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On the Mechanism of Higher Alcohol Formation over Metal Oxide Catalysts

I. A Rationale for Branching in the Synthesis of Higher Alcohols from Syngas

TERRY J. MAZANEC

The Standard Oil Company, Alternate Energy and Coal Research, Pleasant Valley Laboratory, Independence, Ohio 44131

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A new mechanism for the synthesis of alcohols from synthesis gas is proposed based on recent observations from surface spectroscopy, catalysis, and synthetic organometallic chemistry. Stepwise transfer of hydrogens to coordinated CO and chain growth by CO insertion provide the primary pathway for the construction of higher alcohols over metal oxide catalysts. The insertion of a carbon monoxide into a surface-bound aldehyde is proposed as the primary carbon–carbon bond forming step in the chain growth. A competing carbon–carbon bond-forming step is the reaction of a surface n^3-enolate with a surface alkoxide. This condensation reaction is critical for providing product distributions deviating from those predicted by simple polymerization schemes. A novel rationale is proposed to explain the selectivity to branched products. The relative stabilities of the enolate precursors to the various alcohols and the relative rates of the 1,2-shift reactions of methyl and hydrogen are the rate-controlling mechanistic features which regulate selective formation of branched higher alcohol products. The mechanism is related to the dehydration of secondary alcohols to 1-olefins catalyzed by basic metal oxides.

INTRODUCTION

It has been known for over 60 years that the reaction of carbon monoxide and hydrogen over certain alkalized metal oxides gives rise to alcohols (*1*). The product mixture obtained from this reaction is rich in branched higher alcohols, predominately isobutanol. Thus the reaction must be occurring by a mechanism other than the "carbide" polymerization scheme of Fischer and Tropsch since the distribution does not obey the Anderson–Schulz–Flory distribution and results in an abundance of branched products.

Several mechanistic proposals have been advanced to account for the unique product distribution obtained in these reactions. One of the earliest was that of Frolich and Cryder (*2*) who ascribed the formation of higher alcohols to the condensation of lower alcohols, e.g.,

$$2CH_3CH_2OH \rightarrow n\text{-Butanol} + H_2O.$$

The condensation mechanism was described by Graves (*3*) as including (i) higher alcohol formation from two lower alcohols, (ii) dehydration preferentially at the α carbon, except in the case of methanol, and (iii) dehydration at CH_2 groups in preference to CH_3 groups, and not at all on CH groups. Negishi (*4*) also adhered to the condensation mechanism, with the added feature that methyl groups α to the alcohol function were proposed to be particularly reactive.

Morgan *et al.* (*5*) described an aldol condensation starting with formaldehyde condensing to glycolaldehyde and proceeding through successive hydrogenations, dehydrations, and reductions to obtain the higher alcohols. Branching was thought to occur by the successive condensation of two molecules of formaldehyde with the β carbon of a single acetaldehyde molecule. Natta *et al.* (*1*) proposed that an alkali alkoxide reacted with CO to give the next

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higher carboxylate which is reduced to the alcohol.

More recently, Vedage *et al.* (*6*) have proposed a mechanism which incorporates features of aldol condensation, carbonylation, and Canizzaro reactions of two aldehydes to account for the product slate obtained over alkali-doped Cu/ZnO catalysts. And Smith and Anderson (*7*) have quantitatively described the higher alcohol distribution based on a scheme in which one- or two-carbon species can add to the growing intermediate to give the higher products. Growth at the α or β carbon atom was proposed, and more rapid β addition was postulated to account for the selectivity to branched products. The nature of the species involved in chain growth was not discussed.

It must be remembered that the product distribution obtained in these reactions is closely related to that found in isosynthesis experiments; indeed, operation of isosynthesis at low temperature (<375°C) results in substantial yields of branched alcohols, and operation of the process at higher temperatures results in the formation of branched hydrocarbons, primarily isobutylene and isobutane (*8*). Isomerization of straight-chain paraffins was ruled out as a possible mechanism of the isosynthesis by consideration of the isobutane/*n*-butane ratio, which deviated sharply from the equilibrium ratio.

