Kinetics of the Formation of Symmetrical Wax Esters from the Corresponding Alcohols with the Use of Hydrobromic Acid and Hydrogen Peroxide

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ABSTRACT: The primary aliphatic alcohols *n*-octanol, *n*-decanol, and *n*-dodecanol have been converted to their corresponding symmetrical esters by using HBr and H_2O_2 in the absence of a solvent. The reaction was carried out at 30, 40, and 50°C and at mole ratios of alcohol to HBr of 1:0.1, 1:0.2, 1:0.3, and 1:0.5. The rate of the reaction was found to increase with increase in the reaction temperature and concentration of HBr. The maximal conversion of *n*-octanol was 72% at 40°C and a mole ratio of *n*-octanol to HBr of 1:0.5. The kinetics of the reaction have been established, and the reaction was found to be first-order with respect to alcohol and bromine concentration in the organic phase, and second-order with respect to both. The second-order rate constants for *n*-octanol, *n*-decanol, and *n*-dodecanol are 27.08, 32.58, and 37.42 mL mol^{-1} min^{-1}, respectively, at 40°C. The activation energy for the esterification reaction of *n*-octanol was found to be 16.32 kcal mol^{-1}.

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KEY WORDS: *n*-Decanol, *n*-dodecanol, HBr, H_2O_2, *n*-octanol, wax esters.

The high-molecular-weight esters generally known as wax esters have a number of applications such as their use as lubricants for high-speed machinery and in pharmaceuticals, cosmetics, and food additives. This has increased the importance of the synthesis of analogs of natural esters of these kinds such as sperm whale oil, carnauba wax, and jojoba oil (1).

The ester production methods are based on the reaction between an alcohol and acid to form the ester and water. The classical method uses a mineral acid such as sulfuric acid as a catalyst. The use of sulfuric acid as a catalyst has various problems, including formation of undesirable products (2). Often, the product obtained is colored because of the high temperature of the reaction. The catalytic system based on cobalt salts avoids the above-mentioned problems and reduces production costs. A kinetic study of the synthesis of *n*-octyl octanoate using cobalt chloride as a catalyst has been reported (3). The direct formation of esters by the oxidation of primary alcohols by hemiacetal oxidation has also been studied (4). Attempts were made to synthesize wax esters from lard oil as possible sperm oil replacements (5). The solvent-free esterification reaction between stearic acid and stearyl alcohol has been examined with a montmorillonite clay as a catalyst (6). The production of symmetrical wax esters by one-step oxidation of a fatty alcohol by hydrogen peroxide using Re_2O_7 as a catalyst has been reported (7).

In the recent past, wax esters have been synthesized by enzyme-catalyzed reactions (8–13). The high catalytic activity and substrate specificity of enzymes make their use a rapidly growing field in organic synthesis. Though the enzyme-catalyzed reactions have advantages of lower reaction temperatures and eco-friendliness, these reactions are not yet commercially viable for wax ester synthesis.

Primary aliphatic alcohols, R–CH_2OH, react with H_2O_2 under mild conditions in a two-phase liquid–liquid system with ethylene dichloride as a solvent in the presence of Br_2 or HBr to yield selectively the corresponding esters. The following mechanistic steps have been suggested by Alessandre and Fabriele (14): (i) oxidation of HBr by H_2O_2, liberating bromine in the aqueous phase; (ii) extraction of bromine into the organic phase; (iii) formation of the acyl bromide by reaction of the alcohol with a stoichiometric amount of Br_2; (iv) alcoholysis of the acyl bromide to give the ester; and (v) extraction of liberated HBr from the organic phase to the aqueous phase. The large excess of HBr can lead to substitution bromination of the alcohol, thus reducing the overall selectivity of the oxidation:

$$\text{R–CH}_2\text{OH} + \text{HBr} \rightarrow \text{R–CH}_2\text{Br} + \text{H}_2\text{O} \qquad [1]$$

In the catalytic process, the oxidation of HBr by H_2O_2 in the aqueous phase and extraction of HBr formed in the organic phase into the aqueous phase are very fast. These reduce the concentration of HBr in the organic phase substantially and hence no formation of alkyl bromide, as indicated by the above reaction, is detected in the organic phase. The intermediate aldehyde, R–CHO, is more reactive toward bromine than the starting alcohol (14).

