The Kinetics of the Esterification Reaction Between Castor Oil and Oleic Acid

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In this study, esterification of castor oil with oleic acid was investigated in view of the reaction kinetics under various conditions. Potassium hydroxide, *p*-toluenesulfonic acid and tin chloride ($SnCl_2 2H_2O$) were used as catalysts. Reaction was carried out at 200°C, 225°C and 250°C by using equivalent proportions of the reactants. For tin chloride, experimental data fitted the second-order rate equation, while for the other catalysts the obtained data fitted the third-order rate equation.

KEY WORDS: Castor oil, esterification, kinetics, oleic acid.

Castor oil consists largely of glycerides of ricinoleic acid (12-hydroxy octadecenoic acid). The presence of a hydroxyl group in addition to an olefinic linkage in this predominating fatty acid provides castor oil many reaction possibilities (1,2). Among these reactions, esterification occupies a very important place in the manufacture of industrially useful materials. For instance, in the manufacture of non-drying alkyd resin, castor oil is esterified with phthalic anhydride (3). Fatty acid esters of castor oil, as well as acetylated castor oil, were reported previously as the starting materials for the preparation of dehydrated castor oil (4,5). Additionally, secondary esters of castor oil formed with drying oil fatty acids were also studied in order to obtain a material with drying oil properties (6). In all these studies, the conditions to reach a given low acid value were determined, but the subject was not investigated in view of the reaction kinetics. However, closely related to the esterification of castor oil with fatty acids is the condensation reaction between ricinoleic acid molecules. In the kinetic study, this reaction was found to be second order (7).

The purpose of the present study was to develop the rate equations for the esterification of castor oil with oleic acid under different conditions. The reaction was carried out at 200°C, 225°C, and 250°C with and without catalyst. The catalysts used were potassium hydroxide, *p*-toluenesulfonic acid monohydrate and tin chloride ($SnCl_2 2H_2O$).

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, 2.1; saponification value, 178; hydroxyl value, 166.4; iodine value, 84.6. Oleic acid was analytical grade from Riedel deHaen with acid value of 200 and iodine value of 92. Other reagents were analytical grade from Merck (Darmstadt, Germany).

Experimental setup. 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. The esterification reaction was conducted in concentrated solution by using 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. In the case of catalyzed reactions, 0.1% of the catalyst based on oleic acid was initially added to the oleic 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 (8). Oleic acid concentration was expressed as weight percentage as determined from the acid value and equivalent weight of the acid (282.47). A correction for loss of water and catalyst, if necessary, was applied to each sample.

RESULTS AND DISCUSSION

The integral method was applied to correlate the experimental data. For this purpose, a differential rate equation based on the disappearance of the functional groups was constructed by assuming that the reaction is irreversible under the applied conditions. In fact, this assumption was also made by Dunlap and Heckles (9) in the esterification reaction between glycerol and oleic acid, where the same stirring rate and inert gas flow rate were applied.

The rate constant calculations were based on second- and third-order kinetics. Since in this study the concentrations of functional groups are equal, *i.e.*, [COOH] = [OH] = c, second- and third-order reaction rates can be represented by equation 1 and equation 2, respectively (10).

$$kt = 1/c - 1/c_0 \qquad [1]$$

$$2kt = 1/c^2 - 1/c_0^2 \qquad [2]$$

To test equations 1 and 2, 1/c and $1/c^2$ were plotted against t, respectively. In view of the difficulty of establishing the concentration in mole per liter at the applied temperatures, the oleic acid concentration was expressed as weight percentage. In fitting a straight line to the experimental data, least square approximation was applied and in each case the standard error of estimate(s) and coefficient of determination (r^2) were determined (11). The value of $r^2 \times 100$ indicates the percentage of original uncertainty explained by the linear model (11). The obtained results are shown in Figures 1–4. As can be seen from Figure 4, the reaction catalyzed with tin chloride followed second-order kinetics. On the other hand, the data obtained from the reactions catalyzed with *p*-toluenesulfonic acid and potassium hydroxide, as well as those from uncatalyzed esterifications, fitted the third-order reaction rate equation better. In the *p*-toluenesulfonic acid-catalyzed reaction at 250°C, there is an increase in oleic acid

