SHORT COMMUNICATION

Effects of Lewis Acid Catalysts on the Esterification Kinetics of Castor Oil with Oleic Acid

A. Erdem-Şenatalar*, E. Erencek, M. Tüter and **A.T. Erciyes**
Istanbul Technical University, Department of Chemical Engineering, 80626 Maslak, Istanbul, Turkey

The effects of two Lewis acid catalysts, tin chloride and cobalt chloride, on the kinetics of the esterification reaction between castor oil and oleic acid have been investigated. Uncatalyzed and catalyzed reactions were carried out both in the presence of excess oil and with equivalent amounts of reactants at various temperatures. The reaction, with respect to castor oil concentration, is first-order in all cases, whereas with acid concentration the reaction was observed to change from second-order for the uncatalyzed reaction to first-order for tin chloride-catalyzed and to zero-order for cobalt chloride-catalyzed reactions. The order (with respect to acid) also changed with temperature for the cobalt chloride-catalyzed reaction.

KEY WORDS: Castor oil, cobalt, esterification, kinetics, Lewis acid catalysts, oleic acid, tin chloride.

The presence of hydroxyl groups, in addition to olefinic linkages in the structure of castor oil, provides many additional reaction possibilities (1,2). Among these, esterification reactions are important and can be used for the production of many industrially important products, such as nondrying alkyd resins and materials with drying oil properties (3–6).

Kinetic studies on the conventional esterification of castor oil or ricinoleic acid are limited (7,8). The uncatalyzed esterification reaction between castor oil and oleic acid followed third-order kinetics in a recent study, where the reaction was also carried out in the presence of added catalysts, such as potassium hydroxide, *p*-toluene sulfonic acid and tin chloride (8). Potassium hydroxide showed essentially no catalytic activity, and *p*-toluene sulfonic acid was somewhat more effective. Tin chloride, which was previously reported (9) to have an outstanding catalytic activity in the esterification between glycerol and peanut oil fatty acids, was the most effective catalyst. The total order of reaction decreased to two in the presence of tin chloride (8).

The effects of tin chloride and another Lewis acid catalyst, cobalt chloride, on the kinetics of the esterification reaction between castor oil and oleic acid were investigated in the temperature range of 200–250°C. Uncatalyzed and catalyzed reactions were carried out in the presence of excess oil to determine the orders of reaction with respect to the acid concentration. Equivalent reactant ratios were also used to determine their total orders.

EXPERIMENTAL PROCEDURES

Materials. Castor oil was obtained by cold-pressing seeds of Turkish origin. The main characteristics of the oil were: refractive index (n_D^{20}), 1.4780; acid value, 0.44; saponification value, 178; hydroxyl value, 163.1; and iodine value, 84.6. Oleic acid was of analytical grade from Riedel de Haen (Hannover, Germany) with an acid value of 199 and an iodine value of 92. Other reagents were of analytical grade from Merck (Darmstadt, Germany).

Experimental set-up. Esterification reactions were carried out in a four-necked flask equipped with a stirrer, a thermometer, an inert gas inlet tube and an air condenser.

Esterification of castor oil with oleic acid. Reactions were conducted with equivalent proportions of the reactants and excess of the oil. In the preliminary experiments, which were carried out for the determination of the necessary "excess," molar ratios of [OH]/[COOH] of up to 20:1 were tried. Neutralization of the oil prior to the experiments was necessary for the reactions carried out with excess oil. Castor oil was placed into the reaction flask and heated under agitation to the reaction temperature. Oleic acid was heated separately to the reaction temperature and then added to the reaction flask. For catalyzed reactions, 0.1% of the catalyst based on reactants was used. The necessary amount of catalyst, calculated on an anhydrous basis, was initially added to the acid. The stirring rate was adjusted to 200 rpm, and nitrogen was passed over the surface of the reaction mixture at a rate of 200 mL/min to provide an inert atmosphere and to remove water. Samples were withdrawn at predetermined time intervals and cooled immediately by immersion into cold water. Acid values of the samples were determined (10). In view of the difficulty of establishing the concentration in mole per liter at the applied temperatures, the oleic acid concentration was expressed in terms of weight percentage as determined from the acid value and equivalent weight of the acid (282). A correction for loss of water was applied to each sample. Each experiment was carried out twice to check for the reproducibility of the results.

