

THE HYDROGEN-CARBON DIOXIDE REACTION

Sir:

Smith and Hirst [*Ind. Eng. Chem.*, **22**, 1037 (1930)] observed that hydrogen and carbon dioxide formed carbon monoxide and water over methanol catalysts at atmospheric pressure.

We have been able to confirm this reaction and in addition obtain the regular methanol formation simultaneously using an unsupported zinc-copper-aluminum catalyst under pressure at high temperatures. This catalyst was not particularly active but served as an indication of the course of the reaction. For example, with an initial gas mixture of 27% CO₂, 71% H₂ and 2% N₂ at 325° and 1700 lb. pressure, the effluent gas contained 4% CO and calculations showed an exact agreement with the water found in the condensate compared with the amount produced in the formation of the methanol by the regular reaction.

This suggests that the primary step in the synthesis of methanol from carbon dioxide and hydrogen involves the reduction of carbon dioxide, and the nature of the catalyst determines the extent to which the resultant carbon monoxide will be hydrogenated. Experimental results indicate that as the activity of the catalyst decreases the methanol reaction is most affected, as illustrated by an increase in the carbon monoxide percentage and a decrease in methanol as the catalyst aged. Experiments with this same catalyst using water gas gave appreciable amounts of carbon dioxide in the exit gas.

This observation coupled with the apparent formation of a copper carbonyl during the same reaction suggests a new mechanism for the synthesis of methanol which will be discussed later.

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THE ADDITION OF SODIUM ENOL ALKYL MALONIC ESTER TO BENZAL-ACETOPHENONE

Sir:

In a recent communication [Michael and Ross, *THIS JOURNAL*, **52**, 4598 (1930)] it was shown that addition of sodium enol methylmalonic ester to crotonic ester resulted in a 60% yield of α,β -dimethyl- γ -carbethoxyglutaric ester and it was concluded that the methyl group migrated directly in the addition process. Holden and Lapworth [*J. Chem. Soc.*, 2368 (1931)] have suggested that the primary addition compound may be converted into the final product through the intermediate formation and decomposition of the cyclobutanone structure II