Chloroacetoxylation of Oleic Acid—A Kinetic Study

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ABSTRACT: The kinetics of the addition reaction of chloroacetic acid to oleic acid (chloroacetoxylation) in the presence of sulfuric acid as a catalyst were investigated. The reactions were carried out at the same concentration of both reactants at various temperatures and catalyst content. The reaction time ranged from 30 min up to 12 h, and the reaction course was observed by determining mainly iodine value, and chlorine content of the oil samples at 30-min intervals. The experimental data fitted the reversible second-first order rate equation for bimolecular-unimolecular type reactions. The reaction constants of the forward and reverse reactions were obtained at temperatures 70 and 80°C. The effect of sulfuric acid content on the reaction constant was investigated at 70 and 80°C.

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KEY WORDS: Chloroacetic acid, chloroacetoxylation, kinetics, oleic acid, reaction constants.

Vegetable oils and their component fatty acids represent an attractive renewable source for the production of useful chemicals. Their reactivity needs to be enhanced by introducing additional functionalities into the fatty acid molecules (1,2). So far, a variety of chemical and biochemical reactions have been used for conversion to value-added products such as hydroxystearic fatty acids and their derivatives (3–5). These compounds are used in greases, lubricants, detergents, and chemical additives. A good review of the literature concerning the production, properties, and uses of the above acids is given by Lower (6).

This work is part of a research project aimed at the production of methyl monohydroxystearates and their derivatives from oleic acid through chloroacetoxylation reaction followed by methanolysis of the addition product. Methyl monohydroxystearates are important as intermediate chemical products, and one of their most interesting applications is in the production of surface-active agents from natural products, such as sucrose esters (7). In addition, 9- or 10-monohydroxystearic acids could be used as substitutes for 12-hydroxystearic acid, derived from castor oil, which is an important high-temperature lubricant (8). The introduction of a hydrophilic group, such as a hydroxyl group, into the middle of the hydrocarbon chain of the oleic acid molecule reduces its hydrophobicity and can improve the hydrophilic–lipophilic balance (HLB) ratio of surfactants based on oleic acid (9). The synthesis of monohydroxystearic acids from oleic acid has been achieved chemically by different reactions including mainly hydroboration of methyl oleate, formoxylation, or acetoxylation as well as enzymatically (2,3,6). We have already studied, under different conditions, the addition of chloroacetic acid to the double bond of oleic acid and methanolysis of the addition product to methyl monohydroxystearates (10). So far, kinetic studies on the chloroacetoxylation of oleic acid or other unsaturated fatty acids do not exist.

In the present work, the kinetics of the chloroacetoxylation reaction of oleic acid was investigated. Reactions were carried out in stoichiometric proportions of reactants in the presence of catalyst (sulfuric acid) at temperatures of 70 and 80°C to determine the order of reaction. The effect of sulfuric acid content were also examined. The recovery of unreacted chloroacetic acid was achieved by precipitation in petroleum ether at 0°C, and this separation method is suggested as an alternative solution to the expensive process of production of anhydrous low molecular weight acids (formic and acetic acids). Extraction with water and distillation are generally applied for the separation of the components of these reaction mixtures (11).

MATERIALS AND METHODS

Materials. Oleic acid (pure; Merck, Darmstadt, Germany, Art. 471 with an acid value of 199 and an iodine value of 90, mean oleic acid content 85%), chloroacetic acid (Merck, Art. 412, 99%), sulfuric acid (Merck, 96–98%), petroleum ether (Merck, 40–70°C), and additional reagents (such as Na_2SO_4, $NaHCO_3$) were of very pure grade. The reagents used in analytical tests are described in the relevant literature.

Experimental setup. Chloroacetoxylation reaction was performed in a spherical three-necked flask equipped with a mechanical stirring system, a thermometer, and a condenser. The flask system was placed in a constant-temperature water bath (±0.5°C). Schoeniger apparatus was used for chlorine analysis (12,13).

