concentrations of OH groups and ester groups remained constant.

For each reaction, the three forward rate equations were integrated to give three equations expressing each glyceride concentration in terms of the three forward rate constants. Microsoft Excel’s Solver feature was then used to calculate the rate constants using the glycerol/triglyceride mass balance for the fourth equation. The Solver iterated different values for the rate constants (k_1, k_2, and k_3) until the squared error, S, between the calculated model values and the experimental values was minimized.

$$S = \sum([\mathrm{TG}]_{\mathrm{exp}} - [\mathrm{TG}]_{\mathrm{calc}})^2 + ([\mathrm{DG}]_{\mathrm{exp}} - [\mathrm{DG}]_{\mathrm{calc}})^2 + ([\mathrm{MG}]_{\mathrm{exp}} - [\mathrm{MG}]_{\mathrm{calc}})^2$$

Error Calculation

For each temperature, the average values of the three rate constants were obtained from the five runs. Each average value was then entered back into its relevant reaction Solver model and four new squared errors were calculated. These new errors were either the same or slightly larger than the original values. For each temperature the five squared errors (for the five runs) were then averaged. Finally, the model error, *N*, for each temperature was obtained by taking the square root of this average.

Results and Discussion

Activation Energies and Model Errors

Figure 1 shows a typical reaction profile, in this case for 40 °C. The trends are consistent with the three sequential reactions. Numerous experiments showed that the base

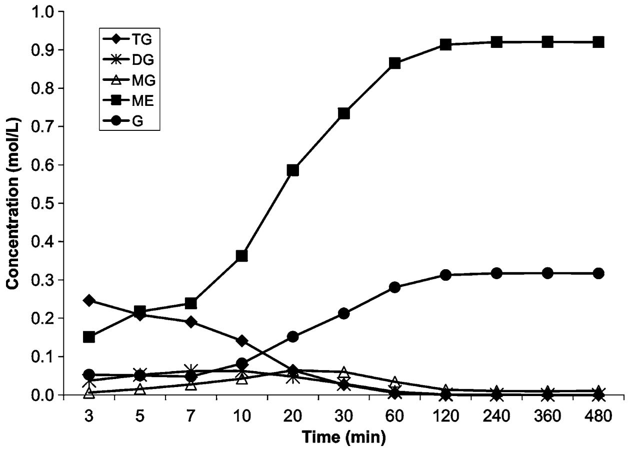

Fig. 1 Reaction profiles of triglycerides (TG), diglycerides (DG), monoglycerides (MG), methyl ester (ME) and glycerol (G) at 40 °C

concentration barely decreased during the runs. For example at 40 °C the base concentration fell less than 5% in 8 h. This may not be so when either hydroxide catalysts are used or significant moisture is present, in which cases the irreversible attack of hydroxide ion on the ester bonds can then form soaps with a corresponding decrease in the base concentration. All the runs, except for those at 23 °C, reached equilibrium before 480 min. The reaction at 50 °C reached equilibrium at or before 120 min. For all equilibria the monoglyceride concentration was typically 1.1 wt% with the diglyceride and triglyceride concentrations being significantly less. Therefore, close to 99% of all the triglyceride bonds were cleaved. This observation was justification for ignoring the reverse reactions in the kinetic modeling. The forward rate constants, k_1, k_2 and k_3 and their 95% confidence limits as well as their model errors, N, are shown in Table 1. The model errors are similar for all four temperatures and lie in the second decimal place of all three rate constants; therefore the sequential model is an excellent fit to the observed concentration/time data. It is useful to first consider the activation energies of each reaction. The least squares Arrhenius plots of the natural logarithms of the rate constants (k_1 and k_2) against the reciprocal of temperature, are shown in Fig. 2. Because the corresponding plot for ln k_3 against reciprocal temperature falls very close to that for ln k_2, it has been plotted separately in Fig. 3. The slopes of these linear graphs are the activation energies (E_a), divided by the universal gas constant (R) i.e. $\ln k = -E_a/R\mathrm{K} + \ln A$, where A is the pre-exponential factor of each reaction; therefore the activation energies for the three sequential steps are virtually identical (63 kJ mol^{-1}). This is consistent with the intermediates in each of the sequential reactions being structurally similar. These intermediate anions, which are formed by the attack of methoxide ions, contain a tetrahedral carbon atom that is attached to a methoxyl group, a long chain alkoxy group, a glyceride group and a negatively charged oxygen atom [10].

