

formed acetic acid with the excess methanol present.) Little conversion of the methyl iodide promoter is found.

At higher pressures (runs 4 and 5) essentially total conversion of methanol is obtained even at only 10–30% of the methyl iodide levels used in the runs at atmospheric pressure. At high methanol conversions, some consumption of the methyl iodide promoter to form acetic acid and hydrogen iodide occurs. Hydrogen iodide can be used in place of methyl iodide as the promoter. The carbonylation reaction is also effective in the presence of a hydrogen diluent (runs 6–8). No reduction products such as acetaldehyde or ethanol are found in any of these runs. The

increased feed rates used in runs 6–8 could account for the decreased conversions observed.

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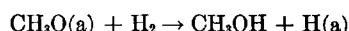
On the Mechanism of the Synthesis $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$

The catalytic synthesis of methanol from hydrogen and carbon monoxide has been the subject of many investigations (1), first with regard to the equilibrium constant of the reaction and later with regard to the rate and mechanism (2).

Rate measurements have led to various conclusions as to the rate determining step in the reaction. Temkin *et al.* (3) suggested that the rate of adsorption of the reacting gases on the catalyst determined the rate of production of methanol, while Natta *et al.* (4) postulated that the surface reaction was rate determining. Ogino *et al.* (1) based their rate equation on the assumption that the desorption of the product methanol was rate determining. Saida and Ozaki (2) found that their data could be explained equally well by at least two mechanisms: One mechanism requires the attack of a hydrogen molecule on formaldehyde, while in the second a CH_3O radical is formed from chemisorbed hydrogen and CO , and then reduced to methanol by another chemisorbed hydrogen atom, the latter step being rate determining.

Tsuchiya and coworkers (5) also sug-

gested the formation of a CH_3O radical on the catalyst, having found that H_2 and CO are adsorbed on the catalyst in a mole ratio of 3:2. This would require a rate determining step in which the radical is attacked by a hydrogen molecule, forming methanol and a chemisorbed hydrogen atom:



It thus appears that data specifically indicating the rate determining step can help clarify the mechanism of the synthesis.

In the course of synthesizing methanol (for vapor pressure measurements) on a commercial catalyst (6), a system, previously saturated with CO and H_2 , was used to produce CD_3OD . The synthesis was carried out at 250°C and a pressure of 60 psia, in a glass system similar to that described by Beersmans and Jungers (7). The CO and D_2 were supplied to the system from cylinders of the compressed gases (8); the $\text{D}_2:\text{CO}$ ratio was 2:1. Circulation was maintained by thermal convection and the product was collected in a liquid air-cooled trap.

The catalyst vessel was first evacuated

to remove free hydrogen and the D_2 -CO mixture was then added at operating temperature and pressure. Methanol was prepared in batches of 2-5 ml, in order to follow the protium-deuterium content of the product. After each batch the catalyst was reevacuated.

The isotopic composition of the hydrogen in the methyl and the hydroxyl groups of the methanol was determined by comparing the areas of the protium peaks in the N. M. R. spectrum of the product methanol with the areas found in the spectra of standard solutions in CCl_4 of methanol of normal isotopic composition.

Figure 1 shows the protium concentration in the methyl and hydroxyl groups of the methanol batches (in the order of production from right to left). As can be seen, the protium concentration in the product methanol (particularly in the methyl group) diminished gradually with each batch produced. Also, the protium concen-

tration in the methyl group was always significantly higher than that in the hydroxyl group of the methanol, i.e., protium is preferentially incorporated in the methyl group of the product.

According to the findings of Tsuchiya *et al.* (5) protium is present on the catalyst in the form of methoxy radicals. The difference in the isotopic constitution of the hydroxyl and methyl groups is an indication of a difference in the sources of the hydrogen in the two groups. Considering that the rise in deuterium content in the methyl group is slower than that in the hydroxyl group, one may assume that the methoxy radical is formed first, incorporating protium from the catalyst and that this is followed by the addition of hydrogen, forming methanol, and the desorption of the product. Since the chemisorbed methoxy radical is most probably immobile (9), on isotope effect in the reaction between a methoxy radical and a chemisorbed

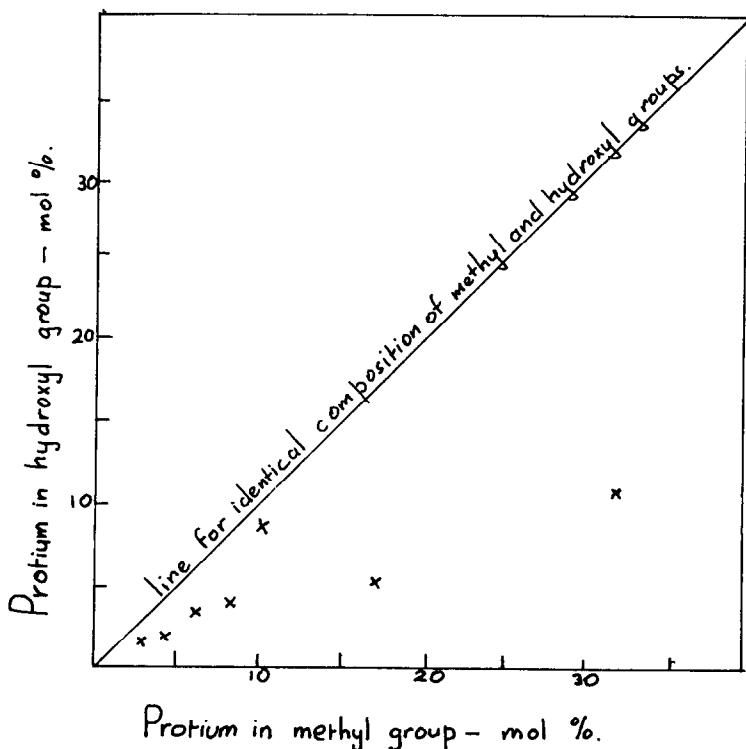


FIG. 1. Comparison of protium concentrations in the methyl and hydroxyl groups of the methanol synthesized. (Order of samples from right to left.)

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.

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^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.