Kinetics of the Reaction of Isopropenyl Acetate and Stearic Acid to Form Isopropenyl Stearate[1]

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ABSTRACT

A mathematical kinetics model has been developed for the reaction of stearic acid with isopropenyl acetate to form isopropenyl stearate. Though the reaction is reversible, the kinetics can be described mathematically most simply by a pseudo first order irreversible reaction model. The model predicts the rate of formation of isopropenyl stearate as a function of time, temperature, catalyst concentration and equilibrium concentration of isopropenyl stearate. Equilibrium is determined from an empirical equation as a function of the ratio of the original concentration of the reactants. Temperature has little effect on the equilibrium.

INTRODUCTION

In 1949, Phillips (1) reported the synthesis of enol esters from isopropenyl acetate (IPA) and carboxylic acid anhydrides. In 1962, Rothman et al. (2) reported the interesterification of stearic acid (SA) with IPA to give isopropenyl stearate (IPS).

Due to the relative ease with which IPS acylates difficultly acylatable compounds (3,4) with little by-product contamination, the development of an economically feasible process for the production of IPS should promote commercial interest and increase the utilization of long chain fatty acids. The development of a process to make IPS from SA and IPA is in progress.

To this end, a kinetics model of the reaction was developed. The term model is used in the sense that it is a sufficiently accurate representation of reality to permit the engineering design of a continuous bench scale reactor and aid in the subsequent scale up. It was not the purpose of this study to develop a formal chemical mechanism. The stoichiometric model used was the simplest not conflicting with experimental data.

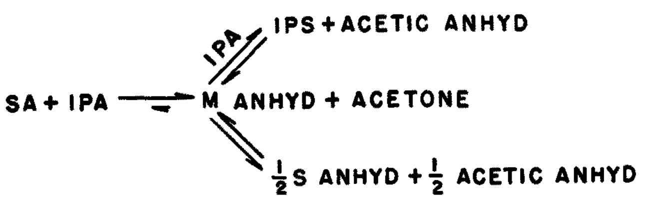

FIG. 1. The chemical model. Stearic acid (SA) reacts with isopropenyl acetate (IPA) to form mixed anhydride (M Anhyd) and acetone. The M Anhyd reacts with excess IPA to form isopropenyl stearate (IPS) and acetic anhydride and decomposes to stearic anhydride (S Anhyd) and acetic anhydride.

EXPERIMENTAL PROCEDURES

Reagents

Isopropenyl acetate (Matheson, Coleman and Bell) was purified by distillation. Stearic acid from Humko Products was recrystallized once from acetone.

Procedure

Stearic acid was weighed into a round bottom flask, IPA added, and the system heated to within 5 C of the desired temperature. Sulfuric acid catalyst was added and the heat of solution rapidly (ca. 15 sec) increased the temperature to the desired level.

The reaction time was considered as the time from when the H_2SO_4 catalyst was added since there was no reaction until the catalyst was added. Before sampling, two drops of triethylamine quenching agent were placed in a 7 ml sample vial. About 2 ml of reaction mixture was withdrawn by a capillary pipette and placed in the sample vial. The contents were mixed and the vial plunged into dry ice.

After several minutes the sample was placed under vacuum (300-500μ Hg absolute pressure) for 2-3 hr to remove all volatiles (IPA, acetone, acetic anhydride and acetic acid). An accurately weighed dried sample which consisted only of the nonvolatiles IPS, SA, mixed anhydride and stearic anhydride was dissolved in 100 parts CS_2 ($\sim$1% w/v) and analyzed according to the procedures of Calhoun and DellaMonica (5) for IPS and SA. A total of