RESULTS AND DISCUSSION

The reaction is assumed to be irreversible under the applied conditions, as found in previous studies employing similar reaction conditions (8,11).

The amount of excess oil necessary for determination of the reaction order with respect to the acid concentration was found by a series of uncatalyzed experiments with starting [OH]/[COOH] molar ratios in the range 1:1 to 20:1. Because the accuracy of the differential method is lower as compared to the integral method, the latter was used, and the order was scanned with 0.01 intervals for the best correlation coefficient (12). The best fits, obtained by applying the method of least squares, of some experiments and their correlation coefficients are listed in Table 1.

The order of reaction varied with the initial ratio of oil to acid in the range employed (1:1 to 20:1) and seemed to stabilize around second-order when the amount of oil in the starting mixture was about fifteen times the amount of acid or more. The reaction rate was assumed to be independent of the concentration of the castor oil for these mixtures, and the initial oil-to-acid ratio of 20:1 was employed for further experiments to determine the order of reaction with respect to the acid concentration alone.

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*To whom correspondence should be addressed.

TABLE 1

Reaction Orders Yielding the Best Fit for Some Experiments with Various Amounts of Excess Oil

Initial [OH]/[COOH] ratio (mole:mole)	Reaction order	Coefficient of determination (r^2)
10:1	1.29	0.9994
15:1	1.97	0.9962
15:1	1.88	0.9997
20:1	1.95	0.9960

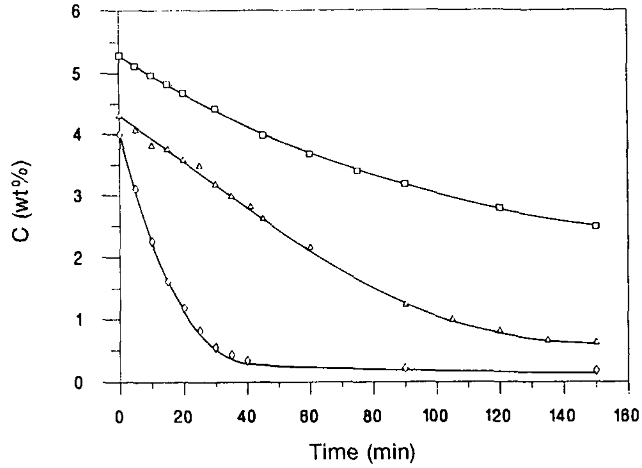

FIG. 1. Change of oleic acid concentration with time for the experiments at 225°C with excess oil in the initial mixtures. □, Uncatalyzed; = ◇ , $SnCl_2$-catalyzed; △, $CoCl_2$-catalyzed.

Figure 1 shows the acid concentration vs. time data for the uncatalyzed and catalyzed reactions with excess oil in the starting mixtures. The reaction proceeded much faster with the addition of catalysts, especially of tin chloride. In fact, in the presence of tin chloride, the reaction seemed to have been completed in about 40 min. On the other hand, the rate of the cobalt chloride-catalyzed reaction decreased significantly after about 90 min.

The integral method was applied to test the zero-, first-, second- and third-order kinetics by plotting C_A, $\ln C_A$, $1/C_A$ and $1/C_A{}^2$ vs. time, respectively, where C_A is the concentration of the acid. The quality of the fit was judged based on the values of the coefficient of determination, r^2, and the standard error of estimate, s (13).

