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Mechanism of Ethanol Formation: The Role of Methanol

Fischer–Tropsch synthesis produces both hydrocarbons and oxygen-containing products such as alcohols and aldehydes. Homologation of methanol has been proposed as the chain propagation reaction of higher alcohols (*1, 2*). Rh is an effective catalyst to produce methanol and ethanol from CO + H_2 under mild conditions (*3*). Using the isotopic tracer method, we have shown that methanol formation from CO + H_2 catalyzed by Rh/TiO_2 occurs by a nondissociative CO mechanism (*4*) and that ethanol is not produced by enol condensation or CO insertion to adsorbed methyl species, and we have proposed a CO insertion into an adsorbed carbene as a more likely mechanism (*5*). In this paper we show that methanol can act as an intermediate in ethanol synthesis under Fischer–Tropsch synthesis conditions catalyzed by Rh/TiO_2 though it is a minor route.

Three wt% Rh/TiO_2 (0.10 g) was used in an all-glass internal recycle reactor. The catalyst was reduced for 15 hr in 380 Torr (1 Torr = 133.3 N m^{-2}) of H_2 at 573 K and cooled to room temperature and evacuated. Then 25.0 Torr of $^{13}C^{16}O$, 14.2 Torr of $^{12}CH_3{}^{16}OH$, and 498 Torr of H_2 were added to the reactor in that sequence at 300 K because methanol decomposes readily at high temperature in the absence of CO. The reactor was then heated to 422 K for reaction. Product analysis was by gas chromatography. Condensable product was collected in a cold trap and analyzed by both proton and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. All of the NMR spectra were obtained using a Bruker WM 250 NMR spectrometer operating at a field strength of 5.875 Tesla, which results in proton resonance at 250.13 MHz and ^{13}C resonance at 62.9 MHz. D_2O was added to the product to provide an internal lock. All spectra were referenced to methanol. ^{13}C spectra were obtained using broad band proton decoupling. The Nuclear Overhauser Effect was suppressed to insure quantitative data. The ratio of the concentrations of the alcohols in the product was calculated from the integrals of the NMR peaks. Details of experimental procedure are given elsewhere (*4*).

Added methanol inhibited the rate of CO hydrogenation by about tenfold. For 15.8% CO conversion, the product distribution (mole%), except for methanol, was methane, 75.0%; ethane, 3.52%; propane, 2.15%; propylene, 0.06%; *n*-butane, 0.63%; butenes, 0.12%; *n*-pentane, 0.24%; pentenes, 0.03%; *n*-hexane, 0.15%; ethanol, 18.0%; and 1-propanol, 0.12%. This product distribution was very similar to that of previous experiments (*4*) though the fraction of higher hydrocarbons produced was somewhat smaller. The partial pressure of methanol was 13.3 Torr after reaction.

Product ethanol can be composed of four possible isotopic species (Table 1). The ^{13}C NMR spectrum of the condensed product is shown in Fig. 1. $^{13}CH_3{}^{13}CH_2OH$ (A) gives rise to the two doublets centered at 16.7 and 57.8 ppm. These resonances occur as doublets, because of the carbon–carbon coupling. $^{13}CH_3{}^{12}CH_2OH$ (B) produces the weak singlet at 16.7 ppm. And $^{12}CH_3$ $^{13}CH_2OH$ (C) produces the weak singlet at 57.8 ppm. The singlet at 48.8 ppm is due to $^{13}CH_3OH$, which is generated by the reaction and is also present at natural abundance in the starting material.

The ratios of A : B : C (Table 1) calculated from the ^{13}C NMR analysis were 1.00 : 0.096 : 0.233. The difference between B and C is a key to reaction pathway inter-

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TABLE 1

Isotopic Composition of Ethanol from $^{13}C^{16}O$ Hydrogenation in the Presence of $^{12}CH_3{}^{16}OH$ Catalyzed by Rh/TiO_2[a]

Isotopic species	Designation	Statistical isotopic composition			Experimental composition[a]
		CO hydrogenation only	Methanol homologation only	90% hydrogenation plus 10% homologation	
$^{13}CH_3{}^{13}CH_2{}^{16}OH$	A	81	0	73	72
$^{13}CH_3{}^{12}CH_2{}^{16}OH$	B	9	0	8	7
$^{12}CH_3{}^{13}CH_2{}^{16}OH$	C	9	90	17	17
$^{12}CH_3{}^{12}CH_2{}^{16}OH$	D	1	10	2	4

[a] Reaction conditions: batch reactor; temperature = 422 K, catalyst 3.0 wt% Rh/TiO_2, 14.2 Torr $^{12}CH_3{}^{16}OH$, 25 Torr $^{13}C^{16}O$, and 498 Torr H_2 are added at RT, $^{13}C^{16}O$ contained 90% ^{13}C.

pretation. The proton spectrum of the methyl protons of the ethanol isotopic species is shown in Fig. 2. Species having a ^{12}C at the methyl position give rise to the set of peaks at around 1.1 ppm. The six larger peaks correspond to $^{12}CH_3{}^{13}CH_2OH$ (C) (proton–proton coupling ~ 7 Hz and two-bond carbon–proton coupling ~ 4.6 Hz). The three weak peaks correspond to $^{12}CH_3$ $^{12}CH_2OH$ (D). Species (A) and (B), having a ^{13}C at the methyl position, produce the two more intense set of peaks on either side of the center set. The separation between these two sets is due to the directly bonded proton-carbon coupling (126.8 Hz). The fine structure arises from the smaller proton–proton and two-bond carbon–proton coupling.