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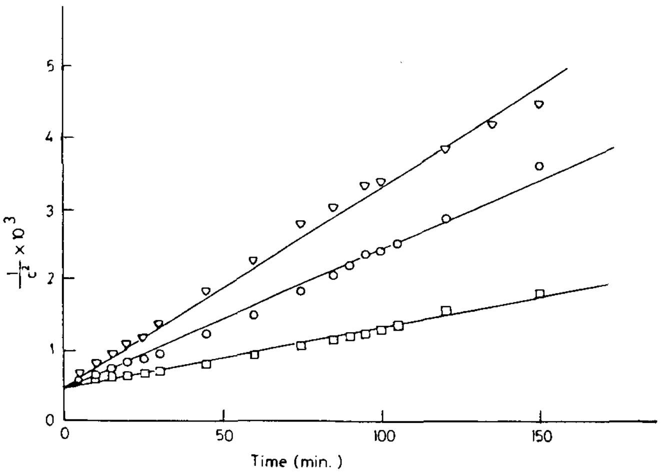

FIG. 1. Rate of uncatalyzed reaction of castor oil with oleic acid: □, 200°C, s (standard error of estimate) = 3.7865 × 10^{-5}, r^2 (coefficient of determination) = 0.9911; ○, 225°C, s = 8.6284 × 10^{-5}, r^2 = 0.9918; ∇, 250°C, s = 1.1730 × 10^{-4}, r^2 = 0.9929.

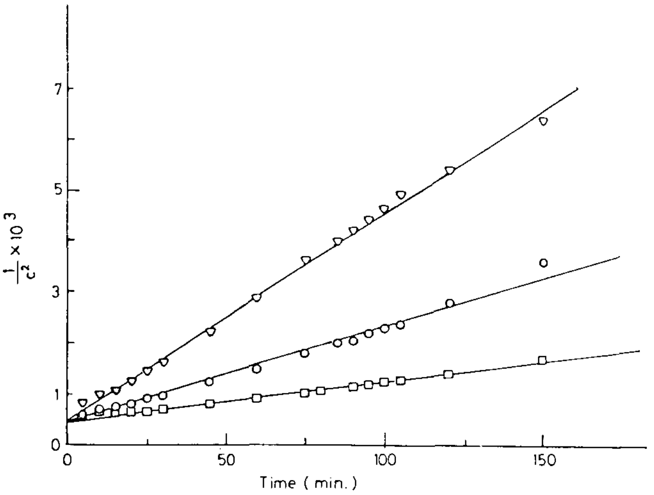

FIG. 2. Rate of potassium hydroxide-catalyzed esterification of castor oil with oleic acid: □, 200°C, s (standard error of estimate) = 2.3969 × 10^{-5}, r^2 (coefficient of determination) = 0.9956; ○, 225°C, s = 1.0607 × 10^{-4}, r^2 = 0.9867; ∇, 250°C, s = 9.0097 × 10^{-5}, r^2 = 0.9978.

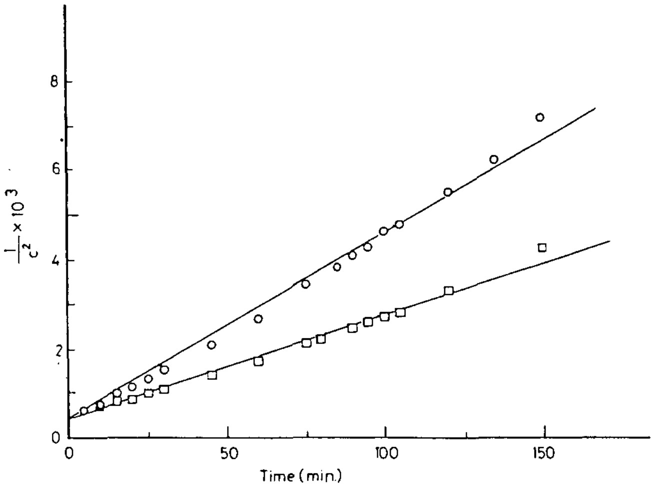

FIG. 3. Rate of *p*-toluenesulfonic acid-catalyzed esterification of castor oil with oleic acid: □, 200°C, s (standard error of estimate) = 1.1916 × 10^{-4}, r^2 (coefficient of determination) = 0.9888; ○, 225°C, s = 2.0710 × 10^{-4}, r^2 = 0.9907.