Herein a mechanism is proposed which accounts for the product distribution obtained in alcohol synthesis experiments over metal oxides. Recent observations from surface spectroscopy, catalysis, and synthetic organometallic chemistry are brought together to demonstrate how the branching which predominates in higher alcohol and isosynthesis products can be explained on the basis of a single mechanistic proposal. The rationale for branching proposed can also be successfully applied to the dehydration of secondary alcohols to 1-olefins catalyzed by metal oxides.

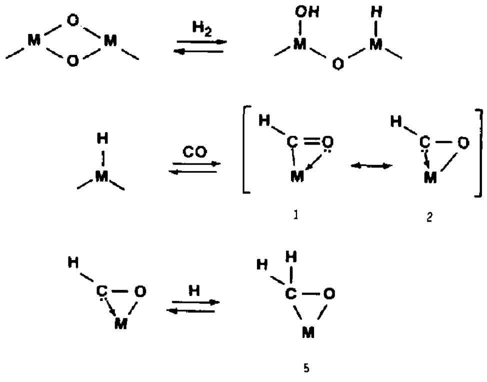
RESULTS AND DISCUSSION

A. The Mechanism of Chain Initiation

The first step in any synthesis gas reaction must be activation of the reactants by the catalyst surface. Hydrogen has been shown to undergo heterolytic cleavage (Scheme 1) on ZnO to give Zn–H and Zn–OH groups as detected by infrared spectroscopy (*9*). Other metal oxides which have long been known to catalyze alcohol synthesis reactions have recently been shown to activate hydrogen in a similar fashion. For example, evidence has also been obtained for the heterolytic cleavage of H_2 over ThO_2 to give Th–H and two types of Th–OH species (*10, 11*).

Adsorption of carbon monoxide on metal oxides has been carefully studied (*12*). Recent spectroscopic work has shown that the CO adsorbed on ZnO is bound through the carbon to a Zn^{2+} ion, the C–O vector makes a 30′ angle with respect to the surface, and the bound CO possesses a stronger C–O bond than free CO (*13*).

Coadsorption of carbon monoxide and hydrogen changes their individual adsorption behaviors on these oxides, probably through the formation of surface complexes (*14*). Infrared measurements and chemical trapping experiments have confirmed the existence of several species on ZnO, among them a formyl (*15*). Formation of a formyl group by hydride migration to a coordinated CO in a model system has been re-



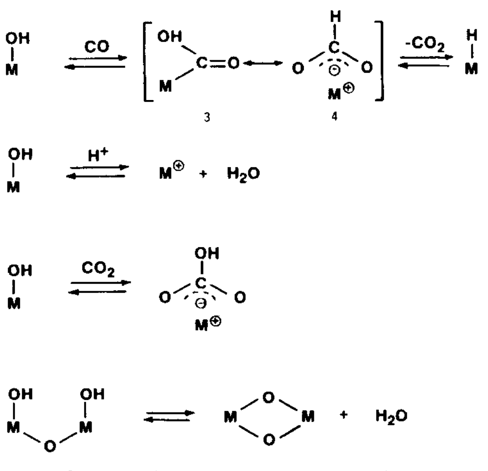
SCHEME 1. Chain initiation.

ported for $ThH[Cp^*]_2[OR]$ (R = $C[C(CH_3)_3]_2H$ or 1,5-$[C(CH_3)_3]_2$-C_6H_3 and $Cp^* = (CH_3)_5C_5$), which undergo rapid exchange with gaseous CO in solution at −40°C (*16*). Indeed, hydride migration was reported to have a lower activation energy than alkyl migration by about 7 kcal/mol. These formyls are thought to be stabilized by interaction of the oxygen of the formyl with the oxophilic metal, and several valence bond structures are able to be drawn (**1** and **2** in Scheme 1).