Only the downfield half of the proton spectrum, corresponding to isotopic species (A and C) containing ^{13}C in the methylene position, can be clearly resolved (around 3.9 ppm) (Fig. 2, insert); the remaining resonances occur under the methanol peaks.

The ratio of A : B : C, known from the ^{13}C NMR, was used to solve the linear equation system from the ^1H NMR; results are given in Table 1, as Experimental Composition. Repeat NMR analysis gave reproducibility within about 1%. Under the experimental conditions used here, approximately 90% of the ethanol was formed from CO + H_2;

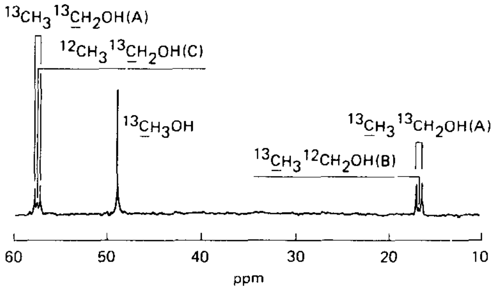


FIG. 1. $^{13}C\{^1H\}$-NMR analysis of product ethanol from $^{13}C^{16}O + H_2 + {}^{12}CH_3{}^{16}OH$ reaction catalyzed by Rh/TiO_2. Reaction conditions: batch reactor, 422 K, 14.2 Torr $^{12}CH_3{}^{16}OH$, 25 Torr $^{13}C^{16}O$, and 498 Torr H_2 (added at RT).

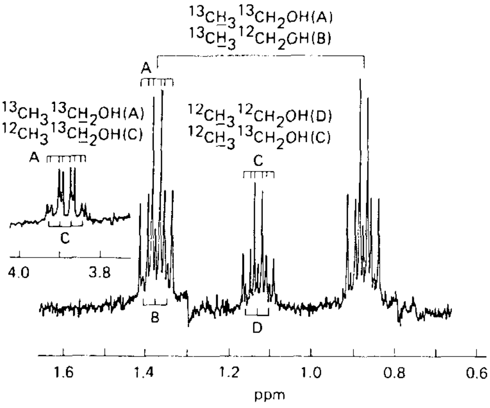
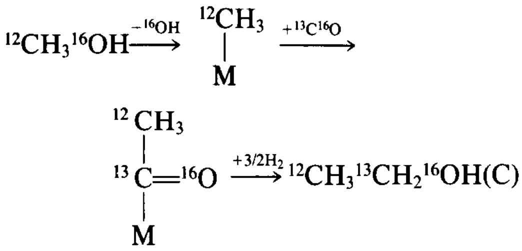


FIG. 2. ^1H-NMR analysis of product ethanol from $^{13}C^{16}O + H_2 + {}^{12}CH_3{}^{16}O$ reaction catalyzed by Rh/TiO_2: methyl and methylene regions.

at most only 10% was formed via the added $^{12}CH_3OH$.

The methanol at the end of the reaction contained 2.7% $^{13}CH_3OH$, as compared with 1.1% $^{13}CH_3OH$ (natural abundance) for the methanol added as determined from the ^1H NMR. This increment of $^{13}CH_3OH$ corresponds to synthesis from $^{13}CO + H_2$.

The ^{13}C distribution in C_2H_5OH shows that the carbon atom from the CH_3OH is incorporated as the CH_3 portion and that the inserted CO goes to the CH_2OH portion. This is consistent with previous studies, and the accepted reaction mechanisms in homogeneous systems (*2, 6, 7*). We speculate that the reaction mechanism may be similar to that for homogeneous homologation in this respect but not necessarily in other details.



$$^{12}CH_3{}^{16}OH \xrightarrow{-^{16}OH} \underset{M}{\overset{^{12}CH_3}{|}} \xrightarrow{+^{13}C^{16}O} \underset{M}{\overset{^{12}CH_3}{^{13}C={}^{16}O}} \xrightarrow{+3/2H_2} {}^{12}CH_3{}^{13}CH_2{}^{16}OH(C)$$

The mechanism of ethanol formation from CO + H_2 was studied by the isotopic tracer method. Enol condensation and CO insertion into surface methyl do not explain the isotopic composition of ethanol (*5*). Ethanol is produced mainly from CO + H_2 directly. CO insertion into methyl acts as a minor route to produce ethanol, and methanol homologation as a route to produce ethanol. We infer that a different mechanism or different sites are involved for the two reactions catalyzed by Rh/TiO_2. The 10% contribution of methanol homologation to ethanol synthesis suggests that methanol is not an important intermediate in ethanol synthesis from CO + H_2, catalyzed by Rh/TiO_2 at approximately atmospheric pressure. At higher pressures, where methanol and ethanol synthesis are to be practiced commercially, methanol homologation could be a much more significant contributor to ethanol synthesis (*6, 7*), as, for instance, in the I.F.P. higher alcohols process (*8*).

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