The present work deals with direct conversion of primary aliphatic alcohols to their corresponding esters with the use of HBr and H_2O_2. A model overall reaction for wax ester synthesis is

$$2\ \text{R–CH}_2\text{OH} + 2\ \text{H}_2\text{O}_2 \rightarrow \text{R–COO–CH}_2\text{R} + 4\ \text{H}_2\text{O} \qquad [2]$$

where R is C_nH_{2n+1}; in the present work, n = 7, 9, and 11. The reaction was carried out in the absence of a solvent. This has a

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number of advantages. First, it eliminates the need for the solvent recovery step. Second, when ethylene dichloride is used as a solvent, substantial loss of the solvent takes place during the processing and separation owing to the volatility of ethylene dichloride. Finally, elimination of the solvent from the process reduces the reactor volume considerably. The information about this reaction in the literature is limited to a single set of reaction conditions (14). Thus, the effects of different parameters such as the reaction temperature and the mole ratio of the reactants are not available in the literature. In view of this, the present paper presents an investigation of the effects of various operating parameters on the progress of the reaction and the kinetics of the direct esterification reaction of alcohols.

MATERIALS AND METHODS

Materials. n-Octanol (99% purity), hydrogen peroxide (H_2O_2) (30% wt/vol), and *n*-decanol (99% purity) were purchased from S.D. Fine-Chem Ltd. (Mumbai, India). *n*-Dodecanol (lauryl alcohol) (98% purity) was supplied by Godrej Soaps Ltd. (Mumbai, India). Hydrobromic acid (HBr) (49%) was purchased from Merck India Ltd. (Mumbai, India).

Experimental procedures. All experiments were carried out batchwise in a borosilicate glass reactor of 65 mm i.d. and 400 mL capacity, with four baffles and a six-blade turbine-type impeller (22 mm diameter). The reaction temperature was maintained constant by immersing the reactor in a constant-temperature water bath.

A predetermined quantity of aqueous HBr (60 mmol, unless otherwise stated) was added (as a 49% aqueous solution) to the reactor placed in the constant-temperature water bath. A measured quantity of H_2O_2 (300 mmol) was then added, followed by addition of the alcohol (200 mmol). All the reactants were preheated to the reaction temperature before being added to the reactor.

Samples were withdrawn from the reaction mixture at predetermined time intervals (30 min, 60 min, etc.) and the progress of the reaction was monitored by analyzing the organic phase by a titrimetric method. After 10 h, the stirring was stopped, and the organic and aqueous phases were allowed to separate in a separatory funnel.

The samples withdrawn from the reaction mixture were allowed to separate into two phases (organic and aqueous) in an ordinary glass tube. The separated phases were carefully drained. The organic phase was immediately analyzed by the titrimetric method. The phase separation with subsequent draining took about 3 min. To check whether an appreciable amount of reaction would take place during this step, the two separated phases were retained in the tube for 15 min prior to draining and analysis of the organic phase. The results of the analysis were practically the same as those obtained when the phases were separated in less than 3 min. Thus, the phase separation was sufficient to ensure that practically no reaction occurred during this stage.

Analysis. Conversion of the alcohol to the ester was determined by a titrimetric method. This titration method is a modification of the official Ester Value method (15). An accurately weighed quantity of the organic phase and a measured quantity of aqueous NaOH were added to a conical flask containing methanol. The mixture was refluxed for 2 h in order to hydrolyze the ester completely. The excess of NaOH in the mixture was then estimated by titrating against standardized HCl (reading A). The same quantity of aqueous NaOH added in the above step was titrated separately with standardized HCl (reading B). The organic phase also contains unreacted Br_2/HBr. The difference between B and A corresponds to the amount of NaOH consumed by the hydrolysis of the ester and the reaction with Br_2/HBr in the organic phase. The amount of Br_2/HBr in the organic phase was determined by titrating a weighed sample of the organic phase dissolved in chilled methanol (~10°C) with NaOH. Using these results, the amount of ester present in the organic phase was estimated.

Gas chromatography (GC) analysis. Qualitative analysis of the organic phase was carried out by using a gas chromatograph (Chemito; Mumbai, India) equipped with a flame-ionization detector. A 2-m long and 1/8″ diameter OV-17 column was employed. The injector and the detector were maintain at 325°C, and the oven temperature was maintained at 120°C for 4 min. The temperature was then elevated to 290°C using a ramp rate of 30°C/min.

The GC analysis showed that the organic phase of the reaction mixture did not contain carboxylic acid, aldehyde, or alkyl bromide at detectable levels. Only two peaks were observed, one for the unreacted alcohol and the other for the ester. The identification of these peaks was verified by comparison with authentic samples.

