

# The mechanism of hydrogenolysis and isomerization of oxacycloalkanes on metals

## XV. <sup>1</sup> Transformation of ethyl- and vinyloxirane on Cu–SiO<sub>2</sub>

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### Abstract

The isomerization and hydrogenolysis of vinyloxirane and, for comparison, those of ethyloxirane were studied on a Cu–SiO<sub>2</sub> catalyst at 373 K in a recirculation reactor, at various hydrogen pressures and in the presence of deuterium. It was established that in the case of ethyloxirane, the dominating reactions are deoxygenation associated with the formation of 1-butene and isomerization resulting in the formation of butanal. In the case of vinyloxirane, the enlargement of the oxirane ring to a five-membered ring also takes place in addition to deoxygenation and isomerization. Olefins are formed on Cu(0) while isomerization occurs on copper–copper oxide interfaces. The experimental results allow the identification of the probable reaction pathways leading to the formation of the individual products. © 1998 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Hydrogenative ring opening of oxiranes has been studied extensively. The reaction has both theoretical and practical significance (see in part XIV). Additionally, oxiranes show exclusively ring opening under very mild conditions (low temperature and hydrogen pressure) without any side reaction. Methyloxirane is probably one of

the most popular reactants in catalytic chemistry. Its hydrogenative transformation is a frequently used model reaction for characterisation of metal catalysts.

Relatively few data are available in the literature regarding the transformation of oxiranes on Cu catalysts [2–7]. No experimental observations have been published at all on the transformation of vinyloxirane on copper catalysts. Information on the catalytic conversion of vinyloxirane in the presence of hydrogen has also been scarce. The isomerization and hydrogenolysis of the oxirane ring are catalyzed by Rh complexes [8,9]. Selective hydrogenation of the

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<sup>1</sup> For part XIV, see Ref. [1].

<sup>2</sup> This is a unit of the Center for Catalysis, Surface and Materials Science.

double bond has been observed in the case of Pd and Ir complexes [10]. The application of metal catalysts (Rh, Pd, Pd–Au, Pd–Re) has been the subject of patents [11–16] describing the selective hydrogenation of the C=C bond. In the case of Raney–Ni catalyzed hydrogenation of steroid–vinyloxiranes, hydrogenolysis of the oxirane ring has been observed [17].

The study of C=C bond containing oxiranes has a special significance, since the presence of two functional groups within the same molecule makes possible the investigation of the selectivity of catalytic hydrogenolysis and hydrogenation which is important from the point of view of synthetic chemistry on the one hand and for the understanding of the mechanism of metal catalyzed reactions on the other. For these two purposes, a deeper understanding of the hydrogenation and hydrogenolysis of vinyloxirane was chosen as the aim of the present study. These data may yield valuable information on the reaction mechanisms as well as on the nature of the active sites of the copper catalyst.

## 2. Experimental

### 2.1. Materials

Vinyloxirane and ethyloxirane were purchased from Fluka and Aldrich, respectively. Prior to use, they were purified by several cycles of freezing–degassing–thawing.

A 6.36% Cu–SiO<sub>2</sub> (*D* = 14%) was prepared by ion exchange [18,19]. Preparation and characterization of the catalyst have been described [20]: silica gel (Strem, large pore, 120–230 mesh) was immersed in a tetramminecopper(II) solution at pH 11. After 24 h, the blue product was washed thoroughly with water, dried at 393 K (24 h) and decomposed at 773 K in air (3 h). The catalyst was reduced in flowing hydrogen (20 cm<sup>3</sup>/min), with heating to 673 K at a heating rate of 8% min, with a 2-h hold at this temperature, and then cooled in hydrogen. The number of surface Cu atoms was determined

through reaction with N<sub>2</sub>O at 363 K, using a GC pulse method. Pretreatment was performed in the circulation reactor, the catalyst was treated at 26.6 kPa hydrogen or deuterium for 1 h at 573 K.

### 2.2. Methods

Measurements were carried out in a circulation reactor [21]. The volume of the reactor was 69 cm<sup>3</sup> and that of the entire system, 170 cm<sup>3</sup>. The reactor was heated by an air thermostat. In the case of hydrogenolysis, analysis was carried out by a gas chromatograph (HP 5890) equipped with a flame ionization detector. For studies on deuterolysis, a gas chromatograph (HP 5890) with a quadruple mass selective detector (HP 5970 MSD) was attached to the system. Separation was done in a Carbowax 20 M capillary column (HP-20 M). Data were processed by CSW and HP 5970 chromatogram analysis programs.

Hydrogen used for the measurements was generated in a Matheson type 8326 electrolysis apparatus equipped with a Pd diffusion cell. Deuterium was obtained by a General Electric 15EHG generator (the purity of D<sub>2</sub>O was 99.8%). Deuterium was deoxygenated by a Model 1000 Oxygen Trap (CRS, USA).

