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Formation of Higher Alcohols from Methanol in the Presence of Metal Acetylides

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It has been found that methanol can be converted to higher-molecular-weight alcohols in the vapor phase in the presence of a metal acetylide. Isobutyl alcohol is the predominant higher alcohol formed. Significant amounts of ethanol, propanol, butanol, 2-methylbutanol, and 2-methylpentanol are also produced. In addition to higher alcohols, a significant portion of the methanol is converted to CH_4, CO, and H_2. The overall product distribution is a function of the metal acetylide employed and the reaction conditions. ^{13}C labeling studies have conclusively shown that the source of the carbon in the higher alcohols is the methanol, not the metal acetylide. However, studies indicate that the process is not catalytic, presumably due to the fact that under reaction conditions, the metal acetylide is converted to other species which are not catalytically active. Attempts to determine the fate of the acetylide and the catalytic activity of the resultant species are described. A mechanism consistent with experimental observations is presented to explain the high selectivity to isobutyl alcohol and similarities to the heterogeneous isosynthesis catalysts are discussed.

INTRODUCTION

Although catalytic processes for the conversion of synthesis gas and/or methanol to useful hydrocarbons and oxygenates are well known, the mechanistic details of many of these transformations are not well understood. For example, the mechanism of C–C bond formation in the zeolite-catalyzed methanol to gasoline process has been the subject of much attention (*1*, *2*). Similarly, the mechanism of the Fischer–Tropsch reaction remains the topic of considerable debate (*3*, *4*). Although they have received considerably less attention than their Fischer–Tropsch counterparts, the isosynthesis catalysts (*5–9*) also are capable of converting synthesis gas to valuable higher-molecular-weight hydrocarbon and oxygenated products. These catalysts derive their name from the high selectivity to iso products, particularly iso-C_4 products, observed under ordinary operating conditions. As such, the distribution of products is quite different from that obtained in the Fischer–Tropsch reaction, and the mechanism of C–C bond formation over these catalysts also is not well understood.

The present study focuses on C–C bond formation from methanol in the presence of metal acetylides. It has been observed that methanol can be converted to useful higher alcohols by contacting it in the vapor phase with a metal acetylide such as CaC_2. Although the formation of these alcohols is not catalytic and thus of limited commercial value, the mechanistic results described herein may be relevant to C–C bond formation in the isosynthesis.

EXPERIMENTAL

The vapor-phase reaction of methanol with metal acetylides was examined in a quartz flow reactor at atmospheric pressure in the temperature range 300–450°C. The metal acetylide in powder form was supported on a porous frit inside a fused-quartz tube obtained from Quartz Scientific Inc. (20 mm i.d., 23.6 mm o.d., 18 in. length, No. 3 porosity frit 7 in. from one end). The quartz tube was heated inside a vertically mounted Lindberg furnace.

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The methanol was delivered at a set flow rate, usually 0.1 or 0.05 ml/min, using a liquid syringe pump (Sage Pump Model 355) and was vaporized prior to entering the reactor by passing it through a length of 1/16-in. stainless-steel tubing wrapped with electrical heating tape. The methanol was passed upward through the catalyst bed in the presence of a low flow of helium carrier gas. A Brooks mass flow controller (Model 5841-1A2ZZ1) was used to control the helium flow which was usually set at 10 ml/min.

Liquid products were collected at periodic intervals in an ice-cooled trap and analyzed by gas chromatography. The analysis of alcohol mixtures was performed on a Hewlett–Packard Model 5710A gas chromatograph with a sample size of 0.5 μl. The 6-foot column (5% Carbowax 20M, 60/80 Carbopack B from Supelco) was kept at 80°C for 0 min, heated at 8°C/min to 250°C and kept at 250°C for 8 min. Methylbenzoate was used as an internal standard.

The effluent gas usually passed through a wet test meter and was collected either in a 10-liter gas sampling bag (Calibrated Instruments, Inc.) or over water in an inverted 2-liter graduated separatory funnel. The gas mixture was analyzed using a Carle Model 357-A Series S gas chromatograph equipped with both FID and TC detectors.

$^{13}CH_3OH$ was purchased from Merck Isotopes and GC–mass spectra were recorded on a Finnigan Model 4024 mass spectrometer. X-Ray diffraction patterns were obtained using a Philips' powder diffractometer.

CaC_2, Na_2C_2, CeC_2, and LaC_2 were all purchased from Alfa. The calcium carbide was crushed to a fine powder before use. $Mg(OEt)_2$ was also purchased from Alfa and $NaOCH_3$ was obtained from Fluka AG, Switzerland.