Klier recently reported that small amounts of alkali accelerate the rate of methanol formation over Cu/ZnO catalysts (*17*). This could be a reflection of the increased rate of production of the formyl species when the oxygen atom of CO is coordinated to an alkali cation. Assistance of this sort was demonstrated by Shriver *et al.* for the Lewis-acid-accelerated alkylation of CO, and by other recent examples (*18*).

In addition to the interaction with metal hydrides to produce formyl species, the adsorbed CO interacts with both metal and hydroxide (or oxide) ions to generate formate species (**3** and **4** in Scheme 2) (or CO_2^{2-}). Formate has been observed on ZnO exposed to CO/H_2 (*15*).

Vedage *et al.* have demonstrated the role of hydroxide in the production of formate species over Cu/ZnO catalysts by observing an accelerated rate of exchange among labeled and unlabeled CO after the injection of water (*17*). Rapid scrambling of labeled oxygen in $CO_2/CO/H_2$ mixtures over Cu/ZnO catalysts has also been reported by Kung *et al.* (*19*).



SCHEME 2. Water–gas shift reaction.

For ZnO definitive proof of the interaction between CO and surface oxygen ions comes from the rapid exchange of ^{18}O label between labeled CO and unlabeled surface oxide sites at 300–350°C (*20*), and for ZrO_2 from the reduction of CO to labeled formate and methoxide by surface OD groups (*21*).

On the working catalyst there will be both hydride and hydroxide species present on the surface, and so both formyl and formate are likely to be present. Formate can be reduced to formyl by hydrogen as proposed by Klier and co-workers (*17*), or the two can interconvert by interaction with a surface oxide ion.

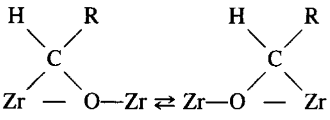
Although many discrete metal formyl complexes are known, most are very unstable with respect to decarbonylation. The complex $[(\eta_5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}CHO)(\mu\text{-}H)$ (*22*) contains a formyl which is stabilized by further coordination of the oxygen and carbon atoms to a second tantalum atom. On metal oxide surfaces the formyl moiety could obtain additional stability by interaction with one or more metals at a surface defect or vacancy. Acyls bound in this manner have been reduced to bridging aldehydes by the action of hydride donors (*23*). Muetterties and Stein pointed out that the Zn–H present on the surface of ZnO should be sufficiently hydridic in nature to effect this reduction as well (*24*). Thus a metal oxide surface provides the appropriate environment for partial stabilization of formyl species as well as the hydridic hydrogens necessary for their reduction to formaldehyde.

A well-characterized model for the first steps of CO reduction on a metal oxide surface is the reaction of CO with $[(Cp)_2Zr\ HCl]_n$ to give $[(Cp)_2ZrCl]_2(\mu\text{-}CH_2O)$ (*25*). This molecule has a bridging formaldehyde moiety in which the O atom of the formaldehyde bridges the two metals and the methylene fragment is bonded to the O and one Zr. Formaldehyde bound to a metal oxide surface could easily be stabilized in this fashion.

Other examples of this type of bonding of formaldehyde to metal complexes have been reported in the last few years (*26*). They can be viewed as having a side-on bonded formaldehyde where both carbon and oxygen interact with one metal atom and the oxygen atom interacts with a Lewis acid center (the second Zr). If the oxygen atom of the aldehyde is considered to be part of the metal oxide lattice, then these complexes appear as models for alkylidene species bound to a metal oxide surface.

Formaldehyde has frequently been hypothesized to be an intermediate in alcohol synthesis, either as the free molecule or as a surface-bound structure (*27*). The likelihood of finding free formaldehyde under alcohol synthesis conditions is slim due to thermodynamic limitations, but these considerations do not apply to surface structures. Sapienza *et al.* have postulated the "oxide mechanism" wherein an oxygen-bound formaldehyde is the key intermediate in synthesis gas reactions, but their structure is more accurately described as an oxymethylene since metal–carbon interactions are discounted (*28*).

