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The Mechanism of Hydrogenolysis and Isomerization of Oxacycloalkanes on Metals

IV. Mechanism of Transformation of Oxiranes on Cu Catalyst[1]

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The mechanism of isomerization of methyloxirane to propanal and acetone was studied on a Cu catalyst. During the transformation, the deoxidation reaction causes the oxidation of the catalyst surface, and Lewis acid site-basic site pairs are produced. Propanal is formed predominantly on these centers. The rate of formation of such active centers, and hence that of propanal, is maximum on the partially oxidized surface. Acetone is formed on the reduced metal surface. Both reactions may be regarded as hydroisomerization.

INTRODUCTION

Hydrogenolysis and isomerization of the oxiranes are well-known reactions (*1–11*). Cleavage of the bond adjacent to the substituent leads to the formation of a primary alcohol or aldehyde, while cleavage of a more distant bond gives a secondary alcohol or ketone (Scheme 1).

The regioselectivity of the transformation of oxiranes depends mainly on the catalyst. On Cu, primarily the C–O bond adjajacent to the substituent is split; on Pt and Pd mainly a more distant C–O bond undergoes cleavage (*5*). An explanation of why the regioselectivity on Cu is different from that on Pt or Pd demands a knowledge of the mechanism of the reaction.

Relatively few data from the literature are available on the transformation of oxiranes on Cu catalysts. The initial studies showed that methyloxirane isomerizes to propanal (*12*). Acetone formation too was reported later (*5, 13*). Alcohol formation was also demonstrated on Cu (*5, 6, 13*); indeed, at high hydrogen pressure alcohol is the main product (*14, 15*). Little attention has been paid to the mechanism of hydrogenolysis and isomerization on Cu. The inductive effect of the methyl substituent has been stated to be the reason why the C–O bond adjacent to the substituent is split (*16*).

Besides hydrogenolysis and isomerization, oxirane also undergoes deoxidation on Cu, and alkene is formed (*17*). The reaction pathway of deoxidation is illustrated in Scheme 2 (*18*).

Our survey of data from the literature led us to conclude that additional experimental data were needed if the mechanism of transformation on Cu is to be interpreted.

EXPERIMENTAL

A 6.8% Cu/SiO_2 catalyst was used; this was prepared as in (*19*). Before measurement, the catalyst was heated in a stream of hydrogen at a rate of 10 K min^{-1} to 423, 473, or 523 K, maintained at each temperature for 1 h, and then cooled to the reaction temperature during evacuation. The specific surface area of such a pretreated catalyst was 7 $m^2\ g^{-1}$ Cu.

The copper oxide catalyst was prepared in a similar way, but the thermal treatment

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[1] Part III to be published.

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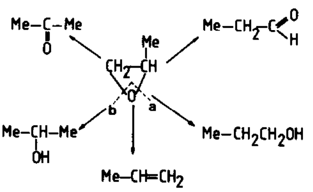


SCHEME 1

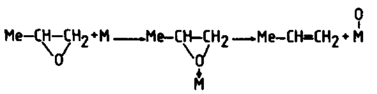
was carried out *in vacuo*. The Cu catalyst was prepared as in (*20*). The specific surface area of the reduced catalyst was 3.4 m^2 g^{-1} Cu. The catalysts were characterized through reaction with nitrous oxide at 363 K, using a single pulse method (*21*). The methyloxirane used was a product of BDH.

Measurements were made in a circulation reactor; 175 cm^3 in volume; the volume of the reactant sample was 0.3 cm^3. A Carlo Erba Fractovap 2150 gas chromatograph was used for the analysis. The chromatographic column was 0.5 m 20% ODPN/Chromosorb-W at 293 K, and 1.5 m 15% Reoplex 400/Chromosorb-W + 20% ODPN/Chromosorb-W at 313 K. The retention data are found in Table 1.

Data were processed with a Perkin–Elmer Sigma 10 integrator. The hydrogen used in the measurements was produced with a Matheson 8326 electrolysis apparatus equipped with a Pd diffusion cell.