RESULTS

Higher Alcohol Formation

Calcium carbide has been used in conjunction with conventional Cu–Zn methanol synthesis catalysts to convert synthesis gas to a mixture rich in methanol and isobutyl alcohol. Furthermore, it has also been reported that at elevated temperatures and pressures, it is possible to convert methanol to isobutyl alcohol using only CaC_2 (*10*). Unlike these earlier experiments which were conducted under pressure in a batch autoclave, the experiments described herein were carried out in a quartz flow reactor at atmospheric pressure in the temperature range 300–450°C. The metal acetylides employed were CaC_2, Na_2C_2, CeC_2, and LaC_2.

When vaporized methanol was contacted with a metal acetylide at 400°C, gas chromatographic analysis indicated that the effluent liquid contained appreciable amounts of higher alcohols. The distribution of alcohols for the various acetylides is summarized in Table 1, where the selectivity values denote the carbon mole percentage, i.e., the percentage of the carbon in all the higher alcohols in a particular alcohol. Isobutyl alcohol was the predominant higher alcohol for all the metal acetylides with lesser amounts of ethanol, 1-propanol, 1-butanol, 2-methylbutanol, and 2-methylpentanol also being formed.

It can be seen from the data in Table 1 that the distribution of alcohols changed with time on stream. This is best illustrated by the data for LaC_2, which is depicted graphically in Fig. 1. The selectivity to iso-

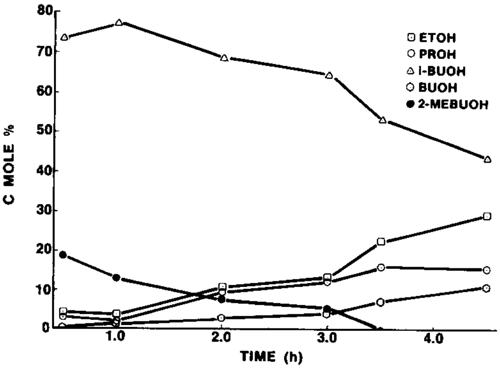


FIG. 1. Changes in alcohol selectivity with time for the reaction of LaC_2 and CH_3OH at 400°C.

TABLE 1

Distribution of Liquid and Gaseous Products from the Reaction of Methanol and Metal Acetylides at 400°C

Acetylide	Contact time (s)	Time (h)	$\%CH_3OH$ to ROH	Alcohol selectivities						Gas make			
				EtOH	PrOH	i-BuOH	BuOH	2-Me BuOH	2-Me C_5-OH	$\frac{C_2H_2}{ROH}$	$\frac{CH_4}{ROH}$	$\frac{CO}{ROH}$	$\frac{H_2}{CO}$
CaC_2	3.3	1	1.6	15.3	18.0	52.5	4.7	6.3	3.4	0.8	0.15	0.7	3.1
		2	1.9	11.1	16.2	57.1	2.8	4.4	2.6	0.6	0.07	0.8	2.3
		3	1.7	12.1	15.4	56.4	2.9	5.9	4.6	0.5	0.08	1.1	2.0
		4	1.9	12.5	15.3	55.6	3.0	6.0	4.6	0.3	0.08	1.2	2.1
Na_2C_2	5	1	0.4	9.5	18.0	52.0	5.1	15.1	—	0.7	3.9	3.2	33.4
		2	1.3	16.7	22.5	43.8	4.3	8.3	—	—	0.7	1.7	7.1
		3	1.3	19.8	23.5	41.5	5.4	5.5	—	—	0.5	1.6	4.3
		4	1.2	23.0	22.4	42.1	6.7	5.7	—	—	0.4	1.3	4.1
LaC_2	1.6	0.5	2.0	4.3	3.1	73.7	—	18.9	—	0.05	1.4	7.7	2.3
		1	1.8	4.0	2.2	77.4	1.7	13.1	—	—	1.7	8.4	2.3
		2	1.3	10.6	9.7	68.7	3.1	7.7	—	—	1.7	8.6	2.5
		3	1.0	13.2	12.3	64.6	4.5	5.6	—	—	2.2	12.9	2.2
		3.5	0.6	27.6	16.3	53.5	7.6	—	—	—	3.2	20.6	2.2
		4.5	0.3	29.3	15.6	43.8	11.3	—	—	—	4.1	27.9	2.4
CeC_2	1.6	0.5	1.9	3.5	—	69.9	—	21.9	4.7	0.03	7.3	8.3	2.6
		1.0	1.3	3.7	1.7	75.6	—	19.0	—	—	8.9	16.9	2.0
		1.5	1.3	4.8	3.4	76.8	—	15.1	—	—	8.6	18.9	2.0

butyl alcohol often tended to pass through a maximum initially and then decrease with increasing time on stream. At the same time, the selectivity to ethanol and 1-propanol increased relative to isobutyl alcohol. At long reaction times, the selectivity to ethanol was also observed to increase relative to 1-propanol. The selectivity to 1-butanol paralleled that of ethanol, while the selectivity to 2-methylbutanol and 2-methylpentanol decreased with time.