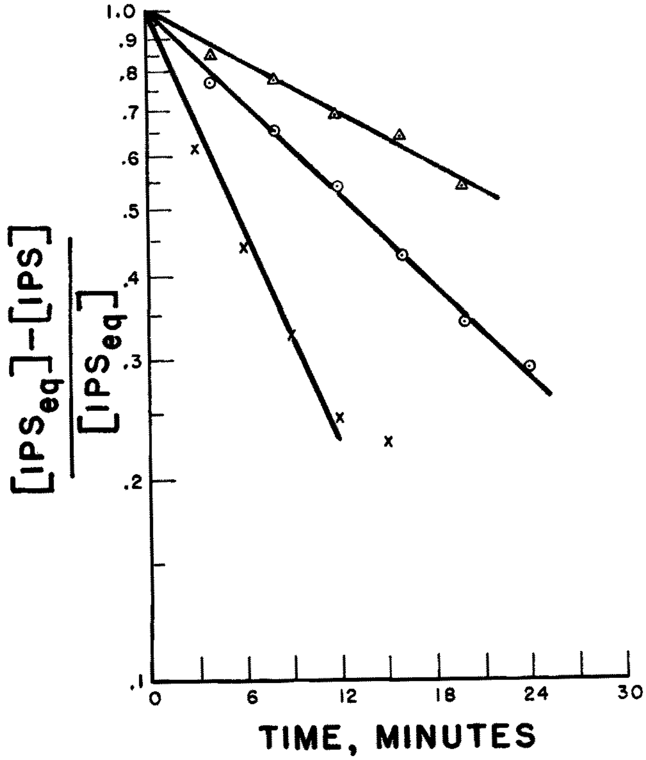

FIG. 2. Three typical sets of experimental data plotted as the integrated form of the rate equation (symbols in nomenclature) vs. time to test the fit of a pseudo first order irreversible reaction scheme.

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[1] Nomenclature: c = empirical constant; $[CAT_0]$ = initial H_2SO_4 concentration, gm moles/10 kgm solution; E = activation constant, cal/gm mole; [SA] = stearic acid concentration, gm mole/10 kgm solution; $[SA_0]$ = initial stearic acid concentration, gm mole/10 kgm solution; [IPA] = isopropenyl acetate concentration, gm mole/10 kgm solution; $[IPA_0]$ = initial isopropenyl acetate concentration, gm mole/10 kgm solution; [IPS] = isopropenyl stearate concentration, pseudo-mole fraction; $[IPS_{eq}]$ = equilibrium isopropenyl stearate concentration, pseudo-mole fraction; k = rate constant, 10 kgm/gm mole/min; K_c = equilibrium constant; P = probability; R = gas constant, 1.987 cal/gm mole °K; T = temperature, °K; θ = time, min.

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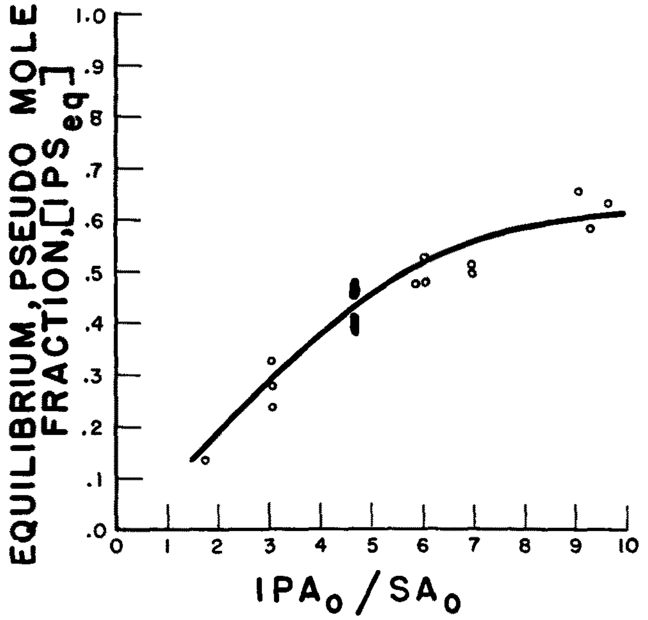

FIG. 3. Equilibrium concentration of isopropenyl stearate (IPS), expressed as the pseudo mole fraction [IPS_{eq}], plotted as a function of the ratio of the original concentration of the reactants–original concentration of isopropenyl acetate [IPA_0] divided by the original concentration of stearic acid [SA_0].