Comparison of Rate Constants and Pre-exponential Factors

It is clear from Table 1 that the rate constants for the reactions of the triglycerides were significantly different and less than those for the diglycerides and monoglycerides. Given that the intermediates for each step were the same (see above), and if all the glyceride ester groups behaved as if they were part of a pool, then k_1, k_2 and k_3 should have been in the ratio of 3:2:1, thereby reflecting the moles of ester groups in a mole of each glyceride. If, on the other hand, the triglycerides and diglycerides artificially increased the concentrations of the ester groups in the vicinity of their respective molecules, then the numerical values 3 and 2 in the above ratio would be higher. For either case, it is clear from Table 1, that k_1 and k_2 were both considerably smaller than they should be relative to k_3; and that k_1 was smaller than k_2 than it should be. The activation energies for the three reactions were the same, in which case the anomalies must be due to the pre-exponential factors, A, for the three steps (see above). Pre-exponential factors are a product of the collision frequencies of the reactants and the fraction of these collisions that lead to reaction. Collision frequencies (and hence the fraction which lead to reaction) can only be calculated for reactions in the gas phase when small molecules, which have known cross-sectional areas, are involved. However, for our three sequential reactions we can say with some certainty that the cross-sectional areas of all the ester groups are the same, even if they are solvated; therefore any differences in the pre-exponential factors for the three steps must be due to steric effects on the collision frequencies and the fraction of collisions which lead to reaction. The values of the pre-exponential factors were 0.78×10^{12}, 1.92×10^{12}, and 3.49×10^{12}, respectively, for the three successive reactions. Therefore, each glyceride chain has the effect of significantly decreasing the reaction of methoxide ions with other glyceride chains in the same molecule.

A reaction conducted at 40 °C, in which the methoxide concentration was doubled, gave rate constants (see Table 1) which fell comfortably within the 95% confidence limits of the rate constants for the other five reactions performed at the same temperature. This strongly suggests that the reactions are indeed first order in methoxide ion concentration as predicted from the known mechanism.

As mentioned above, Freedman et al. in their study did not recognize the importance of reaction homogeneity, but

Table 1 Forward rate constants and residual norms for the transmethylation of soybean oil (27:1 methanol/oil molar ratio, 12:1 THF/oil molar ratio, sodium methoxide 0.050 wt% w.r.t. oil

Temperature (°C)	Average rate constants (L mol^{-1} min^{-1}) and 95% confidence limits			Residual norm
	k_1	k_2	k_3	
23[a]	6.3 ± 1.3	15.2 ± 2.8	13.9 ± 2.7	0.067
30[a]	13.6 ± 1.7	35.6 ± 7.5	35.2 ± 10.6	0.076
40[a]	29.1 ± 5.5	68.5 ± 13	60.6 ± 16	0.074
50[a]	54.2 ± 13	136 ± 23	139 ± 29	0.068
40[b]	27.5	64	70	0.069
60[c]	1.7	0.35	0.67	0.048
50[d]	6.4	14.1	27.5	

See footnotes for deviations

[a] Averages and confidence limits are for five runs

[b] 0.10 wt% sodium methoxide w.r.t. oil, one experiment only

[c] Ref. [7], Pongamia oil triglyceride used as reactant. Table 2, line 1 values corrected to methoxide basis, no cosolvent, 10:1 methanol/oil molar ratio, 1.0 wt% potassium hydroxide (based on the oil)

[d] Ref. [6], k_1, k_3 and k_5 values of Table 2 (forward rate constants without shunt mechanism) corrected to methoxide basis, no cosolvent, 6:1 methanol/oil molar ratio, 0.20 wt% NaOH (based on the oil). Reynolds number, $N_{Re} = 6200$

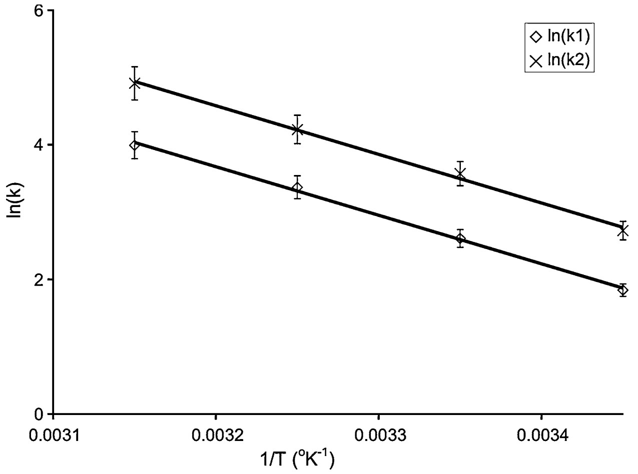

Fig. 2 Arrhenius plots (least squares fits) of ln k_1 and ln k_2 against 1/*K* (each data point is the average from five runs with 95% confidence limits as shown)