The effect of contact time on selectivity among the higher alcohols is summarized for CaC_2 in Table 2. Increasing the contact time from 3.3 to 9 s increased the selectivity to isobutyl alcohol, primarily at the expense of ethanol and 1-propanol. The selectivity to 1-butanol also fell off, but the selectivity to 2-methylbutanol and 2-methylpentanol remained essentially unchanged. Further increasing the contact time to 18 s had little effect on selectivity.

^{13}C labeling studies with $^{13}CH_3OH$ indicated that the source of the carbon in the higher alcohols was the methanol, not the metal acetylide. Figure 2 compares the GC–mass spectra of the isobutyl alcohol formed when $^{12}CH_3OH$ and $^{13}CH_3OH$, respectively, were passed over CeC_2 at 400°C. The shift in the parent ion from 74 to 78 amu when $^{13}CH_3OH$ was employed clearly shows that all four carbon atoms were derived from the ^{13}C-labeled methanol. Similar results were obtained when the spectra of 2-methylbutanol and 2-methylpentanol were compared.

In terms of conversion, the values which appear in the fourth column of Table 1 re-

TABLE 2

Effect on Contact Time on Alcohol Selectivity with CaC_2

Contact time (s)	Time (h)	EtOH	PrOH	i-BuOH	BuOH	2-Me BuOH	2-Me C_5-OH
3.3	3	12.5	15.9	58.0	3.0	6.0	4.7
9.0	3	1.5	3.6	83.8	1.0	5.9	4.2
18.0	5	1.3	3.5	86.1	0.5	4.6	4.0

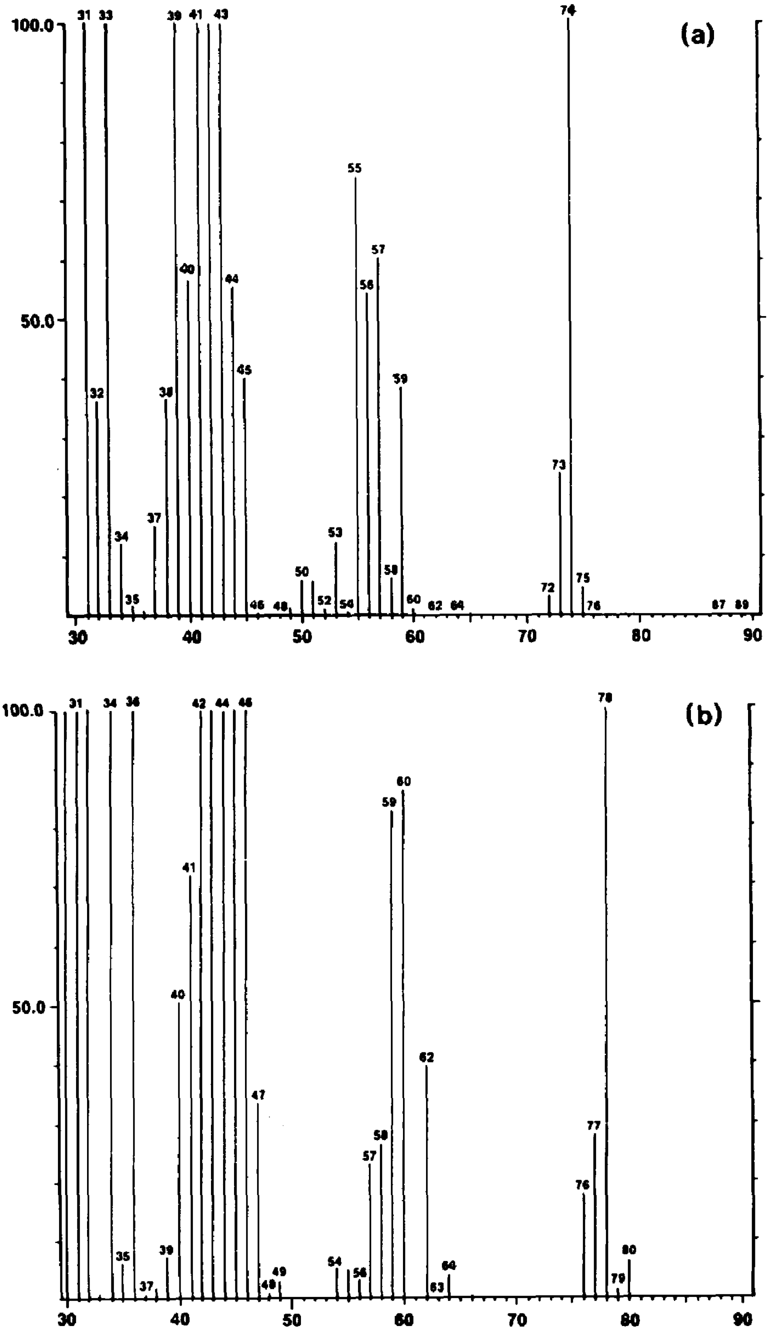


FIG. 2. Comparison of GC–mass spectra of isobutyl alcohol prepared from reaction of CeC_2 with $^{12}CH_3OH$(a) and $^{13}CH_3OH$(b) at 400°C.