An interesting feature of the family of aldehyde-bridged binuclear zirconocene model complexes is the rapid automerization process, or dyotropic rearrangement, which exchanges the alkylidene fragment between the two metals (*29, 30*):



(1)

The barrier to exchange was calculated to be from 7 to 20 kcal/mole depending on the nature of R and the other ligands on zirconium (*30*).

When extended to surface species of a similar structure this represents a convenient low-energy pathway by which alkylidene species can "walk" across a metal oxide surface, or at least between two adjacent metal centers. Sapienza's oxymethylene may represent the transition state in this dyotropic rearrangement.

Evidence for the role of aldehydic species as precursors to alcohols on Cu/ZnO catalysts has been presented by Vedage *et al.* (*31*). They reported that amines added to the feed of methanol synthesis reacted to form *N*-methylamines by intercepting aldehyde intermediates. It was also observed that the water–gas shift reaction was unaffected by the added amine, indicating that the aldehydic species was not involved in the shift.

Further hydrogenation of the bound formaldehyde can lead to methoxy species, methanol and methane. The selectivity between methanol and methane is likely to be a reflection of the relative rates of hydrogenation of the metal–oxygen and carbon–oxygen bonds of the methoxy intermediate, which are determined by the extent to which the bound formaldehyde species interacts through its oxygen atom with a neighboring metal cation. If this interaction is very strong and additional strain is put on the C–O bond by coordination to a metal ion fixed in a rigid lattice structure, then the C–O bond is more susceptible to hydrogenation. If the interaction is weaker and less demanding in terms of strain energy introduced, then oxygenated products are favored.

B. The Mechanism of Chain Growth

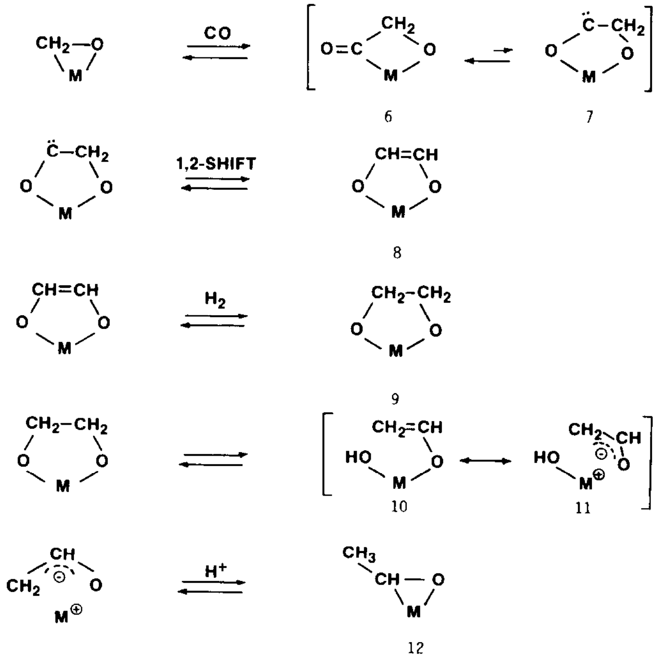
The primary carbon–carbon bond-forming step is proposed to be a CO insertion into the metal–carbon bond of a bound aldehyde to make a cyclic acyl, **6.** The CO insertion can be viewed as CO trapping of Sapienza's oxymethylene transition state structure in the dyotropic rearrangement of a bound aldehyde (vide supra). The rapidity of reaction of the zirconium-bound aldehyde model complexes with CO to produce (η_1-acyl)zirconocene species (*30*) confirms the CO insertion into the metal–carbon bond of the bridged aldehydic compounds first postulated by Wolczanski and Bercaw (*32*) (Scheme 3). Strong kinetic evidence for the CO insertion reaction was also reported for Th–acyl complexes (*33*). For a metal oxide surface, interaction of the acyl with neighboring metal or alkali ions is a potential means of stabilization.

