Studies on Kinetics and Preparation of C_{36} Dimer Acid Esters

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C_{36} Dimer acids were esterified with various short-chain alcohols, namely 2-propanol, n-butanol, n-hexanol, n-octanol, 2-octanol and 2-ethyl-1-hexanol by using sulfuric acid as catalyst and benzene as an azeotropic solvent. Various reaction parameters were standardized. In case of isopropyl esters, acid-to-alcohol mole ratio of 1:5 and sulfuric acid concentration of 2% based on the weight of dimer acids were found to be optimum. In case of straight-chain primary alcohols, namely n-butanol, n-hexanol and n-octanol, 1:2.5 mole ratio of acid to alcohol and 1% by weight of sulfuric acid were found satisfactory. Esterification reaction rates were determined from the fall in acid value of the product. The reaction followed pseudo first order kinetics. The reaction rates increased with the increase in chainlength of straight-chain primary alcohols from n-butanol to n-octanol. The rate of reaction decreased from n-octanol to 2-ethyl-1-hexanol to 2-octanol due to the branching of the chain in 2-ethyl-1-hexanol and secondary nature of the —OH group in 2-octanol.

KEY WORDS: C_{36} Dimer acids, esterification, kinetics, short-chain alcohols.

C_{36} Dimer acid esters are versatile products and are used as lubricants, lubricant additives, surface-active agents and corrosion and rust inhibitors (1). Kinetics of esterification of C_{19} diacids with short-chain alcohols has been reported (2). Most of the literature on preparation and uses of C_{36} dimer acid esters is patented (3–5), and no information is available on kinetics of their esterification. The present work pertains to the standardization of reaction conditions for the preparation of C_{36} dimer acid esters with various short-chain alcohols, namely 2-propanol, n-butanol, n-hexanol, n-octanol, 2-octanol and 2-ethyl-1-hexanol by using sulfuric acid as a catalyst and benzene as an azeotropic solvent to remove water of reaction. Rate studies on the above esterification reactions also have been carried out.

MATERIALS AND METHODS

C_{36} Dimer acids (Empol 1010 grade, Emery Industries Inc., Cincinnati, OH) were 97% pure and had an iodine value below 20. 2-Propanol, n-butanol, n-hexanol, n-octanol, 2-octanol, 2-ethyl-1-hexanol, benzene and sulfuric acid were laboratory-grade reagents. The esterification reactions were carried out in a 500-mL round-bottom flask equipped with a stirrer, a thermowell, the Dean-Stark apparatus and a sampling point. A known weight of C_{36} dimer acids (*ca.* 56 g) and an appropriate quantity of alcohol were charged in the flask and diluted to 250 mL with benzene. The Dean-Stark trap was filled carefully to overflow level with benzene. The reaction flask was heated to the reflux temperature in an isomantle. Sulfuric acid was added at this stage. Samples were withdrawn periodically, washed with water to remove traces of sulfuric acid, extracted with ethyl ether and analyzed for acid value. The reaction was continued until the acid value of the product fell below 2. The product was then cooled and washed with water to remove sulfuric acid. Benzene and excess alcohol in the product were distilled out to get the pure esters.