135 experiments was performed covering a temperature range of 45-130 C, a range of catalyst concentrations of 0.04-1.97 g mole/10 kgm solution, and a range of molar ratios of IPA:SA of 1.8:18.

In a mathematical approach for obtaining reactor design criteria, an understanding of the reaction path is not an absolute necessity. However, for process design where material and energy balances become necessary, a plausible model of the chemistry is essential.

The model suggested by Phillips (1), shown in Figure 1, appears to be a plausible representation of the reaction as the authors observed to date and was therefore adopted. The SA is thought to react with IPA to form mixed stearic-acetic anhydride (M Anhyd) and acetone. The M Anhyd can react in two directions. It reacts with IPA to give the desired product IPS and acetic anhydride. It also spontaneously and reversibly decomposes to stearic anhydride (S Anhyd) and acetic anhydride.

In order to correlate the rate data, the simplifying assumptions were made that the reaction can be treated as a pseudo first order irreversible reaction and concentrations can be expressed as pseudo mole fractions.

The reversible decomposition of M Anhyd to S Anhyd could not be quenched effectively; therefore it was not possible to establish the concentrations of S Anhyd and M Anhyd in the reaction mixture. Since the primary objective of this work was a mathematical model useful for designing a chemical reactor, the study could be designed to circumvent using the M Anhyd and S Anhyd concentrations by restricting the correlation to two steps: (a) the rate of disappearance of SA and (b) the rate of formation of IPS.

RESULTS

The disappearance of SA is a rapid, essentially irreversible reaction (< 5 sec at 90 C). The formation of IPS is much slower (ca. 30 min) and the rate controlling step. It is a reversible reaction with yields typically about 50% (based on SA). The data for the disappearance of SA fit reaction rate equation E-1 (6).

$$\frac{-d[SA]}{d\theta} = 1.97 \times 10^{11}\, e^{\frac{-21122}{RT}} [CAT_0]\,[IPA_0]^2\,[SA]^{1/2} \quad \text{(E-1)}$$

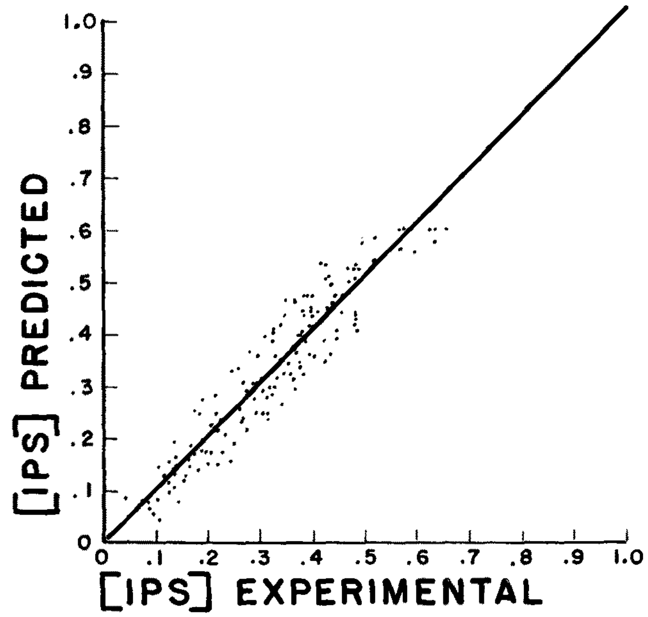

FIG. 4. Fit of the mathematical model to the experimental data plotted as the predicted pseudo mole fraction of isopropenyl stearate [IPS] vs. the experimental pseudo mole fraction of isopropenyl stearate [IPS].

Data for the rate of formation of IPS fit well to a pseudo first order irreversible reaction scheme (7). (While the reaction is evidently reversible, external knowledge of the equilibrium concentration of IPS permits an equation wherein the equilibrium value is an end-point. This treatment is a minor modification of the scheme of Levenspiel [7].)