Deuterolysis was studied in a flow reactor. The deuterium was produced by electrolysis. The catalyst (50 mg 6.8% Cu/SiO_2) was reduced for 2 h at 523 K in a stream of deuterium; 1 ml methyloxirane was then led over the catalyst in a stream of deuterium during 1 h. The deuterium distribution was determined with a Finnigan 1015 SL GC-MS instrument.

For microreactor studies, a microreactor was connected to a gas chromatograph (Carlo Erba Model C ATC/f); details were reported earlier (*22, 23*). The carrier gas used in the measurement was He, freed from oxygen with an Alltech Oxy-Trap. The catalyst (100 mg 6.8% Cu/SiO_2) was reduced for 2 h at 523 K in a stream of hydrogen in the microreactor; He carrier gas was next passed through for 5 min, and a pulse of methyloxirane (2 μl) was then injected into the reactor. The product distribution was determined with the gas chromatograph connected to the microreactor. The products were separated with two columns at 333 K (*23*). After completion of the analysis, a new pulse was injected into the reactor and the entire process was then repeated. The absence of oxygen from the carrier gas was checked by passing the carrier gas through the reactor for 150 min before the first pulse. The result was the same as after the shorter desorption period. In the study of the effect of oxidation, a pulse of air (13 μl) was admitted onto the reduced Cu catalyst at the temperature of the measurement in static operating mode, and oxidation was performed for 5 min.



SCHEME 2

RESULTS

During transformation of oxiranes on a Cu catalyst, mainly the bond adjacent to the substituent is cleaved (Table 2). From Table 2, it appears that propene formation is as great as C–O bond rupture by isomerization and hydrogenolysis. The deoxygenation can affect the overall selectivity of the reaction. During isomerization and hydro-

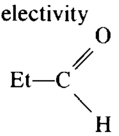
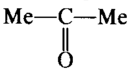
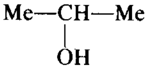
TABLE 1

Retention Times of Products Formed in Transformations of Methyloxirane (Carrier Gas: 30 ml N_2 min^{-1}; Column: Reoplex + ODPN)

Product	Retention time (min)	RRT
Propene	0.97	0.13
Methyloxirane	7.20	1.00
Propanal	10.50	1.46
Acetone	16.5	2.29
2-Propanol	21.5	2.99
1-Propanol	45.1	6.26

TABLE 2

Transformation of Methyloxirane on Cu in a Static Microreactor

	Catalyst	
	Cu	Cu/SiO_2
Temperature (K)	473	523
Rate of transformation ($mol\ m^{-2}\ min^{-1} \times 10^3$)	0.11	1.61
Selectivity		
 $\mathrm{Et{-}C}{\genfrac{}{}{0pt}{}{/\!\!/\, \mathrm{O}}{\diagdown\, \mathrm{H}}}$	22	10
$\mathrm{Et{-}CH_2OH}$	20	33
 $\mathrm{Me{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Me}$	3.5	11
 $\mathrm{Me{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}Me}$	1	0
$\mathrm{Me{-}CH{=}CH_2}$	54	46
b/*a*[a]	0.11	0.25

[a] See Scheme 1.

genolysis, however, only one of the C–O bonds is split. The products (e.g., propanal) do not undergo secondary decomposition either. Thus, the regioselectivity is not influenced by either secondary reactions or deoxidation.