RESULTS AND DISCUSSION

Various parameters, namely acid-to-alcohol mole ratio, weight percent of sulfuric acid based on the weight of the dimer acids, and reaction time for the esterification reactions were standardized. The amount of benzene used in all the experiments was *ca.* 60% of the total volume. This could maintain the reflux temperature at a fairly constant level during the reaction. For example, in experiments using different mole ratios of C_{36} dimer acid and 2-propanol, and various wt% of sulfuric acid (Table 1), the reaction temperature was 75 ± 1°C. Table 1 shows that there is a gradual decrease in the reaction rate constant as the mole ratio of C_{36} dimer acid to 2-propanol is changed from 1:5 to 1:10, but there is only a small variation in the rate constant when the mole ratio is changed from 1:10 to 1:20. This small variation in rate constant at higher mole ratios of alcohol may be due to the excess dilution of the reaction mixture with the alcohol used. Similar results have been reported (2) on esterification of C_{19} dicarboxylic acid and n-butanol in the mole ratio of 1:15 and 1:30. With lower ratios of C_{36} dimer acid to 2-propanol of 1:2.5 and 1:3, the product became darker. When sulfuric acid was increased from 1% to 3% at a dimer acid-to-alcohol mole ratio of 1:5, the reaction rates were found to increase. With 1% by weight of sulfuric acid it took 6 hr to get a product with an acid value below 2, whereas with 2% it took only 4 hr. Thus, the acid-to-alcohol mole ratio of 1:5 and 2% by weight of sulfuric acid were found to be satisfactory for isopropyl ester preparation. When these acid-to-alcohol mole ratio and percent weight of sulfuric acid were used for butyl ester preparations, the reaction was very fast and went to completion in less than 30 min. With lower acid-to-alcohol ratios of 1:3 and 1:2.5 and 1% by weight of sulfuric acid, the reaction was over in *ca.* 1 hr (product acid value below 2). The reaction rates decreased with decrease in the acid-to-alcohol mole ratio

TABLE 1

Rates of Esterification of C_{36} Dimer Acids with 2-Propanol[a]

Acid:alcohol (mole ratio)	H_2SO_4 wt%	Reaction rate constant ($min^{-1} \times 10^2$)	R^2
1:5.0	2	0.70	0.994
1:6.0	2	0.47	0.991
1:7.5	2	0.30	0.992
1:10.0	2	0.22	0.996
1:20.0	2	0.19	0.977
1:5.0	1	0.42	0.993
1:5.0	3	0.83	0.989

[a]Reaction temperature in these experiments was 75 ± 1°C.

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TABLE 2

Rates of Esterification of C_{36} Dimer Acids and n-Butanol[a] with 1% by wt. of Sulfuric Acid

Acid:alcohol (mole ratio)	Reaction rate ($\text{min}^{-1} \times 10^2$)	R^2
1:3.0	3.95	0.991
1:2.5	1.99	0.986
1:2.0	1.90	0.982

[a] Reaction temperature in these experiments was 80 ± 1°C.

TABLE 3

Rates of Esterification of C_{36} Dimer Acids with Different Alcohols at a Mole Ratio of Acid to Alcohol of 1:2.5 and 1% by Weight of Sulfuric Acid

Alcohol	Reaction rate ($\text{min}^{-1} \times 10^2$)	R^2
n-Butanol[a]	1.99	0.986
n-Hexanol[a]	3.89	0.961
n-Octanol[a]	5.33	0.957
2-Ethyl-1-hexanol[b]	1.19	0.956
2-Octanol[b]	0.17	0.958

[a] Reaction temperature in these experiments was 80 ± 1°C.
[b] Reaction temperature in these experiments was 84 ± 1°C.

from 1:3 to 1:2 (Table 2). With a lower mole ratio of 1:2, the product became darker. Hence, for butyl ester preparation the mole ratio of 1:2.5 and 1% by weight of sulfuric acid were found to be ideal. Using these conditions, esters were prepared from the C_{36} dimer acids with n-hexanol, n-octanol, 2-octanol and 2-ethyl-1-hexanol. The reaction rates were found to increase with an increase in chainlength of the normal alcohols from n-butanol to n-octanol. According to Goldschmidt (6,7) and Othmer (8), the protonated alcohol acts as the catalytically active species during the esterification reaction. In the case of longer alcohols, because of their higher basicity as compared to the shorter ones (9,10), the concentration of the protonated alcohol (ROH_2^+) is higher and may lead to a faster reaction, as observed in the present studies. Similar observations were reported by van der Zeeuw (11) in his studies on kinetics of the esterification of phthalic anhydride with straight-chain primary alcohols in the C_4-C_{10} range. With 2-ethyl-1-hexanol and 2-octanol, the reaction rates were slower when compared to that of n-octanol (Table 3). This decrease could be due to the branching in the chain in 2-ethyl-1-hexanol and the change in −OH group position in 2-octanol. The R^2 values reported in all the Tables indicate a fairly good degree of fit to the linear correlation of log acid value *vs.* reaction time data.

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