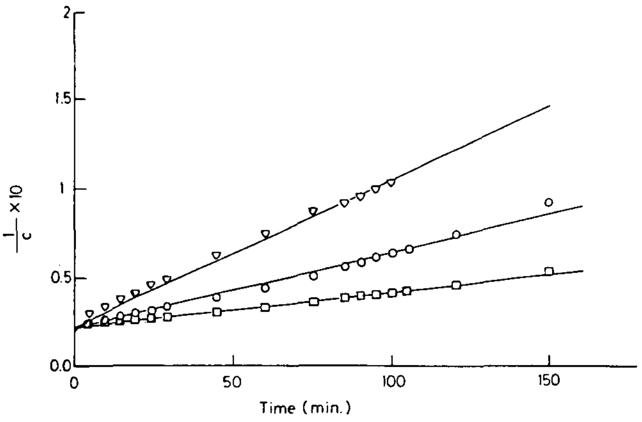

FIG. 4. Rate of tin chloride-catalyzed esterification of castor oil with oleic acid: □, 200°C, s (standard error of estimate) = 4.6280 × 10^{-4}, r^2 (coefficient of determination) = 0.9976; ○, 225°C, s = 2.1180 × 10^{-3}, r^2 = 0.9898; ∇, 250°C, s = 2.2985 × 10^{-3}, r^2 = 0.9942.

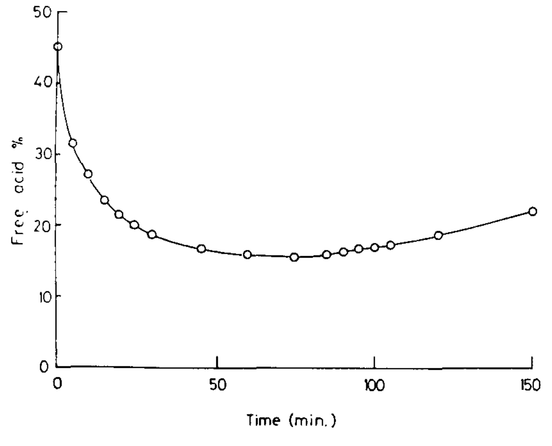

FIG. 5. Change of free fatty acid content during the *p*-toluenesulfonic acid-catalyzed esterification conducted at 250°C.

concentration after 85 min from the beginning (see Fig. 5), and the data did fit neither second- nor third-order reaction rate equations. This might be mainly due to the cleavage of secondary ester groups that are already formed on the ricinoleic acid chain (4–6). In fact, Grummitt and Fleming (5) explained previously that *p*-toluenesulfonic acid lowered the thermal decomposition temperature of acetylated castor oil to 250°C, while this temperature was determined as 270°C and 280°C for phosphoric acid (65%) and sulfuric acid (96%), respectively. Since conjugated double bonds are formed during the splitting process, the above conclusion could be confirmed by the presence of conjugated diene. Therefore, ultraviolet (UV) absorption was measured on a sample taken out after 150 min, and the conjugated dienoic acid content was found to be 9.5% with a Beckman U.V. Spectrophotometer Model

TABLE 1

Rate Constants and Activation Energies for the Esterification of Castor Oil with Oleic Acid Under Different Conditions

Catalyst used in the reaction	Rate constant, k^a, $(\text{wt}\%)^{-2}$ $(\text{min})^{-1}$			Activation energy, E, kcal/mole
	200°C	225°C	250°C	
None	4.21×10^{-6}	9.72×10^{-6}	1.41×10^{-5}	11.95
Potassium hydroxide	3.79×10^{-6}	9.34×10^{-6}	2.03×10^{-5}	16.50
p-toluenesulfonic acid	1.14×10^{-5}	2.07×10^{-5}	—	11.11
Tin chloride	2.01×10^{-4}	4.27×10^{-4}	8.34×10^{-4}	13.98

[a] The units of rate constants for tin chloride-catalyzed reactions are $(\text{wt per})^{-1}$ $(\text{min})^{-1}$.