Bromine partitioning. The oxidation of HBr by H_2O_2 in the aqueous phase liberates bromine, which is then extracted into the organic phase. Br_2 reacts with alcohol to generate HBr, which is extracted back into the aqueous phase. The partitioning of bromine between the organic and aqueous phases was determined at three different temperatures, *viz.*, 30, 40, and 50°C, as follows.

The reaction mixture was stirred for 15 min at a constant temperature. This procedure was the same as described above. The organic and aqueous phases were rapidly separated. A measured quantity of organic phase (5 mL) was added to a conical flask containing a known quantity of methanol at ~10°C. A known quantity of aqueous NaOH was then added to the conical flask; the quantity added was in excess of that required for complete reaction. The unreacted NaOH was titrated against standardized 0.1 N HCl. From the titration reading, the amount of Br_2/HBr (combined) in the organic phase was calculated.

Material balance. In a typical batch experiment, *n*-octanol (26 g, 200 mmol) was reacted at 40°C. The mole ratio of alcohol to HBr was 1:0.5. At the end of the batch reaction time of 10 h, the organic phase was separated from the reaction mixture and washed with water to remove traces of acid. The organic phase was dried and weighed (25.1 g). Analysis of the organic phase showed the ester content to be 72%. Thus the material balance to the extent of 97% based on the initial *n*-octanol was obtained. No attempt was made to separate the alcohol–ester mixture.

RESULTS AND DISCUSSION

The effects of the following variables on the conversion of alcohol were investigated: (i) stirring speed, (ii) mole ratio of reactants, (iii) temperature, and (iv) substrates.

Effect of stirring speed. In liquid–liquid systems, a species that is transferred from the aqueous phase to the organic phase encounters resistance at two stages, *viz.*, (i) upon passing from the bulk aqueous phase to the interface, and (ii) upon passing from the interface to the bulk organic phase. It is important to eliminate these resistances to achieve maximal overall reaction rates. This may be done by increasing the stirring speed. For the reaction under investigation, Br_2 formed in the aqueous phase is transferred to the organic phase, and HBr formed in the organic phase is transferred back to the aqueous phase. At a certain stirring speed, the concentration of the species in the bulk of the phase equals the interphase concentration. At this stage, the mass transfer resistances are eliminated.

To investigate the effect of the speed of stirring, *n*-octyl octanoate was synthesized by reacting *n*-octanol with aqueous HBr and H_2O_2. The experiments were performed at 50°C. Elimination of mass transfer resistance at 50°C also ensures that reactions at 50°C and lower temperatures under similar agitation conditions or speed of agitation are kinetically controlled (16). There was no effect of speed of agitation in the range of 750–2500 rpm on the progress of the reaction (Table 1). Thus, beyond a speed of 750 rpm, the reaction becomes kinetically controlled. However, all the experiments described below were performed above 1500 rpm to ensure that the effects of various operating parameters were evaluated under conditions of kinetic controlled.

Effect of mole ratio of alcohol to HBr. The effect of the *n*-octanol/HBr mole ratio (1:0.1, 1:0.2, 1:0.3, and 1:0.5) was investigated at 40°C. As this mole ratio decreases, the rate of the overall reaction increases (Table 1). As the concentration of HBr in the aqueous phase increases, more bromine is formed. This effectively increases the concentration of bromine in the organic phase, and the rate of the overall reaction increases. It is noted that after 10 h the amount of *n*-octyl octanoate formed is more than that corresponding to the stoichiometric quantity of HBr consumed. It can be seen from the mechanistic steps that as reaction proceeds, HBr is generated in the organic phase. The HBr produced is transferred back to the aqueous phase, where it is reoxidized by H_2O_2 to generate bromine, which drives the reaction forward. The identity of the products was confirmed by comparison with authentic samples. Authentic samples of *n*-octyl octanoate were prepared by reaction of *n*-octanoic acid with *n*-octanol using *p*-toluene sulfonic acid (P-TSA) as a catalyst and toluene as a water entrainer (17).

Effect of temperature. The effect of temperature on the progress of the reaction was investigated at 30, 40, and 50°C, with all other parameters unaltered. The initial rate of reaction increased substantially with temperature when the reaction was carried out at 40 and 50°C (Table 1).

Effect of substrate. Oxidation of *n*-decanol and *n*-dodecanol was also investigated at 40°C. The progress of the oxidation reaction of *n*-decanol was identical to that of *n*-octanol. Slightly lower conversions were observed in the oxidation of *n*-dodecanol under otherwise identical conditions. Results are given in Table 1.

