

# The Formation of Ketones in the Presence of Carbon Monoxide over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>

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The reaction of linear primary alcohols over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> was studied under nitrogen and under carbon monoxide at 285°C and 1 to 65 atm. The principal products for alcohols with  $n$  carbon atoms were, in addition to the corresponding aldehydes, esters with  $2n$  carbon atoms, ketones with  $2n$  carbon atoms, and ketones with  $2n-1$  carbon atoms. Under nitrogen the esters predominated, but under 65 atm of carbon monoxide the principal condensation products were ketones with  $2n$  carbon atoms. Isotopic labeling studies showed that carbon from CO was not incorporated into the esters and ketones, that oxygen, on the other hand, was exchanged between CO and the reaction products, and that the ketones were formed by an aldol-type mechanism. The changes in selectivity observed under carbon monoxide are attributed to changes in the catalyst surface resulting from the removal of lattice oxygen by the CO and the formation of oxygen vacancies. © 1989 Academic Press, Inc.

## INTRODUCTION

Methanol catalysts based on copper and zinc oxide can convert synthesis gas to methanol very selectively (1). At higher temperatures and lower H<sub>2</sub>/CO ratios than those used for the selective synthesis of methanol, substantial amounts of higher alcohols are also produced (2, 3). The formation of the higher alcohols may be accompanied by the formation of other oxygenated species, including aldehydes, esters, and ketones (4, 5).

It is known (6) that alcohols can be converted to esters and ketones over either copper or zinc oxide. Thus, it seems reasonable that the esters and ketones produced from synthesis gas over CuO/ZnO are secondary products formed by the reaction of alcohols. However, the influence on this reaction of synthesis gas, and in particular of carbon monoxide, is not clear.

In the work reported here, the reactions of some primary alcohols catalyzed by CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> were studied under nitrogen and under carbon monoxide to determine the influence of CO on the course of the reactions. Because it was found that

carbon monoxide affects both the type and the distribution of the products, additional studies were made using reagents labeled with carbon-13 to clarify the mechanism of the reaction and to determine whether carbon monoxide is incorporated in the products.

## EXPERIMENTAL METHODS

**Catalyst.** The catalyst used in this study was a CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst (Cu : Zn : Al = 1 : 1 : 0.3 atom ratio, CuO = 43.2 wt%) obtained from UCI (designated C 79-2). The ¼-inch tablets were crushed, sieved to 16/40 mesh size, and calcined in air at 350°C for 4 h.

**Feeds.** Hydrogen (from Linde, 99.99%) was passed through a Deoxo purified to remove traces of oxygen and then through a 4-Å molecular sieve trap to remove water. Carbon monoxide (from Matheson, 99.5%) was purified by passing the gas through an activated charcoal trap to remove possible metal carbonyls. Absolute ethanol was obtained from USI. Reagent grade 1-propanol and 1-butanol were obtained from Mallinckrodt Chemicals and used as received. Carbon-13 labeled ethanol, 1-butanol, and

carbon monoxide were obtained from MSD Isotopes and used as received.

**Apparatus and procedure.** Catalytic tests were performed in a tubular fixed-bed reactor at 285°C and 65 atm. Gas flows were controlled with mass flow controllers and liquids were pumped to the catalyst through the preheater section of the reactor. In a typical experiment, 2.5 ml of catalyst and 7.5 ml of alundum (16/40 mesh size) were mixed and loaded into the reactor to form a 10-ml bed. The bed temperature was raised to 200°C under nitrogen flowing at 2500 GHSV, and the catalyst was reduced at 200°C for 4 h in a stream of 3% H<sub>2</sub> in helium at 5000 GHSV. After reduction, the reactor was purged with nitrogen and the catalyst was heated to 285°C while the pressure was increased to 65 atm. The reactants were then passed over the catalyst at 285°C and 65 atm. The products were passed through a trap at 0°C and liquid samples were collected over 4-h periods. These samples were analyzed off-line using a capillary column with FI detector and a Porapak Q column with a TC detector. Analysis of the off-gas was performed on-line at 20-min intervals using a multicolumn applied automation gas chromatograph (Model 21).