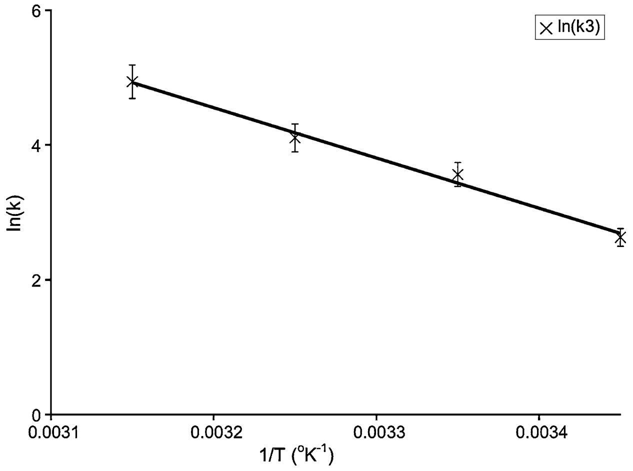

Fig. 3 Arrhenius plot (least squares fit) of ln k_3 against 1/*K* (each data point is the average from five runs with 95% confidence limits as shown)

did note that the transmethylation reaction did not follow the expected kinetics; therefore, they did not quote rate constants. Darnoko and Cheryan [5] recognized that the transmethylation kinetics of palm oil were abnormal and concluded that a kinetic treatment that used a second order dependency on the glycerides fitted their data best; therefore, their rate constants cannot be compared to those obtained in this study. The only other study, in which homogeneity has been claimed throughout, is that of Karmee et al., who studied the transmethylation of Pongamia oil triglycerides using a methanol to oil molar ratio of 10:1, and both 1.0 and 2.0 wt% potassium hydroxide (based on the oil) as catalyst and a temperature of 60 °C [7]. It was claimed that the addition of oxolane did not increase reaction rates. The claim of homogeneity throughout is perplexing given the known phase behaviors of methanol/vegetable oil triglyceride systems. However, the experiments only used 2.0 g samples of triglycerides, in which case it would have been difficult to observe the separate phases, either at the start or end of the reaction. We have no explanation for the reported lack of rate increases either on adding oxolane or doubling the amount of catalyst. Previous workers have reported increases in reaction rates with increasing catalyst concentrations [14]. Karmee et al., like other researchers, used the forms of the rate equations, which contain a first order dependency on the methanol concentration. Despite this, the rate constants so derived by them can be adjusted to the methoxide basis (for comparison) by multiplying them by the ratio of the molar concentration of methanol and that of the methoxide ion at the beginning of the reactions. In order to calculate this ratio it was assumed that all the hydroxide ion was converted to methoxide ion by the equilibrium with methanol. This ratio was approximately 60 when 1.0 wt% KOH (based on the oil) was used in their study. The rate constants for 60 °C, as obtained from line 1 in Table 2 of reference [7], were multiplied by the ratio, and the adjusted values are shown in Table 1. Table 1 also shows that, as expected, our rate constants approximately doubled in value for each 10 °C rise in temperature. If we assume a further doubling on raising the temperature from 50 to 60 °C, then our values of k_1, k_2 and k_3 are approximately 65, 770 and 190 times, respectively, larger than those reported by Karmee et al. This strongly suggests that the earlier study did not involve truly homogeneous behavior. It is highly unlikely that the use of Pongamia oil triglycerides rather than soybean oil would explain the anomaly.

Noureddini and Zhu [6] recognized the non-homogenous nature of the transmethylation reaction and employed various intensities of mixing to facilitate mass transfer at temperatures between 30 and 70 °C. They claimed that all the reactions eventually became homogeneous due to the formation of some methyl ester. At low mixing intensities (Reynolds Number of 3100) there was a lag time of almost 20 min at 70 °C before a significant reaction took place. However, at higher mixing regimes (Reynolds Number of 6200) the lag time essentially disappeared at all temperatures. We suggest that the intermediate diglycerides and monoglycerides, being surfactants, caused emulsion formation, and that this, rather than homogeneity, increased mass transfer. None of the reactions reported by Noureddini and Zhu achieved greater than 90% conversion whereas our homogeneous reactions achieved almost 99%. We attribute their lower value to the formation of glycerol-rich, catalyst-rich phases, which being small would have been difficult to see. Despite this, it can be seen from the results in Table 1 (also adjusted to a methoxide basis) that the reactions observed by Noureddini and Zhu [6] at 50 °C had significantly higher rate constants than those reported by Karmee et al. [7] for Pongamia oil at 60 °C. We doubt that such differences can be attributed to dissimilarities in the fatty acid composition of the two oils At 50 °C and a Reynolds Number of 6200, Noureddini's values of the rate constants were only 5–10 times smaller than those reported in our study, although the reactions only proceeded to 90% completion.

One final comment is necessary. Reaction rates are governed by the activation energies involved to form the intermediates. If the key intermediates are polar, as they are in transmethylation, then they should be stabilized by more polar solvents; therefore it is likely that the use of other solvents such as dioxane, may result in kinetic parameters slightly different from those reported here.

The rate constants, which were derived from this study, provide a benchmark against which the effectiveness of strategies to increase mass transfer in heterogeneous transmethylation, may be compared. They should also be useful in modeling the transmethylation of vegetable oils under conditions that involve complete homogeneity at some time during the reaction.

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