Mechanism and Kinetics of the $CoCl_2$-Catalyzed Esterification Reaction of Castor Oil with Oleic Acid

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ABSTRACT: The apparent orders of the Lewis acid-catalyzed esterification reactions between castor oil and oleic acid are known to change with the catalyst used and with the reaction temperature. A mechanism is proposed in this study to explain the variations (with temperature) in the apparent orders of the cobalt chloride-catalyzed esterification reaction between castor oil and oleic acid. According to the proposed mechanism, an acid-catalyst intermediate forms in an initial, fast quasi-equilibrium step, and this intermediate then reacts with the oil to yield the products and to regenerate the catalyst in the rate-determining second step. A general rate expression, with an acid concentration term and a temperature-dependent constant in the denominator, is derived from the proposed mechanism and is verified with data obtained at different temperatures.

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

Castor oil may undergo many reactions due to the presence of hydroxyl groups in addition to olefinic linkages in its structure (1,2). Among these, esterification reactions that can be used for the production of many industrially important products, such as nondrying alkyd resins and materials with drying oil properties, have special importance (3–6).

Kinetic studies on the conventional esterification of castor oil or ricinoleic acid are limited (7–9). The uncatalyzed esterification reaction between castor oil and oleic acid was observed to follow third-order kinetics in a 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, while *p*-toluene sulfonic acid was somewhat more effective. Tin chloride, which was previously reported (10) 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).

In a recent study, 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 were investigated in more detail (9). Uncatalyzed and catalyzed reactions were carried out both in the presence of excess oil and with equivalent amounts of reactants at various temperatures in the range of 200–250°C. The reaction, with respect to castor oil concentration, was 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. At 250°C, first-order kinetics, with respect to acid concentration, was observed to be similar to the tin chloride-catalyzed reaction.

The change in reaction order with temperature was also observed by Smith and Elliott (11), 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 (12,13) observed a change in order with the extent of reaction in the case of polyesterification between dibasic acids and glycols, which he attributed to a medium effect that arose from the system, becoming progressively less polar as the reaction proceeded.

The differences observed in the reaction orders indicate that these are only "apparent" orders. A mechanism is proposed in this study to explain the variations in the apparent orders of the cobalt chloride-catalyzed esterification reaction between castor oil and oleic acid with temperature. A general kinetic expression is derived from the proposed mechanism and is verified with data obtained at different temperatures.

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).

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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. 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. The catalyst $CoCl_2 \cdot 6H_2O$ was used at 0.1% based on oleic acid. 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 (14). In view of the difficulty of establishing the concentration in moles 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.

RESULTS AND DISCUSSION

Figure 1 shows the acid concentration vs. time data for the cobalt chloride-catalyzed reactions carried out at 200, 225, and 250°C.

The reaction is assumed to be irreversible under the applied conditions, as found in previous studies employing similar reaction conditions (8,9,15). Integral method was applied to determine the total order of reaction in each case, and the quality of the fit was judged based on the values of the coefficient of determination and the standard error of estimate (16,17). The reaction followed first-order kinetics at 200 and 225°C, but second-order kinetics at 250°C, as was expected from previous work (9). It also is known (from previous work) that the order, with respect to acid concentration, changes with the increase in temperature from 0 to 1, whereas the order, with respect to castor oil, is one for all cases.

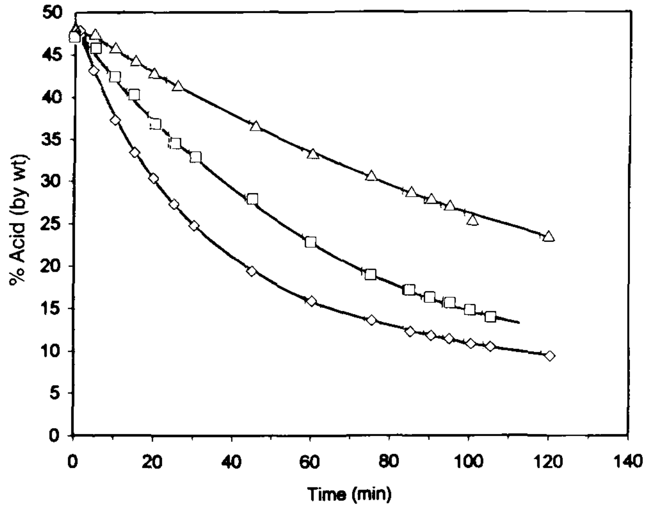

FIG. 1. Change of oleic acid concentration with time: △, 200°C; □, 225°C; ◇, 250°C.

