

hydrogen atom is not to be expected. We have to conclude, therefore, that the hydroxyl hydrogen comes from a different source than that of the methyl hydrogen. As a probable source, one might suggest hydrogen from the gas phase or from a physically adsorbed layer of hydrogen molecules.

According to Tsuchiya *et al.*, the hydrogen on the catalyst is in the form of methoxy radicals. If the hydrogen in these radicals exchanges with gaseous hydrogen more slowly than the rate at which the radicals are reduced to methanol and desorbed, it is understandable that the protium concentration in the methoxy radicals on the catalyst remains about three times (see Fig. 1) that in the surrounding gas.

It thus appears that the step in which the hydroxyl hydrogen is added to the methoxy radical and the product methanol is desorbed is rate determining.

ACKNOWLEDGMENTS

Stimulating discussions with Prof. F. S. Klein are very much appreciated. Thanks are also expressed to Mr. O. R. Gunnerfeldt of Harshaw Chemical Co., Cleveland, U. S. A. for the catalyst, and to Dr. Ervin Glotter of the Chemistry Department, The Weizmann Institute of Science, for the NMR analysis.

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Received November 27, 1968

^aThis paper refers to most of the papers published in the field.

^bThis paper sums up most of the work on rate and mechanism.

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Esterification of Oleic Acid with Butanol Catalyzed by a Cation-Exchange Resin

INTRODUCTION

The ion exchange resin-catalyzed esterification of oleic acid with butanol was investigated by Levesque and Craig (1). The reaction, owing to the slow diffusion rate of the large molecule of the acid, appears to occur only at or near the surface of the resin particles and the data, after the first steps of reaction, fit a bimolecular kinetic equation. A retarding effect of water on the reaction rate was reported.

More recently, the deactivation of the catalyst by water has been emphasized by Bochner *et al.* (2), who investigated the esterification of salicilic acid with methanol. Water was assumed to form hydrated ions with the hydrogen counterions of the resin, which become inactive; a kinetic expression based on the Langmuir-Hinshelwood model, of the form:

$$r = K(\text{Acid})(\text{Alcohol})/[1 + b(\text{H}_2\text{O})], \quad (1)$$

was advanced.

In this paper, experiments which relate the process rate to the water concentration and to the temperature of the reaction mixture, both controlled by the speed of distillation, in the esterification of oleic acid with butanol, are described.

EXPERIMENTAL

Procedure. Three moles of butanol, 0.7 moles of oleic acid and catalyst, amounts corresponding to 9.36 mmoles of hydrogen ions, were placed in a 1-liter flask fitted with stirrer, thermometer, and reflux condenser with water separator and heated at reflux for the duration of the experiment. The heat input to the heater unit was controlled by a Variac and its measurement based on the determination of the distillation speed of butanol. Zero time was taken as the time when refluxing commenced.

Analytical. Portion of the reaction mixture were removed from the flask with a pipet and analyzed. The acid was determined by titration with 0.1 sodium hydroxide solution and the water by vapor-phase chromatography using an internal standard of 20 weight % acetone. The water content in the reflux stream from the condenser was also determined. The Carlo Erba, Mod. C thermal conductivity detector chromatographic apparatus was operated as follows: Column: 4 m in length and 5 mm in diameter filled with 20% Carbowax 1500 supported on Teflon; column temperature: 103°C; evaporator temperature: 180°C; helium flow rate: 3 l/hr.

Materials. The reactants: butanol RP-ACS and oleic acid were Carlo Erba products. The catalyst was a cation exchange resin, Dowex 50W (X2), from 32 to 48 mesh in size. The resin was employed wet (dried on filter paper and containing 79.2 weight % H_2O), and dry (under vacuum).