The data were obtained for a range (3.7–53.3 kPa) of hydrogen partial pressures. The product composition and the transformation rate depend strongly on the hydrogen pressure. Mainly propanal was formed at low hydrogen pressure, and mainly 1-propanol at high hydrogen pressure (Figs. 1, 2). Above a hydrogen pressure of 10 kPa, the rates of propanal and 1-propanol formation varied in opposite directions, but their sum was nearly constant (Fig. 3). Below a hydrogen pressure of 3 kPa, 1-propanol was scarcely formed and the rate of formation of propanal increased with an increase in hydrogen pressure. Propanal is formed even in the absence of hydrogen, but at a lower rate. Acetone was formed only in the presence of hydrogen (Fig. 4). We studied the transformation of a methyloxirane + acetaldehyde mixture on Cu (Fig. 5). It was found that while significant methyloxirane was present (to about 50 min) acetaldehyde was not hydrogenated to ethanol, and, by analogy, gas-phase propanal would not be hydrogenated to 1-propanol. This experiment shows that the propanol formed came from a surface reaction prior to desorption. The data in Fig. 5 show that up to ca. 50 min both propanal and 1-propanol are being formed in nearly equal amounts; however, after 50 min propanal appears to disappear but the amount of 1-propanol does not undergo a corresponding increase. It is probable that under the given conditions only the acetaldehyde is hydrogenated, while the propanal is decarbonylated. Decarbonylation does not occur if methyloxirane too is present in the system (Fig. 1).

Methyloxirane was also transformed on a copper oxide catalyst (Fig. 6), but propanal was the only product in this case.

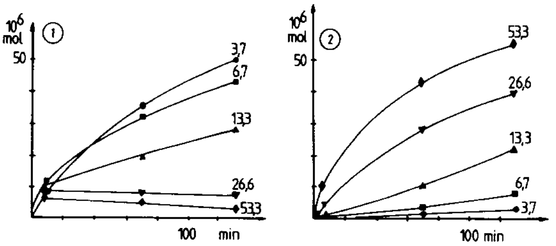


FIG. 1. Formation of propanal from methyloxirane on Cu/SiO_2 at 448 K. ($p_{oxirane} = 3.3$ kPa, $p_{H_2} =$ 3.7–53.3 kPa, catalyst = 3×10^{-2} g.)

FIG. 2. Formation of 1-propanol from methyloxirane on Cu/SiO_2 at 448 K (see Fig. 1).

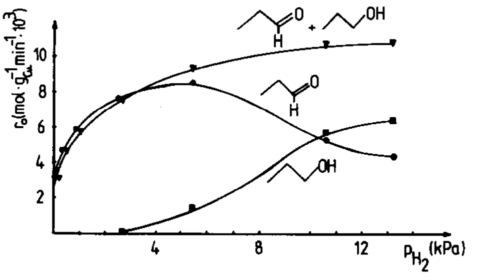


FIG. 3. Initial rates of formation of propanal and 1-propanol on Cu/SiO_2 at 448 K. (p_{H_2} = 3.3 kPa, catalyst = 3 × 10^{-2} g.)

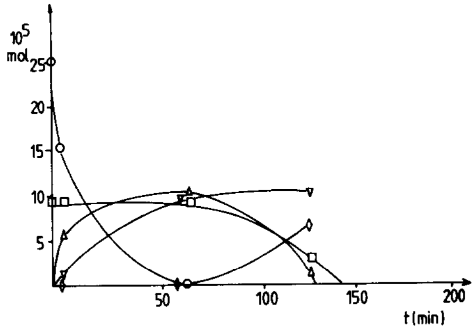


FIG. 5. Transformation of methyloxirane + acetaldehyde mixture on Cu/SiO_2 at 448 K. (p_{oxirane} = 3.3 kPa, p_{H_2} = 13.3 kPa, catalyst = 3 × 10^{-2} g, ○ = methyloxirane, □ = acetaldehyde, △ = propanal, ▽ = 1-propanol, ◇ = ethanol.)

The deuterolysis of methyloxirane on Cu was also studied. No deuterium was found in the untransformed oxirane; that is, the chemisorption of methyloxirane on Cu catalyst was irreversible. The mass spectra of the products are shown in Fig. 7. Figure 7a shows that both deuterated and nondeuterated propanal are present. Propanal-d_1 is formed in the greatest amount; the ratio d_1/d_0 is 2.1. The m/e 29 (HCO^+) indicates that there is no deuterium on C_1. In Fig. 7b, m/e 32 ($CHD{=}OH^+$) points to the presence of deuterium on C_1. From Fig. 7c the main product is acetone-d_1; the ratio d_1/d_0 is 1.5.