It is clear that the changes in the apparent orders should be explained by the reaction mechanism. The variation with temperature of the apparent order, with respect to acid, suggests a more general kinetic expression of the following form for the cobalt chloride-catalyzed reaction, where there is an acid concentration term, C_A, and a temperature-dependent constant, K_1, in the denominator:

$$r_E = \frac{K C_A C_O}{1 + K_1 C_A} \qquad [1]$$

A kinetic expression of this form, where r_E is the rate of esterification, C_O the oil concentration, and K another constant, will result from the two-step mechanism given next, where an acid-catalyst intermediate forms in a fast, quasi-equilibrium step (Eq. 2), and the rate-limiting slow step (Eq. 3) is the formation of ester and water and regeneration of the catalyst, by the reaction between the oil and this intermediate.

$$A + C \underset{k_1'}{\overset{k_1}{\rightleftarrows}} AC^*(\text{fast}) \qquad [2]$$

$$AC^* + O \xrightarrow{k_2} E + W + C(\text{slow}) \qquad [3]$$

A similar mechanism also has been proposed for the Broensted acid-catalyzed esterification (18). According to this mechanism, rate of ester formation can be expressed by the following equation:

$$r_E = k_2 C_{AC^*} C_O \qquad [4]$$

From the quasi-equilibrium condition:

$$C_{AC^*} = K_1 C_A C_C \qquad [5]$$

where K_1 is the equilibrium constant of the first reaction and C_C is the available catalyst concentration, which is equal to the difference of the total catalyst concentration, C_{CT}, and the concentration of the catalyst combined with the acid, C_{AC^*}, at any time as given by Equation 6:

$$C_C = C_{CT} - C_{AC^*} \qquad [6]$$

Combining Equations 5 and 6 and solving for C_C lead to:

$$C_C = \frac{C_{CT}}{1 + K_1 C_A} \qquad [7]$$

By combining Equations 5 and 7 and substituting in Equation 4, the following expression is obtained, which is in the desired form:

$$r_E = \frac{K_1 k_2 C_{CT} C_O C_A}{1 + K_1 C_A} = \frac{K C_O C_A}{1 + K_1 C_A} \qquad [8]$$

The constant in the denominator of Equation 1 is then the equilibrium constant of the first reaction, K_1, and the constant in the numerator is the product $K_1 k_2 C_{CT}$, where k_2 is the specific rate of the rate-determining step, and C_{CT} is the total catalyst concentration. Here, the variation in the relative magnitudes of the two terms present in the denominator is expected to be responsible for the observed changes in the reaction order with respect to acid concentration.

If the amounts of acid and oil remaining in the reactor at any time, t, are denoted by $M_A(t)$ and $M_O(t)$, and their initial amounts by M_{A0} and M_{O0}, respectively, the ratio of the amount of oil consumed by the reaction to that of the acid at any time t can be written as follows:

$$\frac{M_{O_0}-M_O(t)}{M_{A_0}-M_A(t)}=\frac{C_{O_0}-C_O(t)}{C_{A_0}-C_A(t)}=\frac{344}{282} \tag{9}$$

In Equation 9, 282 and 344 are the equivalent weights of oleic acid and castor oil, respectively. The equivalent weight of castor oil is calculated from its hydroxyl value, whereas for oleic acid, the equivalent weight is equal to the molecular weight. Concentrations of the oil and acid at time t, $C_O(t)$ and $C_A(t)$, respectively, and their initial values C_{O0} and C_{A0} are all defined as weight percentages. Solving for $C_O(t)$ from the previous equation:

$$C_O(t)=C_{O_0}+\frac{344}{282}\left(C_A(t)-C_{A_0}\right) \tag{10}$$

On the other hand:

$$C_{O0}=100-C_{A0} \tag{11}$$

Substituting into Equation 10 and rearranging:

$$C_O(t)=100-\left(1+\frac{344}{282}\right)C_{A_0}+\frac{344}{282}C_A(t) \tag{12}$$

Because equivalent reactant ratios ([OH]/[COOH] = 1:1) were used, initial concentration of the acid was:

$$C_{A_0}=\frac{282}{344+282}\bullet 100 \tag{13}$$

Substituting into Equation 12:

$$C_O(t)=\frac{344}{282}C_A(t) \tag{14}$$

Combining Equation 14 with the rate expression:

$$-\frac{608}{282}\frac{dC_A}{dt}=\frac{KC_A\left(\frac{344}{282}C_A\right)}{1+K_1C_A} \tag{15}$$

Solution of the differential equation yields:

$$\frac{1}{K}\left(\frac{1}{C_A}-\frac{1}{C_{A_0}}\right)+\frac{K_1}{K}\ln\left(\frac{C_{A_0}}{C_A}\right)=\frac{344}{608}t \tag{16}$$

The proposed model was tested by fitting the experimental data given in Figure 1 into Equation 16. The calculated values of K and K_1 are listed in Table 1, together with the correlation coefficients of the regressions. The high values of the correlation coefficients indicate that the model can explain the variations in the data at all temperatures.

Because the total catalyst concentration, C_{CT}, was known for each experiment, the value of the rate constant of the rate-determining second step, k_2, also could be calculated for each temperature from the predicted values of K and K_1. The activation energy of the rate-determining step is calculated to be 29.12 kcal/mol from these specific reaction rate (k_2) values, which are listed in Table 1.