RESULTS

The conversion of oleic acid to butyl oleate, X, the water concentration and the temperature of the reaction mixture are plotted against time in Fig. 1. Different initial water contents, obtained by using either wet or dry resin or adding water to the

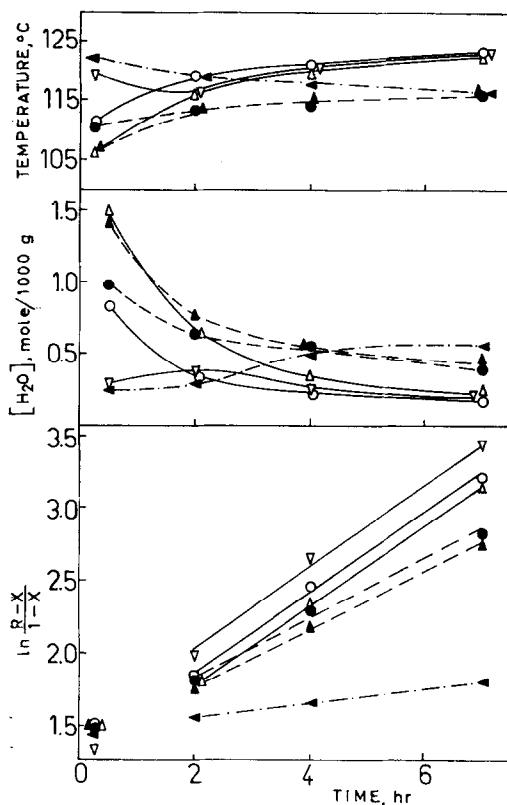


FIG. 1. Conversion, water concentration (mole/1000 g of charge) and temperature of reaction mixture vs time.

R = initial butanol/oleic acid molar ratio in the charge.

Run	Catalyst	Distill. speed (mole/hr)
▲	Uncatalyzed	1.77
○	Wet resin	0.81
●	Wet resin	1.77
△	Wet resin plus 1.78% H_2O	0.81
▲	Wet resin plus 1.78% H_2O	1.77
▽	Dry resin	0.81

charge, and two different speeds of distillation have been employed.

As it seen from Fig. 1, the water concentrations, which are different at the beginning of the experiments, assume with time values which depend only on the speed of distillation. A similar behavior is observed for the temperature of the mixture.

In all cases, the conversion data can be fairly well correlated by a bimolecular

kinetic equation for the last 5 hr when both water concentration and temperature, contrary to what happens in the first steps of the process, assume nearly constant values.

TABLE 1
WATER CONTENT IN REFLUX STREAM

Time (hr)	Distill. speed (mole/hr)	
	0.81 (% H ₂ O)	1.77 (% H ₂ O)
0.25	25.2	20
2	18.7	17.5
4	5.3	17.4
7	2.8	11.8

The higher distillation speed gives the higher water concentration in the reaction mixture. This effect results from the higher dissolved water content in the reflux stream (in Table 1 the % weight H₂O content in samples taken from the reflux at increasing times are shown to depend on the speed of distillation, for wet resin-catalyzed runs). To the higher water concentration and the lower temperature corresponds a lower process rate.

DISCUSSION

Our experimental results are in agreement with Eq. (1), which involves deactivation of the catalyst by water. However,

we should point out that the decrease of the process rate with increasing water concentration must be attributed, in part, to the decrease of the reaction temperature.

The failure of the bimolecular equation to hold over the first steps of reaction, reported by Levesque and Craig (1), may be interpreted on the basis of the variations of the water concentration and of the temperature in the reaction mixture.

The speed of distillation has a marked effect on the process rate, in that it controls the water contents and reaction temperature.

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Received November 26, 1968

The Mechanism of Olefin Disproportionation

Since the initial discovery of olefin disproportionation by Banks and Bailey (1), Bradshaw, Howman, and Turner have published on the mechanism of the reaction (2). The latter authors suggested that the reaction intermediate was a "quasi-cyclobutane." Calderon and workers have recently published on a homogeneous catalyst based upon a tungsten complex. They too proposed a four-center intermediate (3). However, Mol, Moulijn, and Boelhouwer have offered an alternate explanation and have postulated a π -bonded cyclo-

butadiene formed by the transfer of four hydrogen atoms from two olefin molecules to the catalyst surface.

An examination of the structures and distribution of products from a highly selective catalyst (a potassium hydroxide-treated molybdena-alumina catalyst) has given further support for the "quasi-cyclobutane" intermediate. This support is provided by the following experimental observations: 1-octene was converted to ethylene and 7-tetradecene (Table 1); 2-octene was converted to 2-butene and