flect the percentage of methanol converted to higher alcohols, calculated by dividing the total number of moles of carbon in the higher alcohols by the number of moles of methanol fed and multiplying by 100%. With contact times between 1 and 5 s at 400°C, the fraction of methanol converted to higher alcohols was quite low, typically

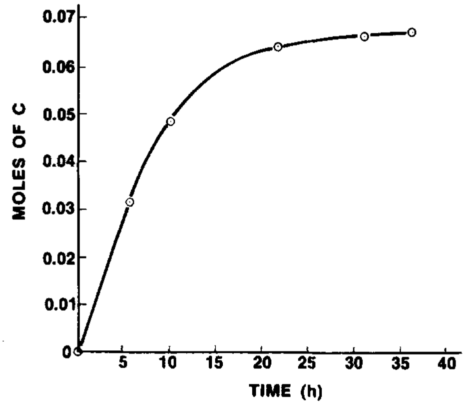


FIG. 3. Formation of higher alcohols vs time for the reaction of CaC_2 and CH_3OH at 400°C.

less than 2%. The data for Na_2C_2, CeC_2, and LaC_2 also show that the conversion decreased with time on stream.

A similar decrease in activity was also observed in a life study conducted with CaC_2 at 400°C. In agreement with the earlier batch autoclave studies (*10*), the life test in the flow reactor indicated that the formation of higher alcohols from methanol was not catalytic. The results of this experiment are presented graphically in Fig. 3, where the *y*-axis denotes the cumulative number of moles of carbon in the higher alcohols. It is clear from this data that higher alcohol production had essentially ceased after 36 h on stream. Conversion fell from a value of 7.7% after 5 h to less than 0.2% after 36 h. The higher initial conversion can be attributed to the 18-s contact time employed in this experiment. The changes in selectivity discussed in Fig. 1 were even more dramatic in the life study such that ethanol became the predominant alcohol in the final samples.

In no case was a turnover number greater than one obtained from any of the acetylides, turnover number being defined as the number of moles of methanol converted to higher alcohols divided by the number of moles of metal acetylide. For example, in the aforementioned life study with CaC_2, the turnover number was 0.35. X-Ray and infrared analysis of the residual solid from this experiment indicated that it was no longer calcium carbide but instead a complex mixture consisting of CaO, $Ca(OH)_2$, and $CaCO_3$. This observation is consistent with the decay in activity with time, because presumably the active material was converted to species which are inactive for higher alcohol formation. When methanol was passed over CaO, $Ca(OH)_2$, and $CaCO_3$ in separate experiments, no higher alcohols were formed.

Gaseous Products

In addition to the higher alcohols, a significant amount of gaseous products were also formed from the interaction of methanol with the metal acetylides. The distribution and yield of gaseous products was dependent on the metal acetylide employed. Usually significant quantities of carbon monoxide, hydrogen, and methane and much smaller amounts of acetylene, ethylene, ethane, CO_2, and higher hydrocarbons were observed. The values in columns 11 to 13 of Table 1 indicate the ratio of the number of moles of carbon in the acetylene, methane and carbon monoxide, respectively, in each gas sample and the number of moles of carbon in the higher alcohols in the corresponding liquid sample. The final column in Table 1 denotes the molar ratio of H_2 to CO for each gas sample.

In general, very little acetylene was present in the gaseous effluent. The greatest yield of C_2H_2 was observed with CaC_2, and its production steadily decreased with time. Only traces of acetylene were observed with the rare earth acetylides. The failure to observe large quantities of acetylene is consistent with the earlier autoclave work (*10*), and at this point, the fate of the carbon in the metal acetylide is not entirely clear. A possible explanation, which is also consistent with the mechanistic discussion later in this article, is that the methanol and the metal acetylide react initially to form the corresponding metal methoxide and acetylene, but that a good portion of the liberated C_2H_2 polymerizes to form carbonaceous residues which remain in the reactor. The tendency of acetylene to polymerize at elevated temperatures (*11*) as well as the dark color of many of the solid residues is supportive of this idea.

For the main group acetylides CaC_2 and Na_2C_2, the gas make was comparable to the higher alcohol yield on a mole of carbon basis. The activity of CaC_2 for gas production, excluding C_2H_2, appeared to be increasing slightly with time while the opposite was true for Na_2C_2. The results with Na_2C_2 were somewhat unique in that a very large volume of H_2 was evolved initially and the H_2/CO ratio remained considerably higher than the value close to two obtained with the other acetylides. These results will be discussed in view of the role of metal alkoxides in the discussion section.