Chloroacetoxylation of oleic acid. Chloroacetoxylation reaction of oleic acid with chloroacetic acid was carried out as follows: A solution of oleic acid, chloroacetic acid, and sulfuric acid (catalyst) was heated at 70 or 80°C with continuous stirring for 0 min to 12 h. The reaction yield in addition product was studied at equimolar concentration of reactants and

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with different catalyst content [1.82, 3.64, and 5.46% (w/w) based on oleic acid]. The hot reaction mixture was poured into petroleum ether and cooled at 0°C to crystallize the unreacted chloroacetic acid, which eventually was removed by filtration. Then, the organic filtrate was washed thoroughly with distilled water to remove the catalyst, it was dried using anhydrous sodium sulfate, and finally it was distilled to remove the solvent. The total yield of addition product (chloroacetoxylated stearic acid) was determined mainly by Wijs method (iodine value) (14) and by chlorine analysis using Schoeniger method. Supplementary analysis of the reaction product included saponification value according to AOCS methods (14). Each experiment was carried out twice to check the reproducibility of the results.

RESULTS AND DISCUSSION

The chloroacetoxylation reaction is the following:

$$\text{oleic acid} + \text{chloroacetic acid} \rightleftharpoons \text{chloroacetoxystearic acid} \qquad [1]$$

or in abbreviated form

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \qquad [2]$$

where *A*, *B*, and *C* correspond to oleic, chloroacetic, and chloroacetoxylated acid, respectively.

The progress of converting oleic acid to chloroacetoxystearic acid at 70°C with 3.64% catalyst content is shown in Figure 1. Similar curves were obtained at different catalyst content and at different temperatures. The iodine value, a measure of the unsaturation of oleic acid, decreases continuously with time and reveals that as the concentration of oleic acid decreases the addition product yield increases. The addition to the double bond in oleic acid was also measured by saponification value determination (a direct measure of the number of chloroacetoxy groups added) and led to similar results. In this case, an increase in saponification value was observed during the reaction.

The effect of catalyst content on the rate of reaction at 80°C is illustrated in Figure 2. It was observed that an increase in catalyst content had a positive effect on the rate of conversion of oleic acid. The effect of reaction time was more pronounced in the first 2 h. The increase of reaction temperature from 70 to 80°C had a positive effect on the rate of reaction. The experimental results were based mainly on the change of unsaturation expressed by iodine value or saponification value. Chlorine analysis gave similar conversion values with mean deviation ±2%.

Chloroacetoxylation of oleic acid by chloroacetic acid was assumed to be a reversible bimolecular-unimolecular second-first order reaction under the applied conditions, since it was observed that the experimental data could be described successfully by the relative equations. The results did not permit application of the integrated forms of rate equations for half-, first-, and second-order reactions. In this case, the following equations can be used for the calculation of the rate constants k_1 and k_2 for the forward and opposing reaction (15,16).

$$\ln \frac{\left[1-\left(x_A \times x_{\mathrm{Ae}}\right)\right] \times x_{\mathrm{Ae}}}{x_{\mathrm{Ae}} - x_A} = \frac{C_{\mathrm{Ao}}\left(1 - x^2{}_{\mathrm{Ae}}\right) k_1 t}{x_{\mathrm{Ae}}} \qquad [3]$$