As described elsewhere (7), isotopic studies were performed with a 2.1-mm diameter stainless-steel reactor mounted on a Hewlett-Packard 5880-A gas chromatograph equipped with a 5970 mass selective detector. In these experiments, 100 mg of catalyst was loaded into the reactor and purged with helium at about 6000 GHSV while the temperature was raised to 200°C. The catalyst was reduced for 2 h in a stream of 8.5% H<sub>2</sub> at 6000 GHSV. After reduction, the catalyst was purged with helium as the temperature was raised to 285°C. Two matched capillary columns were used to separate the products and deliver them to the mass selective detector and to an FI detector. Sampling of the reactor effluent was accomplished on-line with a gas chromatographic valve. This arrangement allowed for simultaneous quantitative and

qualitative analysis of the products. Feed rates were controlled with Matheson mass flow controllers, and the gases were passed through a saturator held at constant temperature to deliver liquid feeds to the reactor (7).

## RESULTS

The products obtained by passing ethanol, 1-propanol, and 1-butanol over the reduced CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst under nitrogen at 285°C and 65 atm are listed in Tables 1, 2, and 3, respectively. As the number of carbon atoms, *n*, of the alcohol increased, the alcohol conversion decreased, from 80% for ethanol to 51% for butanol. For each alcohol the principal products were the corresponding aldehyde with *n* carbon atoms and the ester with 2*n* carbon atoms. Thus, ethanol yielded acetaldehyde and ethyl acetate, propanol yielded propanal and propyl propanoate, and butanol yielded butanal and butyl butanoate. Ketones were also formed but in lesser amounts than the esters; they included the symmetrical ketone containing 2*n*-1 carbon

TABLE 1

Composition of the Liquid Produced by Passing Ethanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at 285°C and 65 atm

Carrier gas	N <sub>2</sub>	CO
Ethanol fed (mmol)	131	148
Conversion (%)	80	96
Composition of liquid (mmol)		
Methanol	0.7	14.1
Ethanol	25.9	5.7
Acetaldehyde	2.9	0.2
Ethyl acetate	28.2	1.4
Acetone	1.6	0.2
Butanone	1.9	2.0
1-Butanol	0.3	1.2
1-Propanol	0.1	1.2
2-Methyl-1-propanol	0.0	2.2
3-Methyl-2-butanone	0.0	1.3
2-Pentanone	0.6	1.9
C6 ketones	1.5	9.0
C7-C9 ketones	0.0	11.7
Water	6.6	0.5

TABLE 2

Composition of the Liquid Produced by Passing  
1-Propanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at 285°C  
and 65 atm

Carrier gas	N <sub>2</sub>	CO
1-Propanol fed (mmol)	119	114
Conversion (%)	62	96
Composition of liquid (mmol)		
Methanol	1.6	4.0
1-Propanol	45.5	4.3
Propanal	4.7	0.4
Propyl propanoate	15.9	1.3
3-Pentanone	2.8	3.5
2-Methyl-3-pentanone	2.8	25.9
2-Methyl-propanal	0.3	8.1
C7 ketones	0.0	2.4
Water	1.9	0.3

atoms (acetone from ethanol, 3-pentanone from propanol, and 4-heptanone from butanol) and the unsymmetrical ketone containing  $2n$  carbon atoms (butanone, 2-methyl-3-pentanone, and 3-methyl-4-heptanone, respectively). With ethanol, homologs containing  $3n-1$  and  $3n$  carbon atoms were also observed.