The acyl can exist in a second valence bond structure, **7**, in which the carbonyl carbon has assumed carbenic character. Through the intermediacy of this carbenic isomer, the cyclic acyl can rearrange to an enediolate, **8**, via a 1,2-shift of a hydrogen. The rearrangement has been confirmed for various zirconium complexes.

This observation underscores the mechanism of formation of the enediolate as postulated by Marks and co-workers (*34*) for closely related thorium and uranium systems. Recent extension of this chemistry to the $(Cp^*)_2Hf$ system ($Cp^* = C_5(CH_3)_5$ (*35*) speaks for its generality among Group IVB metal complexes. The 1,2-shift is a key feature in determining the selectivity of the alcohol catalysts for branched products as will be discussed later.

In recent work it has been observed that for an extensive series of Th–acyl complexes the rate of the 1,2-shift parallels that of the 1,2-shift in related carbene complexes, e.g., $Si(CH_3)_3 > H > CH_3$ (*36–38*), demonstrating the importance of valence structure **7** in determining the reactivity of the acyl. Further support for the carbenic nature of Th–acyls stems from their reaction with phosphines to form ylides (*33*). The relative ability of metal oxides to stabilize the carbenic form of the acyl intermediate as in the model complexes may be an important aspect of their role in higher alcohol synthesis.

Hydrogenation of the enediolate complex is a rapid process in the presence of excess H_2 to produce a coordinated diol, **9** (*35*). Indeed, precedent for the first three steps in Scheme 3 comes from the catalytic homogeneous hydrogenation of coordinated dihapto acyl compounds by a thorium hydride reported by Maata and Marks (*39*).



SCHEME 3. Chain propagation.

Simple dehydration of the coordinated diol by elimination of MOH gives rise to a coordinated enol, **10**. Enols are known to be stabilized by coordination to a saturated and sterically congested Th^{4+} center (*36*). Moreover, the dehydration of alcohols over ThO_2 has been known for many years and has been proposed to proceed through a base-catalyzed elimination mechanism (*40*). Evidence for the ease of this dehydration reaction comes also from the study of the H–D exchange reaction between the CD_3 groups of d^8-isopropanol and the hydroxyls remaining on ZrO_2 (*41*). Another valence bond structure can be drawn for the coordinated enol emphasizing its η^3-enolate character, **11**, which shows how it can be an intermediate in the dehydration as well.

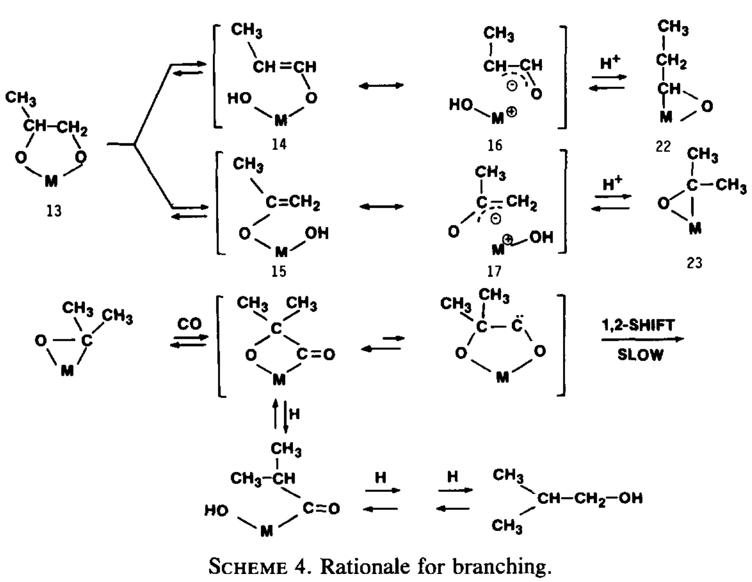
Protonation of the η^3-enolate at the terminal carbon atom leads to what can be considered either as a coordinated aldehyde or as an alkylidene bridging a metal–oxygen bond, **12**. Formation of an aldehyde with one more carbon atom from a coordinated aldehyde completes the cycle for addition of a carbon to the chain.