Assuming the reaction is of the form:

$$\text{M Anhyd} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{IPS}$$

the rate expression is

$$\frac{d\,[IPS]}{d\theta} = k_1'\,[\text{M Anhyd}] - k_2'\,[IPS] \quad \text{(E-2)}$$

As Levenspiel (7) points out, the validity of this correlation can be established if the integrated form of the rate expression, $-\ln[(\text{M Anhyd-M Anhyd}_{eq})/(\text{M Anhyd}_0\text{-M Anhyd}_{eq})]$, can be plotted as a straight line versus time. However, the reactant in this system is M Anhyd and its concentration cannot be reliably determined. Therefore, the rate equation was integrated with the product concentration [IPS] as the dependent variable and the boundary conditions established using the equilibrium relationship. The result is that $\ln\,[(IPS_{eq}\text{-}IPS)/(IPS_{eq}\text{-}IPS_0)]$ is plotted versus time and the slope is changed in sign as shown in Figure 2. The slope equals $-(k_1' + k_2')$.

Due to the uncertainty in the M Anhyd-S Anhyd concentrations, some method was needed to eliminate them from the rate expression and work only with known concentrations of IPS. Therefore the concentration terms were expressed as pseudo mole fractions. Pseudo mole fraction is defined as the molar concentration of a stearoyl component divided by the total molar concentration of stearoyl components in the original reaction mixture [SA_0]. For example, in a 10 kgm reaction mixture having a S Anhyd concentration of 2.5 mole/10 kgm and an original stearoyl concentration of 10 mole SA/10 kgm, the pseudo mole fraction is calculated as (2.5 x 2/10)/(10/10) = 0.5. (The S Anhyd concentration is doubled because there are two stearoyl groups per S Anhyd molecule.)

With concentrations expressed in this manner, [IPS] becomes the pseudo mole fraction of IPS and [M Anhyd] can be expressed as [1-IPS]. Hence, equation (E-2) can be written:

$$\frac{d[\mathrm{IPS}]}{d\theta} = k_1' \, [1\text{-IPS}] - k_2' \, [\mathrm{IPS}] \qquad \text{(E-3)}$$

The reaction rate also depends on the catalyst concentration [CAT], and the rate constants were found to be linear functions of the initial catalyst concentration $[\mathrm{CAT_o}]$.

$$k_1' = k_o + k_1 \, [\mathrm{CAT_o}]$$

$$k_2' = k_o + k_2 \, [\mathrm{CAT_o}]$$

However, there is no reaction without catalyst ($k_o = 0$), and equation (E-3) becomes

$$\frac{d[\mathrm{IPS}]}{d\theta} = k_1 \, [\mathrm{CAT_o}] \, [1\text{-IPS}] - k_2 [\mathrm{CAT_o}] \, [\mathrm{IPS}] \qquad \text{(E-4)}$$

Since the equilibrium constant is $K_c = k_1/k_2$, the individual rate constants can be evaluated with knowledge of an equilibrium constant. No theoretical equilibrium constant could be derived so an empirical equilibrium expression was used. This expression (equation E-5) is unaffected by temperature.

Figure 3 shows how the equilibrium value of IPS varies with the ratio of original reactants ($\mathrm{IPA_o/SA_o}$). By performing a curvilinear regression on these data the following equilibrium equation was determined:

$$y = c_1 + c_2 X + c_3 X^2 \qquad p < 0.001 \qquad \text{(E-5)}$$

where $y = [\mathrm{IPS_{eq}}]$

$X = [\mathrm{IPA_o}]/[\mathrm{SA_o}]$ with limits $1.5 \leq X \leq 10.0$

$c_1 = -0.0612$

$c_2 = 0.1364$

$c_3 = -0.0069$

Therefore,

$$K_c = \frac{k_1}{k_2} = \frac{[\mathrm{IPS_{eq}}]}{1\text{-}[\mathrm{IPS_{eq}}]} = \frac{c_1 + c_2 X + c_3 X^2}{1 - c_1 - c_2 X - c_3 X^2} \qquad \text{(E-6)}$$

and

$$k_1 = K_c k_2 \qquad \text{(E-7)}$$

The reaction rate is temperature sensitive so an Arrhenius relationship is appropriate. It has already been shown that the rate constants in this model vary at a constant temperature with the initial concentration of reactants; but, the ratio (K_c) does not change with temperature. Since

$$k_1 = k_{1_o} e^{-E_1/RT} \quad \text{and} \quad k_2 = k_{2_o} e^{-E_2/RT} \quad \text{then}$$

$$K_c = \frac{k_1}{k_2} = \frac{k_{1_o} e^{-E_1/RT}}{k_{2_o} e^{-E_2/RT}} \qquad \text{(E-8)}$$