When carbon monoxide was used instead of nitrogen the overall alcohol conversion increased and the distribution of products changed substantially. In contrast to the predominance of esters that was observed under nitrogen, ketones were now the main products; moreover, under CO the ketones containing an even number of carbon atoms were formed preferentially. The products obtained by passing each of the alcohols over the catalyst under 65 atm of CO are compared with those obtained under 65 atm of nitrogen in Tables 1, 2, and 3. With ethanol under CO, substantial amounts of higher members of both the series of ketones containing  $kn-1$  carbon atoms and that containing  $kn$  carbon atoms were formed, in addition to the lower members of the series observed under nitrogen. With propanol and butanol under CO the lower members of the series ( $k = 2$ ) were the principal products, and the ketones of even car-

bon number ( $2n$ ) exceeded the ketones of odd carbon number ( $2n-1$ ) by nearly an order of magnitude. In the presence of the hydrogen produced by the dehydrogenation of the starting alcohol, a small fraction of each ketone was converted to the corresponding secondary alcohol. These secondary alcohols are generally not listed separately in the tables, and their yields are included with those of the corresponding ketones.

Both copper and zinc oxide catalyze the dehydrogenation of alcohols (9a); accordingly, the Cu/ZnO catalyst used in this study was very active for the dehydrogenation of primary alcohols to aldehydes. Most of the hydrogen generated in the reaction was recovered (8); some hydrogen was consumed in the hydrogenation of the product ketones to the corresponding secondary alcohols and of the product aldehydes to primary alcohols. Under CO some of the hydrogen was consumed in the synthesis of methanol ( $\text{CO} + \text{H}_2 = \text{CH}_3\text{OH}$ ).

The products of the reactions carried out under nitrogen contained small amounts of water, apparently formed by dehydration of

TABLE 3

Composition of the Liquid Produced by Passing  
1-Butanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at 285°C and 65 atm

Carrier gas	N <sub>2</sub>	CO
1-Butanol fed (mmol)	126	126
Conversion (%)	51	91
Composition of liquid (mmol)		
Methanol	Trace	8.2
1-Butanol	61.4	11.2
Butanal	12.8	1.4
Butyl butanoate	13.9	8.9
4-Heptanone	0.3	1.9
3-Methyl-4-heptanone	0.3	21.4
Dibutyl ether	3.3	5.8
3-Methyl-butanal	0.0	0.3
C5 alcohols	0.0	2.5
C9 ketones	0.0	6.2
C10 ketones	0.0	0.4
Methyl-butanoate	0.0	2.7
Other esters	0.0	1.9

the alcohols. Small amounts of CO<sub>2</sub> were also observed (8). These probably were produced by the reaction of aldehydes with the catalyst (see Eqs. (6) and (7) below). Under CO there was less water and more CO<sub>2</sub>, because the water was consumed in the water-gas shift reaction (CO + H<sub>2</sub>O = H<sub>2</sub> + CO<sub>2</sub>).

The additional carbon dioxide may have formed not only by the water-gas shift reaction, but also by the reaction of CO with the catalyst. Evidence for the formation of CO<sub>2</sub> by the reaction of CO with the reduced catalyst is provided by the following experiment carried out under reduced pressure of CO in a glass vessel. The catalyst was reduced in flowing hydrogen under atmospheric pressure for 5 h at 250°C and was evacuated overnight at 250°C. After the sample was cooled to 25°C under vacuum, the vessel was filled with 100 Torr of CO; it was then heated slowly from 25 to 250°C. The composition of the gases above the catalyst was determined by GC analysis. Gaseous CO<sub>2</sub> was formed at temperatures above 150°C.

The influence of the CO pressure on the distribution of the products formed by the reactions of the alcohols is illustrated by the data shown in Tables 4 and 5. In Table 4

TABLE 4

Influence of CO Pressure on the Reaction of 1-Butanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at 285°C

Reactor	HP	HP	Micro
Pressure (atm)	65	1	1
Contact time (sec)	65	1	1
Composition of liquid (wt%)			
Methanol	3.3	0.7	nd
1-Butanol	10.6	25.4	17.9
<i>n</i> -Butanal	1.3	52.0	57.7
Butyl butanoate	16.2	7.1	8.2
4-Heptanone	2.8	5.9	5.6
3-Methyl-4-heptanone	34.8	4.0	3.3
2-Ethyl-hexanal	0.0	1.4	1.9
2-Methyl-butanal	0.4	0.0	0.1
C5 alcohols	2.8	0.0	0.0
Other	27.8	3.5	5.3