A study was also made of the effect of change in the surface state of the Cu catalyst on the selectivity of transformation of methyloxirane. The measurement was made in a pulse microreactor with helium as carrier gas (Fig. 8).

Following the first pulse, deoxidation was the fastest reaction and propene was formed. In the course of the subsequent pulses, the quantity of propene formed decreased markedly, because of the oxidation of the catalyst surface. The rate of formation of propanal passes through a maximum, whereas that of acetone decreases monotonously. Since the surface area of the Cu^0 continuously decreases because of the oxidation, it may be stated that the rate of formation of acetone decreases continuously with decrease in metal surface area. We repeated the measurement at various temperatures, and similar behavior was observed. The transformation of methyloxirane was also investigated on a partially oxidized Cu catalyst (Fig.9) . It was found that the maximum in the rate of formation of propanal can be eliminated by preliminary oxidation of the catalyst.

The experimental results permit the following conclusions:

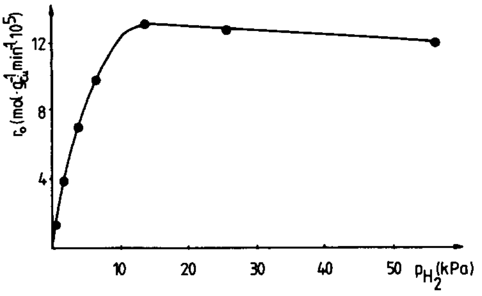


FIG. 4. Initial rate of formation of acetone on Cu/SiO_2 at 448 K (see Fig. 3).

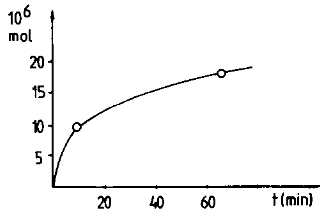


FIG. 6. Transformation of methyloxirane on copper oxide at 448 K. (p_{oxirane} = 3.7 kPa, p_{H_2} = 0 kPa, catalyst = 3 × 10^{-2} g, ○ = propanal.)

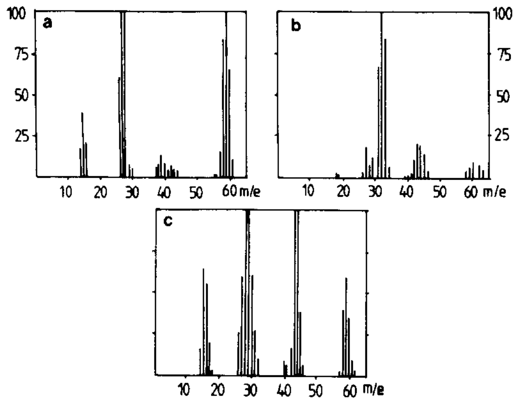


FIG. 7. Mass spectra of products formed in deuterolysis of methyloxirane. (a = propanal, b = 1-propanol, c = acetone, catalyst = 5×10^{-2} g Cu/SiO$_2$, temperature = 523 K.)

—It is probable that two types of isomerization reaction take place side by side.

—One isomerization reaction (electrophilic catalysis) proceeds on copper oxide; the product is exclusively propanal; hydrogen is not needed for the reaction to occur; the reaction probably leads to the formtion of propanal-d_0.

—The rate of the other type of isomerization reaction increases with hydrogen pressure, and at higher hydrogen pressures it becomes the main reaction; this reaction presumably leads to the formation of propanal-d_1 and acetone-d_1.

—Methyloxirane is able to oxidize the Cu catalyst surface, giving rise to new active centers.

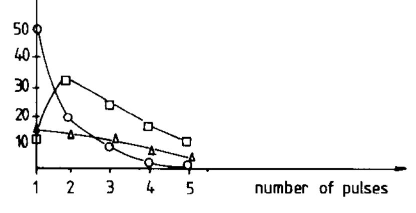


FIG. 8. Transformation of methyloxirane in a pulse microreactor at 448 K. (Catalyst = 0.1 g Cu/SiO$_2$, carrier gas = He, pulse = 1 μl, ○ = propene, □ = propanal, △ = acetone.)