But K_c does not vary with temperature, hence, E_1 must approximately equal E_2 and the assumption must be made that both the forward and reverse reaction rate constants in this model vary at approximately the same rate with temperature. Using this assumption, the individual rate constants were combined and the following modification of the Arrhenius equation derived:

$$k_1 + k_2 = 9.85\,(10^5)\, e^{\frac{-11974.7}{RT}} \qquad p < 0.001 \qquad \text{(E-9)}$$

By solving equations (E-6) and (E-9) simultaneously the individual rate constants, k_1 and k_2, are found. Substituting k_1 and k_2 into equation (E-4) and integrating, the concentration of IPS at any time can be found.

To determine the fit of this model, values of IPS were calculated and checked against the corresponding experimental values as shown in Figure 4. The data scatter indicate that the range of model errors plus random experimental errors is ±.1 pseudo mole fraction. This range was calculated from 163 of 165 data points. However, the data cover a much larger span of experimental conditions than would be expected to be encountered in actual processing. The kinetics study was terminated at this point since a sufficiently accurate model was obtained to design the reactor for a bench scale continuous process.

DISCUSSION

Although the chemical model is quite simple, it must be pointed out that the actual reaction is not. As previously mentioned, various reaction paths to IPS can be postulated. It could be some unique combination of reaction steps that causes the equilibrium to be insensitive to temperature.

Although an empirical relation, equation (E-5), was found to adequately predict equilibrium, limits were placed on the independent variable. The upper limit of 10 mole IPA/mole SA was chosen since the maximum equilibrium value was attained at 10 and remained constant at this value with increases in the independent variable. The lower limit is simply the limit of the experimental data.

The model essentially correlates only the SA and IPS since it was impossible to determine the validity of the M Anhyd and S Anhyd analyses. In the early phases of the study (when the kinetics of the disappearance of SA was studied), S Anhyd was found in the reaction products but not M Anhyd. In the later phases when the rate of formation of IPS was studied it became apparent that M Anhyd was converting to S Anhyd before the analysis could be completed. Acetic anhydride is the byproduct when IPS is formed. It is also the byproduct when M Anhyd converts to S Anhyd. Hence, as the reaction of M Anhyd with IPA to IPS progressed, the excess acetic anhydride probably hindered the decomposition of M Anhyd by shifting the equilibrium. In essence, the M Anhyd was a very unstable component early but developed stability as the reaction progressed. No method was found to accurately determine the concentration of M Anhyd in the reaction mixture.

In addition to the analytical errors as discussed by Calhoun and DellaMonica (5), there were other errors associated with the reaction and sampling. A byproduct of the reaction was an oil which appeared to be a polymer of IPA resulting from the action of H_2SO_4 and heat on the IPA. Infrared shows that the oil has essentially the same absorption peaks as IPA but with different intensities.

Figure 2 shows the data from three typical experiments out of a total of 20, plotted to test the fit of a pseudo first order irreversible reaction scheme. As shown by the bottom line, this model did not fit all the data very well. A good bit of personal judgment had to be exercised in drawing the lines. Early samples were more sensitive to sampling time errors since it took about 15 sec to take a sample and place it in dry ice, and the rate of reaction was much higher early in the reaction. The oily polymer appeared in the later samples. These samples became difficult to dry and the residual oil may have influenced the analysis near equilibrium.

Most of the samples were taken within the first hour of reaction whereas the final (equilibrium) sample was taken several hours later. The later samples may have been affected by the oil and the apparent equilibrium value shifted slightly. In choosing the parameters for a continuous reactor this should have no effect since, as a practical consideration, equilibrium would never be reached in a continuous stirred tank reactor.

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