The rare earth acetylides gave much higher yields of gaseous products than Na_2C_2 and CaC_2. For example, with LaC_2, the combined yield of CO and CH_4 initially was nearly an order of magnitude greater than the higher alcohol make, and the activity for gas production relative to alcohol formation continued to increase steadily with time on stream. ^{13}C-labeling experiments with CeC_2 and $^{13}CH_3OH$ indicated that both the CO and the CH_4 were derived from the methanol. It appears from these results that during the course of the reaction, the rare earth acetylides were converted into species which were catalytically active for the decomposition of CH_3OH to CO and H_2 and the methanation of carbon monoxide.

DISCUSSION

Mechanism of Higher Alcohol Formation

Any mechanism which is postulated to explain the formation of higher alcohols from methanol in this chemistry must account for the high selectivity to isobutyl alcohol which is observed. Negishi at first proposed a mechanism for isobutyl alcohol formation involving the intermediacy of dimethyl ether (*10*), but in later papers he described a "direct dehydration" mechanism (*12*) similar to that of Guerbet (*13*), Frolich (*14*), and Graves (*15*), in which the condensation of lower alcohols produced higher alcohols. We believe that the distribution of higher alcohols formed in the present work is more consistent with the intermediacy of formaldehyde and an aldol condensation scheme similar to that proposed by Morgan (*16*). Indeed, the similarity of the present product distribution to that which arises from the condensation sequence identified by Weiss and Tambawala (*17*) for formaldehyde in the homogeneous, base-catalyzed formose reaction is remarkable, as shown in Fig. 4. Essentially every higher alcohol we have isolated has a counterpart in formose chemistry, both in terms of carbon number and branched character. The observation that the branched 4-carbon polyol 2-hydroxymethylglycerol, **1**, is a

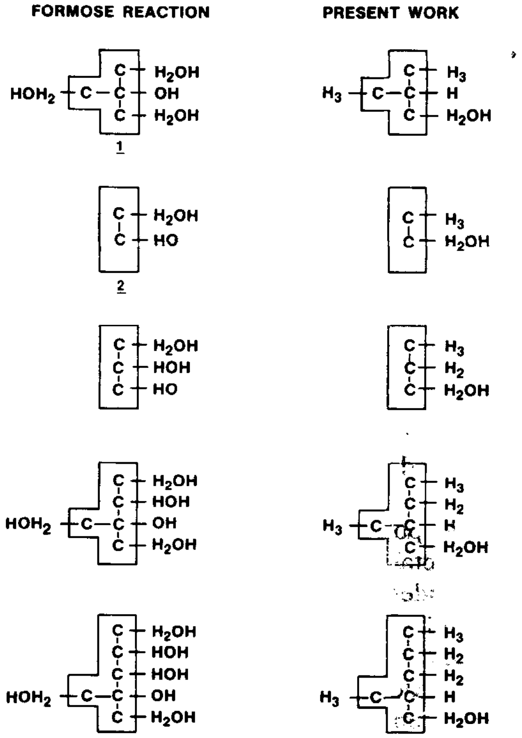
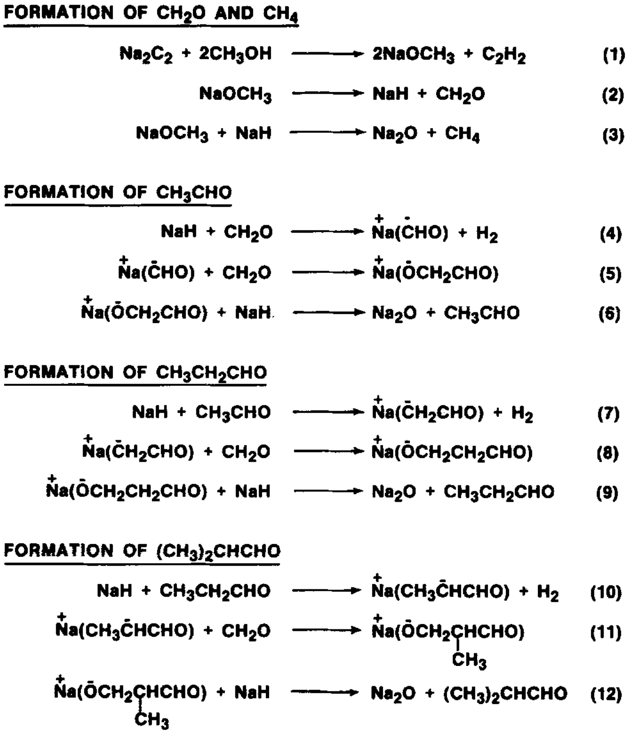


FIG. 4. Structural similarity of principal species identified in the formose reaction (*17*) and higher alcohols formed in the present work.