DB-GT, Munchen, Germany (12). On the other hand, although there was no increase in oleic acid concentration at 250°C in the reaction catalyzed with *p*-toluenesulfonic acid, the data points spread around the regression line. This may be due to the dehydration of castor oil to a small extent, because sulfonic acids have been reported to act as a dehydration catalyst in the preparation of dehydrated castor oil (13,14). In order to verify this decision, the conjugated dienoic acid content of the sample withdrawn after 150 min was determined in the same way and found to be 3%.

Rate constants determined from the slopes of the straight lines shown in Figures 1–4 are presented in Table 1. Energies of activation are also included in Table 1. By evaluating third-order rate constants, it shows that potassium hydroxide shows essentially no catalytic effects while *p*-toluenesulfonic acid is more effective than potassium hydroxide. As mentioned before, the reaction followed second-order kinetics when tin chloride was used as catalyst. This may be due to the mechanism of the reaction. Feuge and coworkers (15) reported previously that tin chloride was outstanding in catalytic activity in the esterification between glycerol and peanut oil fatty acids. They believe that tin chloride reacts initially with free acids and free glycerol to form metal soaps and chlorohydrins and that esterification proceeds through interaction of these two initial reaction products. The chlorides of Al, Sb, Hg, Ni, Mg, Mn, Pb, and Cd did not appear to be capable of reacting in this manner and were relatively poor catalysts for the same reaction (15).

The change in the reaction order with temperature and with the extent of reaction was also observed by others (16–18). For instance, Smith and coworkers explained 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 the second- or third-order rate equations (16). Flory (17,18) observed the change in order with the extent of reaction in the case of polyesterification between dibasic acids and glycols. He attributed this change to a medium effect because the system becomes progressively less polar as the reaction proceeds.

As the result of the above facts, the effect of tin chloride on the order of the esterification reaction between castor oil and oleic acid should be investigated further by considering additional factors, including those inherent in the reaction mechanism.

REFERENCES

1. Achaya, K.T., *J. Am. Oil Chem. Soc. 48*:758 (1971).
2. Naughton, F.C., *Ibid. 51*:65 (1974).
3. Paint Technology Manuals, Convertible Coatings (Oil and Colour Chemists Association), Part 3, edited by C.J.A. Taylor, and S. Marks, Chapman and Hall, London, England, 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 Industrial Research Council of Turkey*, Tubitak Publications No. 388, Ankara, Turkey, 1978, pp. 277–290.
7. Modak, S.N., and J.G. Kane, *J. Am. Oil Chem. Soc. 42*:428 (1965).
8. Cocks, L.V., and C. van Rede, *Laboratory Handbook for Oil and Fat Analysts*, Academic Press, London, England, 1966, pp. 113–117.
9. Dunlap, L.H., and J.S. Heckles, *J. Am. Oil Chem. Soc. 37*:281 (1960).
10. Glasstone, S., and D. Lewis, *Elements of Physical Chemistry*, Macmillan and Co., Ltd, London, England, 1966, pp. 608–613.
11. Chapra, S.C., and R.P. Canale, *Numerical Methods for Engineers with Computer Applications*, McGraw-Hill, New York, NY, 1985, pp. 286–312.
12. Mattiello, J.J., (ed.), *Protective and Decorative Coatings*, Vol. 4, John Wiley and Sons, New York, NY, 1944, pp. 362–405.
13. Alexander, S., U.S. patent 2292902 (1942).
14. Walton, W.T., C.A. Coffey and O.E. Knapp, U.S. patent 2429380 (1947).
15. Feuge, R.O., E.A. Kraemer and A.E. Bailey, *Oil and Soap 22*:202 (1945).
16. Smith, T.L., and J.H. Elliott, *J. Am. Oil Chem. Soc. 35*:692 (1958).
17. Flory, P.J., *J. Am. Chem. Soc. 59*:466 (1937).
18. Flory, P.J., *Ibid. 61*:3334 (1939).

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