C. A Rationale for Branching

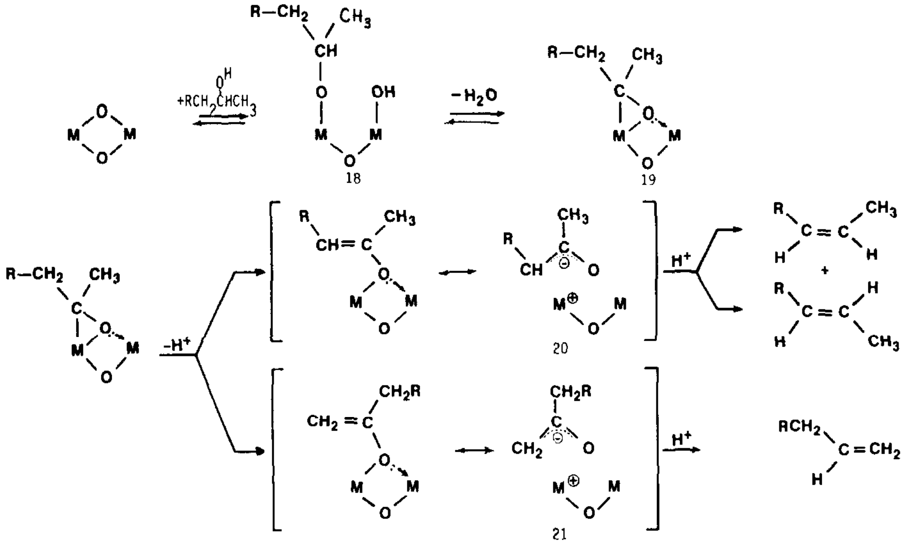
The incorporation of the second CO follows much the same path as outlined for the first CO. When the 1,2-shift occurs there is the chance that either a methyl group or a hydrogen will be transferred; however, the two choices lead to identical structures.

After hydrogenation of the resulting enediolate we are left with a coordinated 1,2-propanediolate, **13** in Scheme 4. This structure can dehydrate in one of two possible directions to give two different enols (**14** and **15** in Scheme 4). When these enols are drawn in η^3-enolate ions **16** and **17**, with the charge delocalized over the oxygen and two carbons, it becomes clear that the less sterically hindered structure is the one with the methyl group on the center carbon atom as compared to the one having the methyl group on the terminal carbon atom. More important are the electronic factors which also favor the electron-donating methyl group being situated on the less electron-rich central carbon atom. There are expected to be more branched enolates in the reservoir of surface species than there are linear species.

Pertinent to the discussion of enolate stability on basic metal oxides is the selective catalytic dehydration of secondary alcohols to 1-olefins observed with ThO_2, ZrO_2, group IIIB, lanthanide, and actinide oxides (*40, 42*). At 350–425°C with each of these



SCHEME 4. Rationale for branching.



SCHEME 5. Mechanism of secondary alcohol dehydration over basic metal oxides.

materials, more than 80% of the olefin formed is 1-olefin (balance *cis*- and *trans*-2-olefin) in the dehydration of 4-methyl-2-pentanol (*42*). The major competing reaction is the dehydrogenation of the secondary alcohol to the ketone, which appears to be highly dependent on the coverage of the surface with hydroxyl groups (*43*). The dehydrogenation reaction is favored at low temperatures.