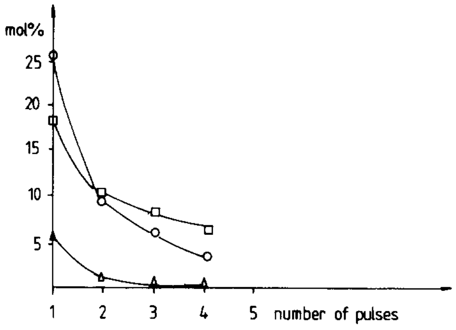


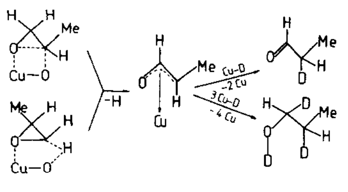
FIG. 9. Transformation of methyloxirane on oxidized Cu catalyst (see Fig. 8).

—The maximum in the rate of formation of propanal indicates that the partially oxidized Cu catalyst is the most active in this isomerization reaction.

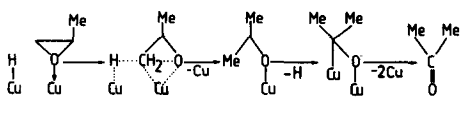
DISCUSSION

A study of the effect of hydrogen pressure showed that mainly propanal was formed at low hydrogen pressure, and mainly 1-propanol at high hydrogen pressure. It was suggested by Sabatier and Durand (*24*) that the oxirane isomerizes to an aldehyde on Ni, and that the resulting aldehyde is hydrogenated to a primary alcohol. Since the desorbed aldehyde is not readsorbed on a Cu catalyst surface covered with oxirane, 1-propanol is not formed through the hydrogenation of propanal. It is probable, however, that both compounds are formed from a common surface species which, depending on the hydrogen coverage, is desorbed in the form of aldehyde or alcohol from the surface.

Our experimental results suggest that the isomerization taking place on the Cu and leading to propanal can be interpreted as in Scheme 3.



SCHEME 3



SCHEME 4

The formation of acetone proceeds in accordance with Scheme 4.

On the basis of the literature observations and conclusions, the following comments may be made in connection with the proposed schemes:

—According to (*25*), zero-valent Cu has little affinity for alcohols. Insertion of oxygen into the surface may create Cu sites of positive valence, promoting adsorption of methanol. The amount of methanol adsorbed on a partially oxidized Cu surface exhibited a maximum at approximately 20% surface coverage by adsorbed oxygen.

—The active sites consisted of a Lewis acid site–basic site pair, a metal site serving as an adsorption site for the alkoxide, and an oxygen site for adsorption of the hydroxyl hydrogen (*26*).

—On analogy with the above, the adsorption of the oxiranes and the cleavage of the oxirane C–O bond may take place in a similar way on the same active centers.

—Depending on the hydrogen coverage, the adsorbed surface species is desorbed as aldehyde or alcohol. The zero-valent Cu atoms surrounding the active center may play an important role in the hydrogen supply.

—The fact that the concentration of the acid site–basic site pairs is maximum on the partially oxidized surface provides a good explanation for the maximum observed in the formation of propanal.

—Through deoxidation, oxirane is able to oxidize the Cu catalyst surface. If the reaction is carried out in the presence of hydrogen, the oxide formed is continuously reduced, and this ensures the partially oxidized metal surface necessary for the maximum catalytic activity.

—Isomerization to acetone takes place only on the metal surface, and its mechanism is similar to that for isomerization on Pt (*22, 23*).

—Isomerization to acetone and isomerization to propanal on the partially oxidized surface proceed only in the presence of hydrogen. Thus, both reactions can be regarded as hydroisomerization (*27*).

Accordingly, methyloxirane is transformed to acetone on the reduced Cu surface, while it undergoes isomerization to propanal on the Cu–copper oxide interface.

ACKNOWLEDGMENTS

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