FORMATION OF CH_2O AND CH_4

$$Na_2C_2 + 2CH_3OH \longrightarrow 2NaOCH_3 + C_2H_2 \tag{1}$$

$$NaOCH_3 \longrightarrow NaH + CH_2O \tag{2}$$

$$NaOCH_3 + NaH \longrightarrow Na_2O + CH_4 \tag{3}$$

FORMATION OF CH_3CHO

$$NaH + CH_2O \longrightarrow \overset{+}{Na}(\overset{-}{C}HO) + H_2 \tag{4}$$

$$\overset{+}{Na}(\overset{-}{C}HO) + CH_2O \longrightarrow \overset{+}{Na}(\overset{-}{O}CH_2CHO) \tag{5}$$

$$\overset{+}{Na}(\overset{-}{O}CH_2CHO) + NaH \longrightarrow Na_2O + CH_3CHO \tag{6}$$

FORMATION OF CH_3CH_2CHO

$$NaH + CH_3CHO \longrightarrow \overset{+}{Na}(\overset{-}{C}H_2CHO) + H_2 \tag{7}$$

$$\overset{+}{Na}(\overset{-}{C}H_2CHO) + CH_2O \longrightarrow \overset{+}{Na}(\overset{-}{O}CH_2CH_2CHO) \tag{8}$$

$$\overset{+}{Na}(\overset{-}{O}CH_2CH_2CHO) + NaH \longrightarrow Na_2O + CH_3CH_2CHO \tag{9}$$

FORMATION OF $(CH_3)_2CHCHO$

$$NaH + CH_3CH_2CHO \longrightarrow \overset{+}{Na}(CH_3\overset{-}{C}HCHO) + H_2 \tag{10}$$

$$\overset{+}{Na}(CH_3\overset{-}{C}HCHO) + CH_2O \longrightarrow \overset{+}{Na}(\overset{-}{O}CH_2\underset{CH_3}{C}HCHO) \tag{11}$$

$$\overset{+}{Na}(\overset{-}{O}CH_2\underset{CH_3}{C}HCHO) + NaH \longrightarrow Na_2O + (CH_3)_2CHCHO \tag{12}$$

SCHEME 1

predominant product of the formose reaction at intermediate formaldehyde conversion levels is particularly relevant in view of its structural similarity to isobutyl alcohol.

We believe that the formation of higher alcohols from methanol can be explained by invoking formaldehyde as an intermediate in the mechanism shown in Scheme 1, in which Na_2C_2 is used for illustration purposes. In the first step, methanol reacts with the metal acetylide to produce acetylene and the corresponding metal methoxide, which undergoes subsequent thermal decomposition to generate the corresponding metal hydride and formaldehyde. Metal alkoxides have been prepared via the reaction of metal acetylides and the appropriate alcohol (*18*), and the decomposition of methoxides to produce formaldehyde has been reported by several groups (*19–21*). Furthermore, GC–mass spectrometric analysis has indicated the presence of CH_2O in many of our liquid samples.

In agreement with the ^{13}C-labeling studies, the formaldehyde is the source of the carbon in the higher alcohols and the acetylene generated in the first step does not become incorporated. As noted earlier, we believe that a significant fraction of the acetylene polymerizes to form carbonaceous residues which remain in the reactor. The intermediacy of metal hydrides is further supported by the formation of a similar distribution of alcohols when methanol was contacted with calcium hydride at 400°C. The results with CaH_2 reinforce the fact that the methanol is the source of the carbon in the higher alcohols.

The intermediacy of metal alkoxides is evidenced by experiments in which the thermal decomposition of metal methoxides was investigated. When CaC_2 and methanol were reacted in a Parr bomb at 200°C, no higher alcohols were formed but the solid obtained from this experiment displayed absorption bands in the infrared at 1080 and 1030 cm^{-1} characteristic of the C–

O stretching frequencies in metal alkoxides.

When this solid was heated to 400°C under helium, the liquid effluent contained isobutyl alcohol and smaller amounts of ethanol, 1-propanol, 1-butanol, 2-methylbutanol, and 2-methylpentanol. When commercial $NaOCH_3$ was heated above 300°C, decomposition to a black solid began concomitant with the evolution of much H_2 and a lesser amount of CH_4. These results are consistent with the composition of the gaseous effluent in the Na_2C_2/CH_3OH experiment. Isobutyl alcohol was also observed in the liquid effluent of the $NaOCH_3$ decomposition experiment.

The formation of methane is postulated to occur as a result of the chemistry in line 3. In studying the role of metal alkoxides in the decomposition of CH_3OH on tungsten surfaces, Ko *et al.* have linked the formation of methane to an alkoxide hydride intermediate (*21*) and in line 3, a metal methoxide and a metal hydride react to produce the metal oxide and CH_4.