TABLE 5

Influence of CO Pressure on the Reactions of Ethanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> at 285°C

Reactor	HP	Micro	Micro
Pressure (atm)	65	1	1
Contact time (sec)	65	1	1
Feed: Ethanol	Anhydrous <sup>a</sup>	Anhydrous <sup>b</sup>	95% <sup>c</sup>
Product composition (wt%)			
Methanol	11.0	0.0	0.0
Ethanol	6.7	14.5	18.0
Acetaldehyde	0.3	40.4	56.0
Ethyl acetate	1.4	16.5	7.3
Acetic acid	0.0	0.1	7.3
Acetone	0.2	11.2	7.5
Butanal (+ol)	2.2	3.6	0.8
Butanone	3.6	6.1	1.2
2-Pentanone	3.5	3.2	0.4
C6-C9 ketones	52.6	1.1	0.02
Other	18.5	3.4	1.0

<sup>a</sup> Unlabeled ethanol and unlabeled CO.

<sup>b</sup> Unlabeled ethanol and <sup>13</sup>C.

<sup>c</sup> Ethanol-1-<sup>13</sup>C (5% water) and unlabeled CO.

the results obtained by passing 1-butanol over the catalyst under 65 atm of CO in the high pressure unit are compared with those obtained under 1 atm of CO either in the high pressure unit or in the microreactor mounted on the GC-MS (see Experimental Methods). Under the lower pressure, and correspondingly shorter contact time, the reactor effluent contained a lesser amount of condensation products and much more butanal. This indicates that the aldehyde is an intermediate in the formation of esters and ketones from the alcohol. Generally, the selectivity trends among the condensation products were those expected on the basis of the results reported in Tables 1, 2, and 3. In accord with the observations that the formation of ketones is promoted by CO, the selectivity to ketones decreased and that to the ester with 2*n* carbon atoms increased under the lower pressure of CO. And, in accord with the earlier evidence for the beneficial influence of CO on the formation of the 2*n* ketone, the selectivity to 3-methyl-4-heptanone as higher under 65 atm than under 1 atm of CO. There was one unexpected result. The selectivity to 4-heptanone was higher at the lower pressure, indicating that CO exerts a moderately in-

hibiting influence on the formation of the  $2n-1$  ketone.

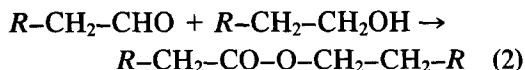
The data in Table 5 indicate similar trends, although a comparison of the distribution of products at high and low pressures of CO is more difficult because at the higher pressure most of the initial reaction products (the  $n$ ,  $2n-1$ , and  $2n$  carbonyl compounds) underwent further reaction. The reactivity of the acetaldehyde was so high that very little acetaldehyde was present in the effluent, most of the  $2n-1$  ketone, the  $2n$  ketone, and the  $2n$  aldehyde was consumed by reaction with acetaldehyde, and more than half of the weight of the effluent was made up of C<sub>6</sub>-C<sub>9</sub> ketones. On the other hand, under low pressure of CO (Column 2 of Table 5) large amounts of acetaldehyde were present in the effluent, and only a small fraction of the effluent was C<sub>6</sub>+ product. This result is consistent with the role of the aldehyde as an intermediate in the formation of esters and ketones. In accord with the trends already observed in Table 4, under 1 atm of CO the selectivity to the  $2n-1$  ketone, acetone, was greater than that to the  $2n$  ketone, butanone.