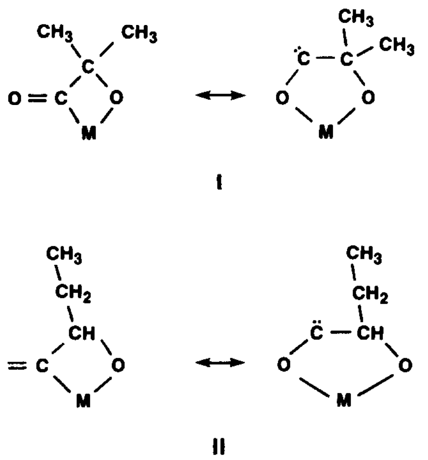
The selectivity of the dehydration reaction can be explained by applying the principle of microscopic reversibility to the same steps as those postulated for higher alcohol synthesis (Scheme 5). A secondary alcohol reacts with the metal oxide surface via addition to a metal–oxygen ion pair. The alcoholate, **18**, is dehydrogenated by transfer of a hydride from the α carbon atom to a nearby metal ion or hydroxyl group to generate a bound ketone, **19**. This step is analogous to a β-hydride abstraction in organometallic chemistry, and has been observed in alcohol reactions over Cu(110) by Bowker and Madix (*44*). In their study adsorbed oxygen enhanced this reaction by providing a low-energy pathway to remove the H atoms as water. On a metal oxide surface there are many oxygen atoms available for hydrogen removal in this manner.

In the next step of the dehydration the resulting bound ketone is deprotonated from the β carbon to give either of two η^3-enolates, **20** and **21**, which can be reprotonated at the α carbon to liberate the olefins. The selectivity to the different olefins is a measure of the relative population of enolates on the surface. The selectivity to 1-olefin demonstrates that its precursor enolate, **21**, is favored over the more highly substituted one, **20**.

In the synthesis of alcohols the enolates, **16** and **17**, are protonated to their respective bound aldehyde structures, **22** and **23**, and the cycle continues via a third CO insertion step to give the acyl structures **I** and **II** (Scheme 6).

These acyls also are subject to undergoing a 1,2-shift reaction. Now, however, the 1,2-shift reaction is different for the two acyls.

In the case of the acyl derived from the "iso" enolate, **I**, there are only methyl groups available for participation in the 1,2-shift reaction. Since the known migratory aptitude of methyl is much lower than that of hydrogen (*36–38*), the "iso"-acyl undergoes competing reactions such as hydrogenation to the alcohol (isobutanol) which can be desorbed from the surface. Precedent for



SCHEME 6. Structures I and II.

the hydrogenation of an acyl of this type has been reported for Zr complexes (*45*). The desorption reaction is not equilibrium limited since the vapor pressures of the alcohols are exceedingly low. The desorption of isobutanol serves as the kinetic drain of alcohols from the system.

On the other hand, **II**, the acyl derived from the "linear" enolate, has a β hydrogen readily available for the 1,2-shift. Thus the acyl is transformed into the enediol and undergoes further chain growth. Hydrogenation to the alcohol is still a competing reaction for this acyl, but the 1,2-shift reaction is rapid and much of **II** goes on to yield higher products.

Thus the differences in the stabilities of the two enolates and the differences in the reactivities of the acyls which result from CO insertion into the enolates favor the selective synthesis of 2-methyl alcohols rather than linear alcohols over metal oxide catalysts.

D. Deviations from Schulz–Flory Distributions

One of the key features of the higher alcohol synthesis and isosynthesis over metal oxide catalysts is the strong deviation of the product mixture from that which is predicted on the basis of a simple Schulz–Flory polymerization scheme. The mixture is relatively low in C_2 and C_3 products but the C_4 and higher products nearly follow that predicted on the basis of a simple polymerization mechanism.