Once the decomposition of the metal methoxide has occurred in line 2 to produce CH_2O and metal hydrides, all the necessary ingredients are present in the reactor for aldol condensation chemistry to take place. Although it is initially tempting to postulate a formose-type mechanism in which the polyols formed by condensation undergo hydrogenolysis to the appropriate alcohol (*22*), the thermodynamics of formose chemistry become unfavorable in the temperature regime of these experiments, i.e.,

$$2\,CH_2O \rightarrow HOCH_2CHO \qquad \Delta G_{673} = 3.8\ \text{kcal/mol} \quad (13)$$

$$HOCH_2CHO + CH_2O \rightarrow HOCH_2CHOHCHO \qquad \Delta G_{673} = 9.6\ \text{kcal/mol.} \quad (14)$$

Furthermore, it is difficult to totally explain the *selective* hydrogenolysis of the formose polyols to the distribution of alcohols obtained, i.e.,

$$HOCH_2CHOHCH_2OH + 2H_2 \overset{?}{\rightarrow} CH_3CH_2CH_2OH + 2H_2O \quad (15)$$

$$HOC(CH_2OH)_3 + 3H_2 \overset{?}{\rightarrow} (CH_3)_2CHCH_2OH + 3H_2O. \quad (16)$$

Recognizing these limitations, the remainder of Scheme 1 depicts an aldol condensation sequence which avoids the formation of polyols and which makes use of surface intermediates to generate aldehydes as the key chain growth species. In lines 4 and 5, the condensation of 2 molecules of CH_2O is catalyzed by the strong base NaH to produce $Na(OCH_2CHO)$ which is in essence a metal-bound glycolaldehyde unit. This intermediate subsequently reacts with a metal hydride to form acetaldehyde and the metal oxide, the hydride transfer here being similar to that which occurred in line 3. The overall reaction to produce acetaldehyde, obtained by summing lines 4 through 6, is

$$2NaH + 2CH_2O \rightarrow Na_2O + CH_3CHO + H_2 \quad (17)$$

for which $\Delta G = -38$ kcal/mol at 400°C. (ΔG values for NaH and Na_2O were obtained from Ref. (*23*), ΔG values for organic molecules were obtained from Ref. (*24*)).

Acetaldehyde possesses two β hydrogens and is capable of undergoing further condensation with CH_2O to produce propionaldehyde as shown in lines 7 through 9. Similarly, propionaldehyde can be converted to isobutyraldehyde using the same sequence of reactions, lines 10 through 12. However, isobutyraldehyde possesses only one β hydrogen and does not participate readily in further aldol condensation reactions; thus a high selectivity to iso-C_4 products would be expected.

The aldehydes formed as a result of condensation could be reduced to the corresponding alcohols by hydride transfer from M–H and proton transfer from a molecule of CH_3OH. Alternatively, reduction could occur via a crossed Cannizzaro reaction (*25*), in which a molecule of CH_2O is concomitantly oxidized to formic acid which could react with labile inorganic species in the system to generate metal formates. This behavior would be consistent with the noncatalytic nature of the reaction in that formates are known to decompose at elevated temperatures to form carbonates (*26*), and in the case of calcium, $CaCO_3$ was present in the solid residue but did not catalyze higher alcohol formation separately. Similarly, the formation of metal oxides in lines 3, 6, 9, and 12 of Scheme 1 is consistent with the decay in activity with time, as once again in the case of calcium, CaO was observed in the residue but did not catalyze the formation of higher alcohols by iteslf.

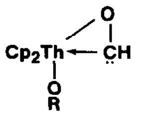
The proposed mechanism is also consistent with the observed increase in selectivity to isobutyl alcohol with increased contact time in that lengthening the residence time allows the acetaldehyde and propionaldehyde an opportunity to undergo further condensation reactions. The changes in selectivity among the higher alcohols with time can be explained if one considers that the concentration of formaldehyde in the system changes with time, particularly as the inorganic species which are capable of producing CH_2O from methanol are depleted.

As noted earlier, the yield of 1-butanol was observed to parallel that of ethanol and its formation is most likely explained by a base-catalyzed dimerization of acetaldehyde, similar to that which occurs in the Guerbet reaction (*27*). This notion is supported by the observation that the thermal decomposition of $Mg(OEt)_2$ at 400°C produced a liquid effluent which contained ethanol and 1-butanol as the predominant species with lesser amounts of acetaldehyde and 1-butyraldehyde.

A mixed-aldol condensation of CH_2O and 1-butyraldehyde would result in the precursor to 2-methylbutanol. The formation of 2-methylpentanol can be explained by dimerization of two molecules of propionaldehyde or alternatively, a condensation of acetaldehyde and propionaldehyde followed by condensation of the linear C_5 oxygenate with another molecule of formaldehyde. As in the case of isobutyl alcohol, the aldehyde precursors to 2-methylbutanol and 2-methylpentanol possess only one β hydrogen and would not be expected to participate readily in further aldol condensation reactions.