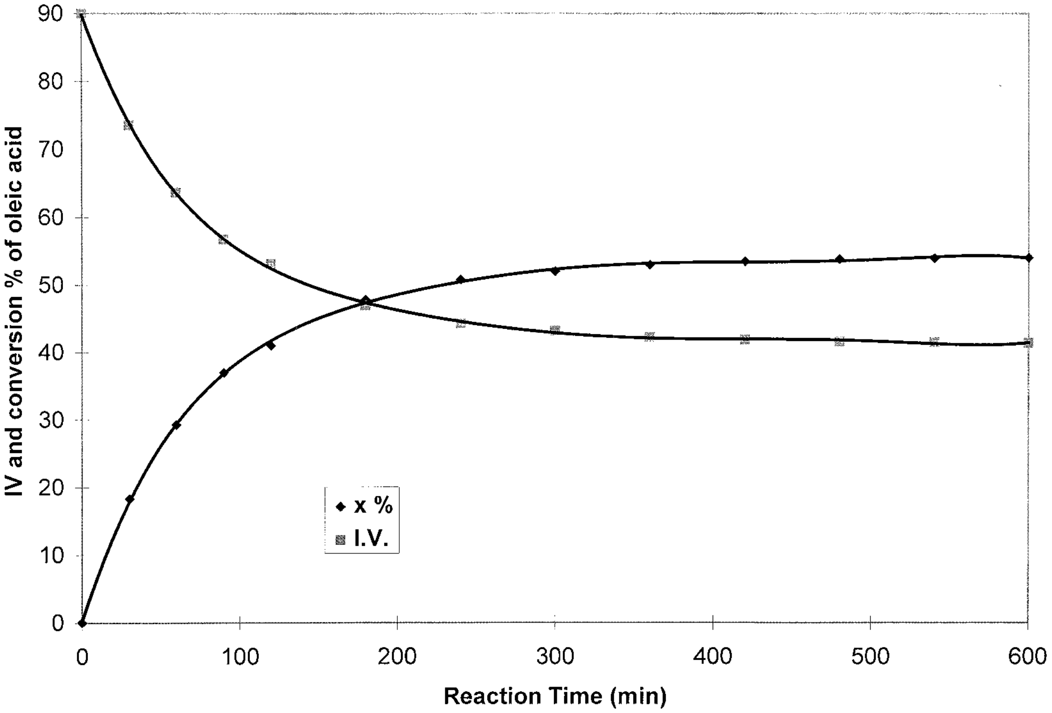

FIG. 1. Iodine value (IV) and conversion (x) (%) of oleic acid during chloroacetoxylation reaction at 70°C and 3.64% catalyst content.

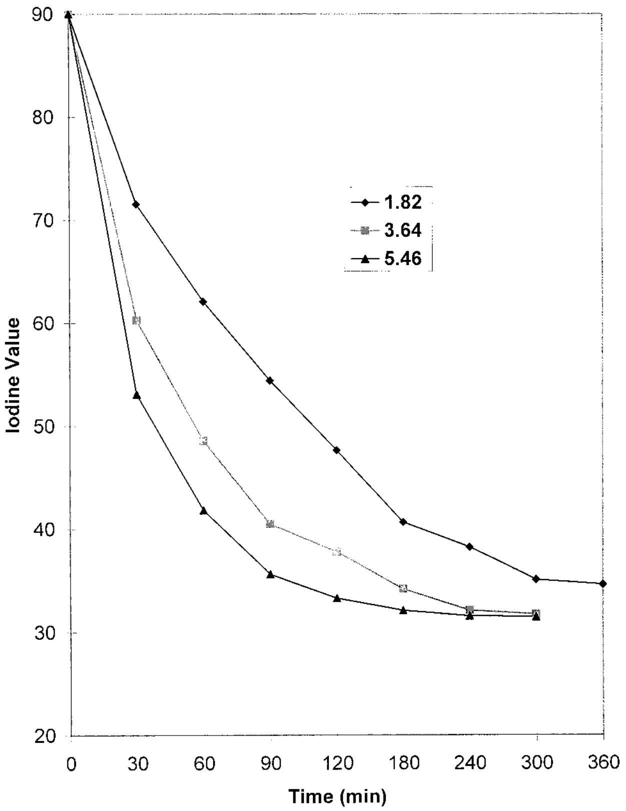

FIG. 2. Effect of catalyst content (% w/w based on oleic acid) on chloroacetoxylation reaction at 80°C.

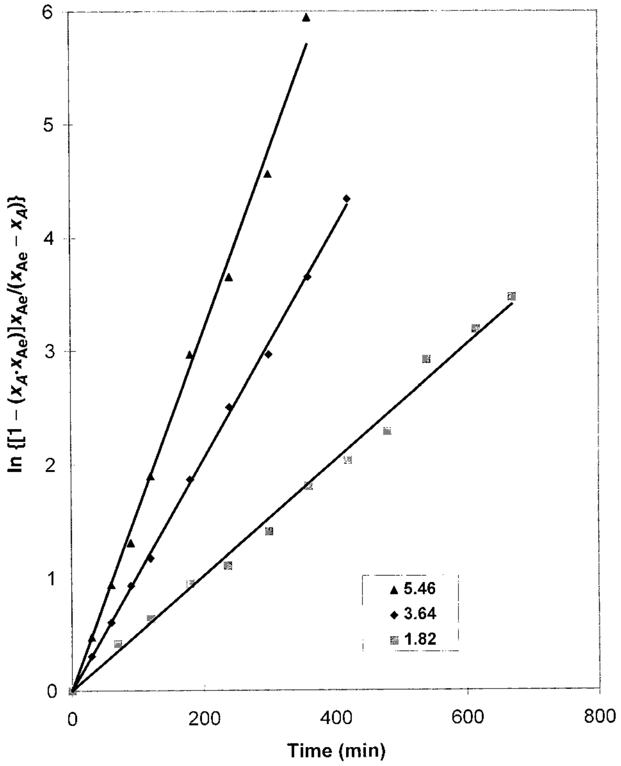

FIG. 3. Plots of the quantity ln $\{[1 - (x_A \cdot x_{Ae})]\ x_{Ae}/(x_{Ae} - x_A)\}$ vs. reaction time at 70°C and in the presence of various catalyst content. See Equation 3.