The most important finding is the change in the value of the equilibrium constant of the first step of the reaction mechanism, K_1, with temperature in accordance with our expectations. The equilibrium constant of this quasi-equilibrium reaction decreased to a small value at 250°C, as shown in Table 1. The significant decrease in the value of K_1 resulted in $K_1 C_A$ values that are 10^{-2} times smaller above 225°C. This decrease in the relative magnitude of the second term in the denominator of the rate equation results in an apparent increase in the reaction order with respect to the acid concentration from zero to one, and in the total reaction order from one to two, when the temperature is increased from 225 to 250°C.

The results indicate that the decomposition of the acid-catalyst intermediate, AC^*, is more favored at higher temperatures for the cobalt chloride-catalyzed reaction, implying higher values of the rate constant of the reverse reaction, k'_1, for the first step.

A system similar to ours is the esterification reaction of oleic acid and oleyl alcohol with the same catalyst, cobalt chloride, the kinetics of which were studied in considerable detail (19,20). The catalyst concentration was observed to be statistically insignificant at higher initial alcohol-to-acid molar ratios (>1), whereas it had a positive influence on conversion at lower (<1) values of this ratio (19). Additionally, the acid conversion increased with decreasing initial acid-to-alcohol ratio at constant initial catalyst concentration (20). These results are also in agreement with the mechanism proposed in this study, the initial step of which involves the formation of an acid-catalyst intermediate.

Recently, a similar two-step mechanism was also reported (21) for the homogeneously catalyzed esterification reaction between levulinic acid and *n*-butanol, the only difference lying in the removal of water and, hence, the assumption of irreversibility for the rate-limiting step in our case.

TABLE 1
Results Obtained by the Application of the Model to Experimental Data

Temperature (°C)	$C_{CT}{}^a \times 10^2$	$K^b \times 10^3$	$K_1{}^c \times 10^3$	$k_2{}^d$	r^e
200	9.9704	6.9027	626.22	0.11055	0.9990
225	9.9163	9.3122	409.33	0.22942	0.9995
250	9.9143	1.4178	6.5134	2.19556	0.9998

[a] $CoCl_2$ concentration on an anhydrous basis, % by wt. [b] $(wt\%)^{-1}$ $(min)^{-1}$. [c] $(wt\%)^{-1}$. [d] $(wt\%)^{-1}$ $(min)^{-1}$. [e] Correlation coefficient.

This study is being continued with experiments on the applicability of the proposed mechanism and kinetic expression for different acid catalysts and other esterification reactions.

REFERENCES

1. Achaya, K.T., *J. Am. Oil Chem. Soc. 48*:758 (1971).
2. Naughton, F.C., *Ibid. 51*:65 (1974).
3. Martin, S.R.W. in *Paint Technology Manuals, Convertible Coatings (Oil and Color Chemists Association)*, edited by C.J.A. Taylor and S. Marks, Part 3, Chapman and Hall, London, 1962, p. 103.
4. Penoyer, C.E., W. von Fischer and E.G. Bobalek, *J. Am. Oil Chem. Soc. 31*:366 (1954).
5. Grummitt, O., and H. Fleming, *Ind. Eng. Chem. 37*:485 (1945).
6. Civelekoglu, H., and A.T. Erciyes, in *Papers Presented at 6th Congress of Scientific and Technical Research Council of Turkey,* Tubitak Publications No. 338, Ankara, 1978, p. 277.
7. Modak, S.N., and J.G. Kane, *J. Am. Oil Chem. Soc. 42*:428 (1965).
8. Erciyes, A.T., L. Dandik and O.S. Kabasakal, *Ibid. 68*:639 (1991).
9. Erdem-Şenatalar, A., E. Erencek, M. Tüter and A.T. Erciyes, *Ibid. 71*:1035 (1994).
10. Feuge, R.O., E.A. Kraemer and A.E. Bailey, *Oil and Soap* 22:202 (1945).
11. Smith, T.L., and J.H. Elliott, *J. Am. Oil Chem. Soc. 35*:692 (1958).
12. Flory, P.J., *J. Am. Chem. Soc. 59*:466 (1937).
13. Flory, P.J., *Ibid. 61*:3334 (1939).
14. Cocks, L.V., and C. van Rede, *Laboratory Handbook for Oil and Fat Analysts*, Academic Press, London, 1966, p. 608.
15. Dunlop, L.H., and J.S. Heckles, *J. Am. Oil Chem. Soc. 37*:281 (1960).
16. Hill, C.G., Jr., *An Introduction to Chemical Engineering Kinetics and Reactor Design*, John Wiley and Sons, New York, 1977.
17. Chapra, S.C., and R.P. Canale, *Numerical Methods for Engineers with Computer Applications*, McGraw-Hill, New York, 1985, p. 286.
18. Groggins, P.H., *Unit Processes in Organic Syntheses*, McGraw-Hill, Kogakuska, Tokyo, 1958, p. 700.
19. Martinez, M., E. Torrano and J. Aracil, *Ind. Eng. Chem. Res. 27*:2179 (1988).
20. Sanchez, N., A. Coteron, M. Martinez and J. Aracil, *Ibid. 31*:1985 (1992).
21. Bart, H.J., J. Reidetschlager, K. Schatka and A. Lehmann, *Ibid. 33*:21 (1994).

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