Kinetics. For a second-order reaction, the following rate equation applies in the present case:

TABLE 1
Effect of Stirring Speed, Molar Ratio of Alcohol to HBr, and Substrate Alcohol on the Progress of the Reaction

Time (min)	Conversion of alcohol[a]									
				Substrate						
	Stirring speed[b] (rpm)			*n*-Octanol[c]						
	750	1500	2500	I	II	III	IV	V	*n*-Decanol[d]	*n*-Dodecanol[d]
20	—	—	0.1	—	—	—	0.21	—	—	—
30	—	0.18	—	0.12	—	—	—	—	—	—
40	—	—	—	—	—	—	0.32	—	—	—
60	0.25	0.24	—	0.15	0.020	0.089	—	—	0.17	0.14
80	—	—	0.29	—	—	—	—	—	—	—
90	—	—	—	—	—	—	0.58	—	—	—
120	0.33	0.37	—	0.3	0.03	0.13	0.61	—	0.28	0.24
160	—	—	0.37	—	—	—	—	—	—	—
180	0.36	0.41	—	—	—	0.16	—	—	0.39	0.36
240	0.39	—	0.43	0.46	—	—	—	0.2	0.44	0.38
300	—	—	—	—	0.04	—	—	—	0.49	0.43
360	—	—	—	0.52	—	0.25	—	0.3	0.50	0.48
480	—	—	—	—	—	0.28	0.68	0.41	—	—
600	—	—	—	—	0.06	0.3	0.72	0.46	—	—

[a] Weight of alcohol converted to esters/weight of original alcohol.
[b] Reaction conditions: 50°C; mole ratio of alcohol (*n*-octanol) to HBr, 1:0.3.
[c] Reaction conditions: stirring speed, 1500 rpm; I: 40°C; mole ratio of alcohol to HBr, 1:0.3; II: 40°C; mole ratio of alcohol to HBr, 1:0.1; III: 40°C; mole ratio of alcohol to HBr, 1:0.2; IV: 40°C; mole ratio of alcohol to HBr, 1:0.5; V: 30°C; mole ratio of alcohol to HBr, 1:0.3.
[d] Reaction conditions: stirring speed, 1500 rpm; 40°C; mole ratio of alcohol to HBr, 1:0.3.

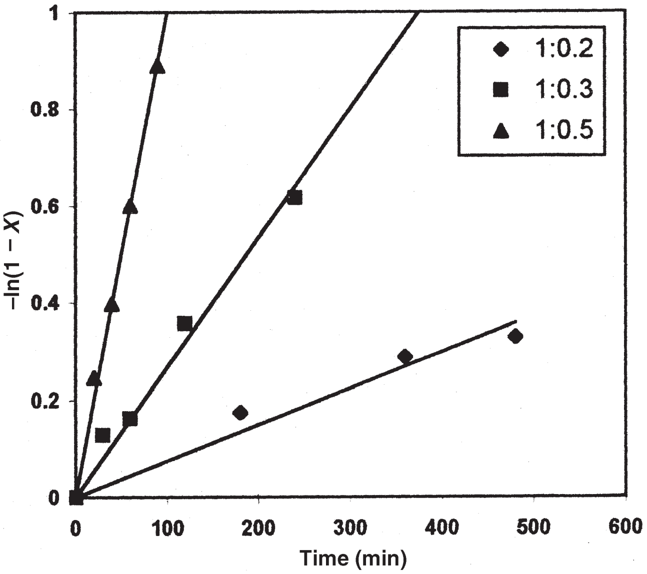

FIG. 1. Plot of $-\ln(1 - X)$ vs. time (min), where X is the fraction of alcohol converted at time t. Initial conditions: 200 *n*-octanol, 300 mmol H_2O_2, 150 mL H_2O, 40°C, 1500 rpm. Mole ratios of alcohol to HBr shown in inset.

$$R = k\,[Br_2]\,[\text{alcohol}] \qquad [3]$$

where R = rate of consumption of alcohol, k = second-order rate constant for the reaction in the organic phase, $[Br_2]$ = concentration of bromine, and [alcohol] = concentration of alcohol.

The concentration of Br_2 in the organic phase can be assumed to be constant, because the HBr formed is immediately extracted into the aqueous phase and bromine is liberated. Because the agitation rates are very high, one can assume that Br_2 gets partitioned rapidly in the organic phase. Thus, at any stage, the concentration of Br_2 remains constant for the given reaction conditions. Thus,

$$R = k'\,[\text{alcohol}] \qquad [4]$$

where $k' = k[Br_2]$.