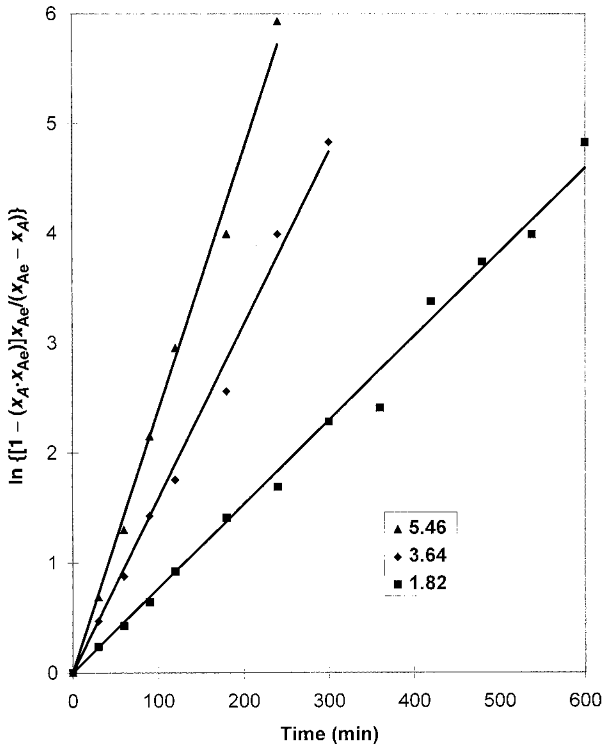

FIG. 4. Plots of the quantity ln $\{[1 - (x_A \cdot x_{Ae})]\ x_{Ae}/(x_{Ae} - x_A)\}$ vs. reaction time at 80°C and in the presence of various catalyst contents. See Equation 3.

$$K = \frac{C_{Ce}}{C_{Ae} \times C_{Be}} = \frac{C_{Ao} - C_{Ae}}{C_{Ae}^2} = \frac{k_1}{k_2} \qquad [4]$$

where x_A and x_{Ae} are the molar fraction of reactant A converted into product at any time t and at equilibrium; respectively, C_{Ae}, C_{Be}, and C_{Ce} (mol/L) are the concentrations of the reactants and the product, respectively, at equilibrium, C_{Ao} is the initial concentration of reactant A (oleic acid) and K is the equilibrium constant of the reaction.

Thus, the integral method was applied to correlate the experimental data and to test the second-first order kinetics by plotting ln $\{[1 - (x_A \times x_{Ae})] \times x_{Ae}/x_{Ae} - x_A\}$ vs. reaction time. In Figures 3 and 4 these plots are presented. In all cases, the plots were linear, with the slopes giving the values of the quantity $[C_{Ao}(1 - x^2_{Ae})k_1/x_{Ae}]$.

TABLE 1
Rate Constants in the Kinetic Study of Chloroacetoxylation of Oleic Acid

Temperature (°C)	H_2SO_4 (%)	$k_1 \times 10^5$ (L mol^{-1}s^{-1})	r^2	$k_2 \times 10^3$ (s^{-1})
70	1.82	2.520	99.3	2.540
70	3.64	5.041	99.9	5.082
70	5.46	7.858	99.6	7.921
80	1.82	5.619	99.2	2.722
80	3.64	11.530	99.2	5.586
80	5.46	17.370	99.4	8.416

For the determination of the reaction order with respect to oleic acid, the values of k_1 were obtained at three different contents of the catalyst (namely 1.82, 3.64, and 5.46 g/100 g) at temperatures of 70 and 80°C. The quality of the fit was judged sufficient based on the values of the correlation coefficient (r^2). The values for the rate constants k_1 and k_2 for the forward and opposing reactions are given in Table 1. The calculated values of the equilibrium constants at 70 and 80°C were 0.992 and 2.064 L mol^{-1}, respectively.

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