The uncatalyzed experiment followed second-order kinetics with respect to the oleic acid concentration. The total order of this reaction was previously reported to be third-order, suggesting that the kinetics should be first-order with respect to the castor oil concentration (C_O), as given in the following rate expression:

$$-r_{A,u} = k_u C_A^2 C_O \qquad [1]$$

When the analysis of the experimental data for the tin chloride-catalyzed reaction carried out in the presence of excess oil was confined to the initial reaction period of about 40 min, a high correlation coefficient was obtained for first-order kinetics. Because the total reaction order for this system is known to be second-order (8), the reaction should also follow first-order kinetics with respect to the castor oil, as in the uncatalyzed system, and the rate expression can be written as follows:

$$-r_{A,SnCl_2} = k_{SnCl_2} C_A C_O \qquad [2]$$

Data obtained from the cobalt chloride-catalyzed reaction with excess oil, on the other hand, yielded the best fit for zero-order kinetics with respect to the acid, indicating that the rate is independent of the oleic acid concentration for this case. The total order of the cobalt chloride-catalyzed reaction was determined to be equal to first-order, both at 225 and 200°C, from the experiments carried out with equivalent amounts of the reactants in the starting mixtures. The rate expression, for this case, then, can be written as follows:

$$-r_{A,CoCl_2} = k_{CoCl_2} C_O \qquad [3]$$

Although the total orders of the uncatalyzed and tin chloride-catalyzed reactions, which are third- and second-order, respectively, generally do not change in the temperature range of 200 to 250°C (8), this is not the case when $CoCl_2$ is used as catalyst. The total reaction order of the cobalt chloride-catalyzed reaction is observed to change at higher temperatures. At 250°C, this reaction follows second-order kinetics, similar to the tin chloride-catalyzed system. The specific reaction rate, k, is on the same order of magnitude, at 250°C, for both Lewis acid catalysts. Table 2 gives a summary of the reaction orders

TABLE 2

Reaction Orders and Rate Constants for the Typical Uncatalyzed and Catalyzed Experiments and the Respective Coefficients of Determination (r^2) of the Regressions

Catalyst	Oil/acid ratio	Temperature (°C)	Order	Rate constant (k)[a]	(r^2)
—	20:1	225	2[b]	1.44×10^{-3}[d]	0.9997
$SnCl_22H_2O$	20:1	225	1[b]	6.57×10^{-2}[d]	0.9974
$CoCl_26H_2O$	20:1	225	0[b]	3.42×10^{-3}[d]	0.9952
—	1:1	225	3[c]	9.72×10^{-6}	0.9918
$SnCl_22H_2O$	1:1	225	2[c]	4.27×10^{-4}	0.9898
$SnCl_22H_2O$	1:1	250	2[c]	8.34×10^{-4}	0.9942
$CoCl_26H_2O$	1:1	225	1	1.15×10^{-2}	0.9983
$CoCl_26H_2O$	1:1	200	1	5.97×10^{-3}	0.9977
$CoCl_26H_2O$	1:1	250	2	7.27×10^{-4}	0.9997

[a] The units are $(wt\%)(min)^{-1}$ for zero-; $(min)^{-1}$ for first-; $(wt\%)^{-1}(min)^{-1}$ for second- and $(wt\%)^{-2}(min)^{-1}$ for third-order reactions.

[b] With respect to the acid concentration.

[c] From previous work for comparison (Ref. 8).

[d] Values including the initial excess oil concentration (kC_O).

and rate constants for the typical uncatalyzed and catalyzed experiments, together with the coefficients of determination.

The change in reaction order with temperature was also observed by Smith and Elliott (14), who reported that the esterification of rosin with pentaerythritol in concentrated solution followed second-order kinetics at 260°C, whereas it appeared to be third-order at 300°C. In addition, data from the reaction carried out at 280°C could be fitted to either second- or third-order rate equations. Flory (15,16) observed a change in order with the extent of reaction for polyesterification between dibasic acids and glycols, which he attributed to a medium effect arising from the system becoming progressively less polar as the reaction proceeded.

The difference in reaction orders with respect to the acid concentration for the two catalysts at the same temperature of 225°C, and the variation with temperature for cobalt chloride-catalyzed reaction, indicate that these are only "apparent" orders. A reaction mechanism and a more general kinetic expression are being sought to explain the changes observed in the apparent orders of Lewis acid-catalyzed reactions between castor oil and oleic acid.

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[Received January 23, 1994; accepted May 24, 1994]