The validity of the pseudo-first-order rate equation (Eq. 4) can be confirmed by plotting $-\ln(1 - X)$ vs. reaction time, t, where X is the fraction of alcohol converted at time t. Figure 1 shows that the reaction is first-order with respect to *n*-octanol. The slopes (k') obtained from Figure 1 were plotted against the concentration of bromine in the organic phase (Table 2).

TABLE 2
Concentration of Bromine in the Organic Phase and Second-Order Rate Constant (*k*) Values[a]

	Concentration of bromine in the organic phase (mol L^{-1})			k (mL $mol^{-1}min^{-1}$)		
Alcohol	30°C	40°C	50°C	30°C	40°C	50°C
n-Octanol	0.125	0.0985	0.0918	8.28	27.08	43.57
n-Decanol	—	0.0798	—	—	32.58	—
n-Dodecanol	—	0.0652	—	—	37.42	—

[a]Reaction conditions: 200 mmol alcohol, 60 mmol HBr, 300 mmol H_2O_2, 150 mL H_2O; stirring speed, 1500 rpm.

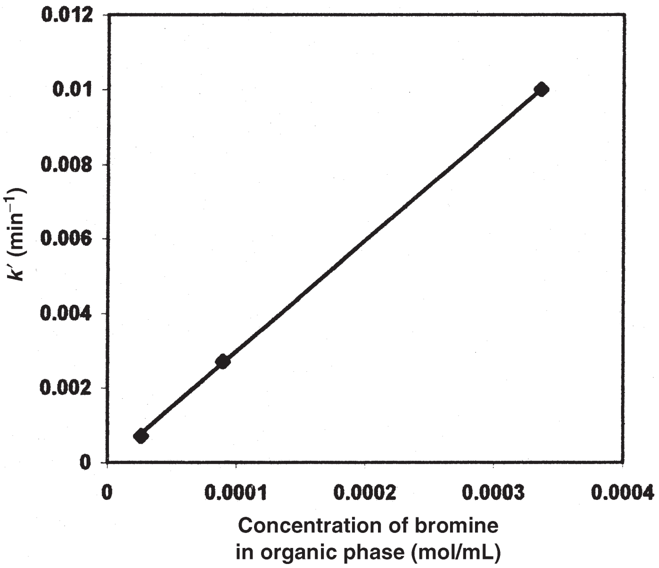

FIG. 2. Plot of k' (Eq. 4) vs. concentration of bromine in organic phase. Initial conditions: 200 mmol *n*-octanol, 300 mmol H_2O_2, 150 mL H_2O, 1500 rpm.

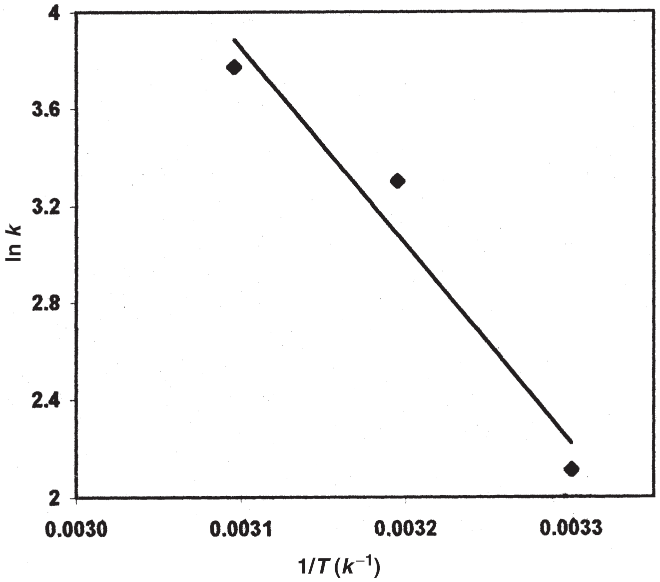

FIG. 3. Arrhenius plot for *n*-octanol. Data from Table 2.

The straight line obtained (Fig. 2) also indicates that the reaction is first-order with respect to bromine concentration in the organic phase. From the slope of this straight line, the second-order rate constant k was evaluated. The values of the second-order rate constant are given in Table 2. An Arrhenius plot for *n*-octanol (Fig. 3) shows the activation energy for the reaction to be 16.32 kcal mol^{-1}. This high value also confirms that mass transfer limitations are absent.

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