The mechanism developed above does not predict deviation of the product from the Schulz–Flory distribution (*46*), but only that branched products will be favored. The CO insertion chain growth step is addition of a monomer to the growing chain. In the absence of competing reactions there should be no deviation from the predicted polymerization distribution. Thus, there must be a competing reaction which is increasing the number of C_4 and higher products at the expense of C_2 alcohols.

The reaction giving rise to increased higher products is a condensation reaction which is faster for the C_2 species than for the C_3 and C_4 species and has no equivalent in the C_1 manifold. This reaction involves alkylation by a nearby alkoxide group of an η^3-enolate at the terminal carbon atom to form an aldehyde. This reaction is most kinetically significant for the C_2 enolate. Of the two C_3 enolates, the more stable one is planar with the methyl group perpendicular to the surface, and therefore much less susceptible to attack. The other C_3 enolate is less abundant but its alkylation leads to intermediates which continue on to secondary alcohols and ketones or to branched C_4 and higher alcohols.

The condensation reactions are slow compared to CO insertion reactions, but are kinetically significant due to the large surface concentration of methoxide groups on the working catalyst (*46*). Condensation reactions of larger alkoxide species are possible but negligibly slow due to the small concentrations of these species on the surface.

A scheme in which ethylene reincorporation in the growing chain competes with polymerization of C_1 fragments in the Fischer–Tropsch synthesis has been analyzed mathematically (*47*). It was calculated that for sufficiently high rates of monomer polymerization compared to ethylene incorporation there could be a dip in the weight distribution at C_2 and little effect on the C_{3+} product distribution. The scheme proposed here is similar except that the fragment which is incorporated into the growing chains is derived from an alcohol and the C_1 polymerization is thought to proceed by CO insertion.

SUMMARY AND CONCLUSIONS

The mechanism described herein provides for the formation of higher alcohols from carbon monoxide and hydrogen by using individual chemical reactions having precedent in organometallic chemistry and surface science. A stepwise transfer of hydrogens to a coordinated carbon monoxide molecule is the primary pathway of alcohol synthesis over metal oxide catalysts. The insertion of a carbon monoxide into a surface-bound aldehyde is proposed as the primary carbon–carbon bond-forming step in the chain growth. A competing carbon–carbon bond-forming step is the reaction of a surface enolate with a surface alkoxide; this may be the mechanism of the aldol condensation reaction over basic metal oxides.

A novel rationale is proposed to explain the selectivity to branched products. The relative stabilities of the enolate precursors to the various alcohols and the relative rates of the 1,2-shift reactions of methyl and hydrogen are the rate-controlling mechanistic features which regulate selective formation of branched higher alcohol products. The enhanced stability of a branched enolate compared to a linear enolate also explains the mechanism of dehydration of secondary alcohols to 1-olefins which is catalyzed by basic oxides. Thus, the mechanism proposed here is versatile enough to predict relative product distributions in related base-catalyzed reactions.

It is well known that different metal oxide catalysts give rise to somewhat different product mixtures in alcohol synthesis, but all of those which are based on nonreducible oxides show high selectivity to branched primary alcohols. As described above the differences can be attributed to the different bonding properties of the various metals to the organic intermediates in the scheme, particularly to the strength of the metal–oxygen bond, but the similarities arise from the generality of the mechanism of the reaction. A detailed analysis of the differences and similarities of the alcohol mixture produced over various metal oxide catalysts is being completed based on a kinetic model rooted in the above scheme. The results will be the subject of a future communication (*46*).

It remains to be seen whether the principles outlined herein can be applied generally to other types of reactions and catalyst systems. A particularly relevant reaction to study is the synthesis of ethylene glycol. It is easy to imagine that the enediolate intermediate invoked here is common to the ethylene glycol reaction.

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Note added in proof. Evidence for the intermediacy of an η^3-enolate in aldol condensation in a model system has recently been reported [J. J. Doney, R. G. Bergman, and C. H. Heathcock, *J. Amer. Chem. Soc.*, **107**, 3724–3726 (1985)].

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