These results can be rationalized on the basis of the following reactions:

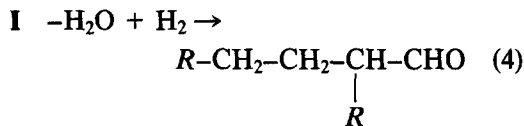
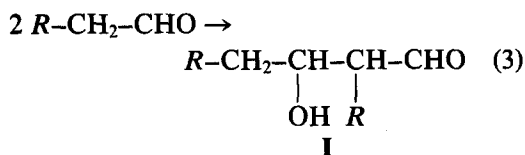
(a) The formation of an aldehyde with  $n$  carbon atoms from the corresponding alcohol:



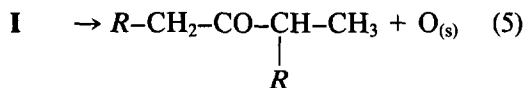
(b) The reaction of the aldehyde with the alcohol to form the  $2n$  ester:



(c) The self-addition of the aldehyde by an aldol-type condensation to yield the  $2n$  aldehyde:

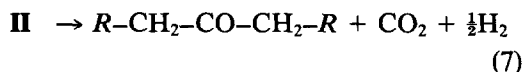
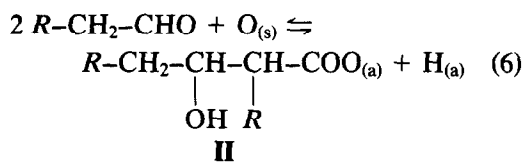


(d) or the  $2n$  ketone



where O<sub>(s)</sub> is a lattice oxygen.

(e) The condensation of the aldehyde that yields the  $2n-1$  ketone



where (a) indicates an adsorbed species.

#### Isotopic Labeling

To clarify further the nature of these reactions, particularly those leading to the formation of the ketones, experiments were performed under atmospheric pressure with <sup>13</sup>C-labeled ethanol, 1-butanol, or carbon monoxide.

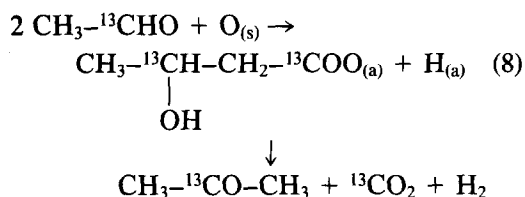
*Ethanol and <sup>13</sup>CO.* The distribution of products observed in an experiment in which unlabeled ethanol was passed over the catalyst under 1 atm of <sup>13</sup>CO is shown in Table 5. There was no evidence that the carbon of the CO was incorporated into any of these products. The MS analyses showed natural abundance of <sup>13</sup>C in all oxygenated compounds (aldehydes, esters, ketones, and alcohols).

On the other hand, oxygen from the carbon monoxide was found in all the oxygenated products. The carbon monoxide contained about 12% oxygen-18. The oxygen-18 content of the oxygenated products is given in Table 6. Exchange of the labeled oxygen of the carbon monoxide with that of the other oxygenated products occurred readily, but complete exchange

was not achieved, so that all the species analyzed contained less than half the exchange equilibrium amount of oxygen-18. Acetaldehyde exhibited the highest level of oxygen exchange. Among the condensation products *n*-butanal contained a higher percentage of labeled oxygen than the other species, which suggests that the butanal exchanged further in the catalyst bed after it was formed. These results point to the aldehydes as the intermediates through which oxygen exchange occurs between carbon monoxide and the oxygenated hydrocarbons.

In these same experiments no unlabeled carbon monoxide was observed among the products, but 66% of the CO<sub>2</sub> was unlabeled. This indicates that the reaction leading to the formation of the 2*n*-1 ketone is accompanied by the formation of CO<sub>2</sub> and not of CO. Evidence that the CO<sub>2</sub> produced in this reaction originates from the carbonyl group of the aldehyde is provided by the following experiments with ethanol-1-<sup>13</sup>C and butan-1-ol-1-<sup>13</sup>C.