Relevance to the Isosynthesis

The high selectivity toward isobutyl alcohol observed in this chemistry is reminiscent of the heterogeneous isosynthesis catalysts which convert carbon monoxide selectively to isobutane and iso-C_4 oxygenates (*5–9*). Many of these catalysts employ thoria or another early transition metal oxide such as zirconia as the active component. In certain instances, the formation of iso-C_4 products from these catalysts has been enhanced by the addition of low levels of alkali.



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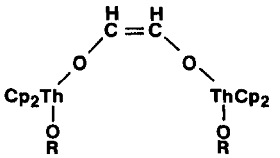
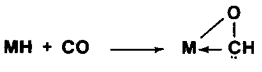


4

HOCH=CHOH

5

In view of the important role of thorium in these catalysts, recent results using Th organometallics are relevant. Thorium alkoxy hydrides have been shown to undergo facile CO insertion to generate the corresponding metal formyl, **3** (*28*). It has been suggested that the oxophilic nature of Th facilitates the reaction and imparts considerable carbene-like character to the formyl. Species like **3** have been shown to react further to form the enediolate dimer, **4.** Similar chemistry has been observed with zirconium hydrides (*29–32*), and the proposed mechanism of enediolate formation in these systems is summarized below (*33*).



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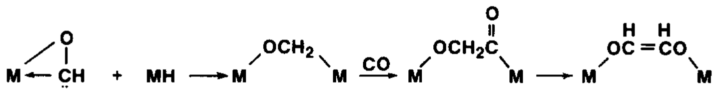
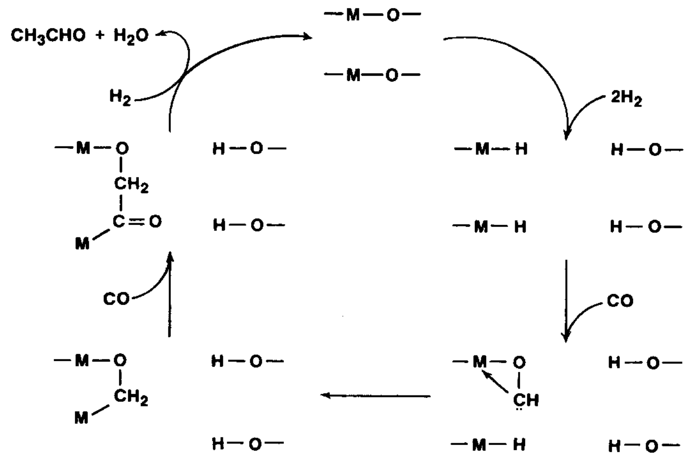


(19)

Much of the unique chemistry observed in these systems appears to proceed through metal-bound formyl or formaldehyde ligands which are stabilized by coordination to the oxophilic metal centers. The structure of the enediolate dimer, **4**, is particularly interesting in view of its similarity to the enol form of glycolaldehyde, **5.** As such the formation of **4** from metal bound formyls is remarkably similar to the initial dimerization of formaldehyde to glycolaldehyde, **2,** in the formose reaction.

This analogy to formaldehyde condensation may be relevant to the iso-C_4 selective heterogeneous catalysts which consist primarily of metal oxides such as ThO_2 and ZrO_2. In view of the organometallic results discussed earlier, Marks has postulated a mechanism for methanol formation (*28*) which involves CO insertion into an M–H bond formed at the surface of a metal oxide such as ZnO which is known to cleave H_2 heterolytically (*34*). As shown in Scheme 2, a similar mechanism can be postulated for the formation of acetaldehyde involving two M–H sites and the proposed intermediates for enediolate formation in the organometallic systems. In view of the isosynthesis, the spectroscopic observation of Th–H bonds on hydrogen-activated ThO_2 (*35*) is particularly relevant to the proposed analogy. We believe in the case of the isosynthesis and the formation of higher alcohols from methanol in the present work that ini-



SCHEME 2

tial C–C bond formation occurs via the intermediacy of metal hydrides and metal-bound formaldehyde and glycolaldehyde species. Whereas in Scheme 1 the formation of the metal oxide in line 6 leads to an irreversible decay in activity, the metal oxide site regenerated in Scheme 2 is capable of further reacting with H_2 to continue the catalytic cycle.

Once the chemistry in Scheme 2 has occurred, a high selectivity to iso-C_4 products would be expected if subsequent base-catalyzed condensation reactions were to proceed at the surface. A recent study has demonstrated the basic character of ThO_2 itself (*36*). Furthermore, it is known that the addition of low levels of alkali enhances the formation of higher-molecular-weight products from certain of these catalysts and in view of the preceding discussion, these basic promoters could also facilitate the necessary condensation reactions.

In view of the observation of surface formyls on zinc oxide exposed to CO and H_2 (*37*) and the recent discussion of the mechanism of formation of isobutyl alcohol over alkali-promoted Cu/ZnO catalysts (*38*), it is possible that the chemistry in Scheme 2 may also be important in systems containing zinc oxide.

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