*Ethanol-1-<sup>13</sup>C.* Within the framework of the reactions postulated earlier (Eqs. (1), (6), and (7)), the formation of acetone, the 2*n*-1 ketone, from ethanol-1-<sup>13</sup>C should proceed as follows:



When ethanol-1-<sup>13</sup>C was passed over the catalyst under 1 atm of unlabeled CO the acetone contained only one label, at the carbonyl carbon, and 32% of the CO<sub>2</sub> produced contained carbon-13. One complication in this experiment was the presence of 5 wt% water in the ethanol feed (see Table 5, column 3), so that considerably more CO<sub>2</sub> was formed from the CO by the water-gas shift reaction than in the previous experiment in which absolute ethanol was used.

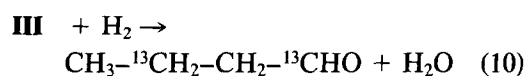
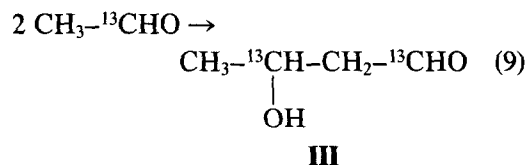
TABLE 6

Oxygen-18 Abundance in the Products of the Reaction of Ethanol with Carbon Monoxide Containing 12 Atom% Oxygen-18

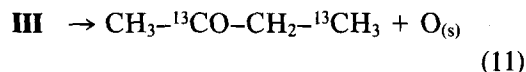
Product	Oxygen-18 (%)	% of Equilibrium <sup>a</sup>
Acetaldehyde	5.6	47
Ethanol	4.3	36
Acetone	3.6	30
Butanone	3.2	27
Ethyl acetate	3.5	29
Butanal	4.3	36

<sup>a</sup> Oxygen exchange equilibrium between CO and reaction products.

Other products of the reaction of ethanol were the 2*n* aldehyde, butanal, and the 2*n* ketone, butanone. In the butanal the carbon atoms 1 and 3 were labeled as expected from classical aldol condensation,



Butanone should also be labeled at the two and four positions, if formed, according to Eqs. (3) and (5):



The butanone was doubly labeled. One label was at the carbonyl carbon and the other in the ethyl group, but it was not possible to distinguish from the fragmentation pattern which of the two carbon atoms of the ethyl group was labeled. A clearer view of the relative arrangement of the reactant molecules in the synthesis of the 2*n* ketone was obtained from the reaction of butan-1-ol labeled with carbon-13 in the one position (see below).

The 3*n*-1 ketone, 2-pentanone, was doubly labeled at the carbonyl carbon and at either the 4 or 5 carbon (again the exact



cies take place by aldol condensations, following two distinct paths, one leading to the  $2n$  ketone and the  $2n$  aldehyde, the other to the  $2n-1$  ketone. The enhancement by CO of the synthesis of these carbonyl compounds is attributable to modifications of the catalyst surface, which enhance the aldol condensation reaction.

These modifications are produced by the reaction of CO with the catalyst. In this reaction oxygen is removed from the catalyst surface and CO is oxidized to  $\text{CO}_2$ . The catalyst is reduced and, therefore, its basicity increases. As a consequence, additional surface sites become capable of removing a proton from the active hydrogen component (9b) of the aldol condensation. It is this increase in the availability of proton acceptor sites, and perhaps their mobility on the surface, that is responsible for the general increase in the yield of the aldol condensation products that was observed in this study when the reaction was carried out under CO.

Carbon monoxide also affected the relative selectivities of the ketones. Under 65 atm of CO there was a sharp increase in the selectivity to the  $2n$  ketone, which can be attributed to an increase in the number of the catalytic sites responsible for its synthesis. These sites can be identified with oxygen vacancies such as those produced by the reaction of CO with the surface.

On the basis of the experimental evidence, the synthesis of the  $2n$  ketone can be viewed as resulting from condensation of two  $n$  aldehyde molecules, accompanied by dehydrogenation of the resulting aldol (I) to a  $\beta$ -keto aldehyde and by reduction of the aldehydic group to a methyl group (see Eqs. (3) and (5)). The first step in the synthesis then is the reaction of the aldehyde through its carbonyl group with a lattice vacancy. The aldehyde thus bound to the catalyst surface constitutes the active hydrogen component of the aldol condensation. The  $\beta$ -ketoaldehyde which is postulated as an intermediate, is also bound to the catalyst at the aldehydic group, and the reduc-

tion step involves the loss of the aldehydic oxygen to the catalyst with healing of the lattice vacancy. This step may be rationalized in terms of hydrogenation of the aldehydic group to an alkoxide, followed by dehydration of the alkoxide and hydrogenation of the resulting alkene group to yield the saturated  $2n$  ketone. Therefore, a substantial pressure of carbon monoxide is necessary to maintain a high concentration of sites (oxygen vacancies) for the synthesis of the  $2n$  ketone. In accord with this requirement, the yield of  $2n$  ketone showed a strong dependence on the partial pressure of CO.

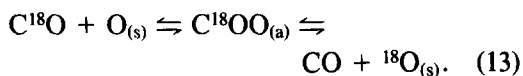
Dehydration, instead of dehydrogenation, of the aldol produces an  $\alpha,\beta$ -unsaturated aldehyde, the expected product of the aldol condensation (9b). Hydrogenation then yields the  $2n$  saturated aldehyde. The presence of both the  $2n$  aldehyde and the  $2n$  ketone in the products indicates that both the dehydrogenation and the dehydration reactions occur over this catalyst. It is not clear whether the  $2n$  aldehyde and the  $2n$  ketone are formed on different sites or on the same site, from which the aldehyde desorbs leaving the vacancy unhealed.

The surface reaction leading to the formation of the  $2n-1$  ketone apparently involves a surface carboxylate. Alcohols and aldehydes react with the surfaces of many metals and metal oxides, including copper (12), zinc oxide (13), and copper-zinc oxide catalysts (14) to form carboxylates. Aldol condensation of the aldehyde with a surface carboxylate results in the formation of a  $\beta$ -hydroxyl carboxylate (II), (Eq. (6)), which may then decompose in one of two ways. Dehydrogenation of the secondary hydroxyl group and protonation of the carboxylate group gives a  $\beta$ -keto acid; such acids decompose with exceptional ease to give a ketone and  $\text{CO}_2$  (9). Alternatively, the dehydrogenation of the hydroxy group may be accompanied by the formation of the  $2n-1$  ketone and a surface formate; the latter may then decompose to give  $\text{CO}_2$ . By either way, the end products are the  $2n-1$



ketone and CO<sub>2</sub>, and if the starting alcohol is labeled at the carbon attached to the oxygen, the carbon atom at the carbonyl group of the ketone and the carbon atom of the CO<sub>2</sub> should be labeled. This labeling is observed in the products of the reaction of ethanol-1-<sup>13</sup>C and of butan-1-ol-1-<sup>13</sup>C.

The surface carboxylate is also a likely intermediate in the exchange between an aldehyde and carbon monoxide. Adsorption measurements (15) indicate that carbon monoxide adsorption on zinc oxide is associated with a surface anion, forming a carboxyl-type species. So, oxygen exchange with the surface can be described by the following equation:



Exchange of the oxygen between the aldehyde and the surface occurs by a similar mechanism through formation of the surface carboxylate.

The adsorption of CO on the same sites on which aldehydes are adsorbed to form the 2*n*-1 ketone also accounts for the inhibition of the synthesis of the 2*n*-1 ketone under high CO pressure.

#### CONCLUSIONS

Over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> linear primary alcohols containing *n* carbon atoms are condensed mainly to esters with 2*n* carbon atoms, to ketones with 2*n*-1 carbon atoms, and to ketones with 2*n* carbon atoms. Under nitrogen the esters predominate, but under substantial pressure of carbon mon-

oxide the principal condensation products are ketones with 2*n* carbon atoms. These changes in selectivity are attributable to changes in the catalyst surface resulting from the removal of lattice oxygen by the CO and the formation of oxygen vacancies.

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