### 2.3. Procedure

Fresh catalyst (20 mg) and 1.33 kPa of vinyloxirane or ethyloxirane were used in each measurement. When hydrogen pressure dependence was studied, the hydrogen pressure was varied within the range of 0–101.3 kPa. The amount of materials were: reactant,  $9 \cdot 10^{-5}$  mol, surface copper atoms,  $2.8 \cdot 10^{-6}$  mol, hydrogen,  $9 \cdot 10^{-5}$  to  $7 \cdot 10^{-3}$  mol. Reaction temperature was 373 K for both compounds. The effect of temperature was studied at a hydrogen pressure of 20 kPa, between 353–403 K.

The initial rates (%/min) and initial turnover frequencies (min<sup>-1</sup>) were calculated. Based on temperature dependence (measured at five tem-

peratures), apparent activation energies were also calculated.

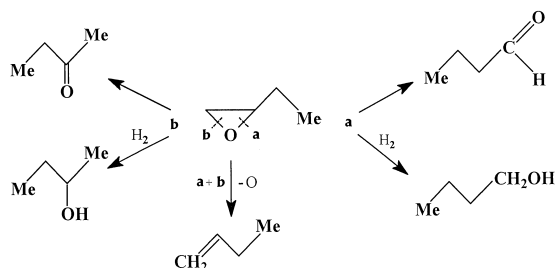
Deuterolysis was performed at a deuterium pressure of 20 kPa and a reaction temperature of 373 K. The data were used for the calculation of deuterium distribution.

### 3. Results and discussion

In the case of substituted oxiranes, the cleavage of the C–O bond adjacent to the substituent gives rise to a primary alcohol or aldehyde while that of the other C–O bond leads to the formation of a secondary alcohol or ketone (Scheme 1). The regioselectivity of the transformation of oxiranes is determined essentially by the metal catalyst applied. While Pt and Pd cleave the molecule from the sterically less hindered direction, Ni and Cu promote cleavage of the sterically more hindered bond [3]. In addition to hydrogenolysis and isomerization, the deoxygenation of the oxirane with the formation of an alkene also takes place [6,22] on Cu.

#### 3.1. Ethyloxirane

The transformation of ethyloxirane on the reduced copper catalyst takes place even in the absence of hydrogen. The elimination of the oxygen atom leads to the formation of 1-butene but at longer reaction time butanal is also observed. This may indicate that the initial event is the oxidation of the copper surface and the



Scheme 1. Reaction pathways in the transformation of ethyloxirane.

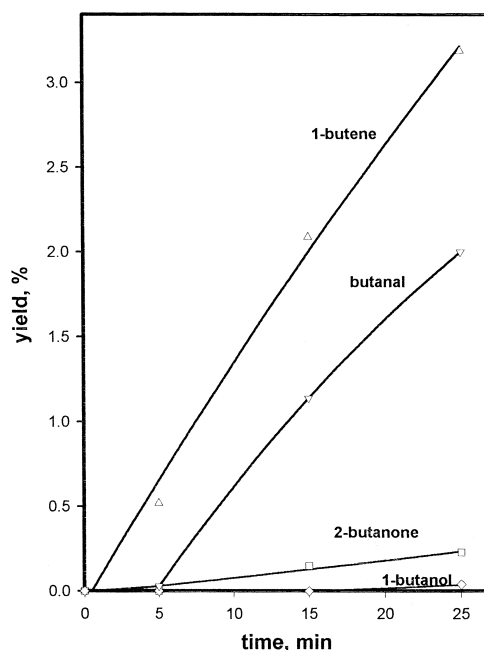


Fig. 1. Transformation of ethyloxirane on Cu–SiO<sub>2</sub> catalyst (catalyst = 20 mg, 373 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 1.33$  kPa).

active sites for the isomerization are formed during the surface oxidation.

As expected, in the presence of hydrogen deoxygenation and the cleavage of the sterically hindered bond are the dominant processes (Figs. 1 and 2).

Owing to the low hydrogenation ability of the Cu catalyst, 1-butene generated during deoxygenation is not converted further to butane. On better hydrogenation catalysts (Ni, Pt, Pd), hydrogenation of butene takes place in every case [1].

Initially, only butanal was detected as the product of the cleavage of the sterically hindered bond. The other product, i.e., 1-butanol appeared only after an extended period; its amount, however, increased with time. Since in the case of a Cu catalyst readsorption of the desorbed aldehyde hardly occurs [6], the process leading to the formation of 1-butanol is probably not the hydrogenation of butanal. It is more likely that both compounds originate from a common surface species.

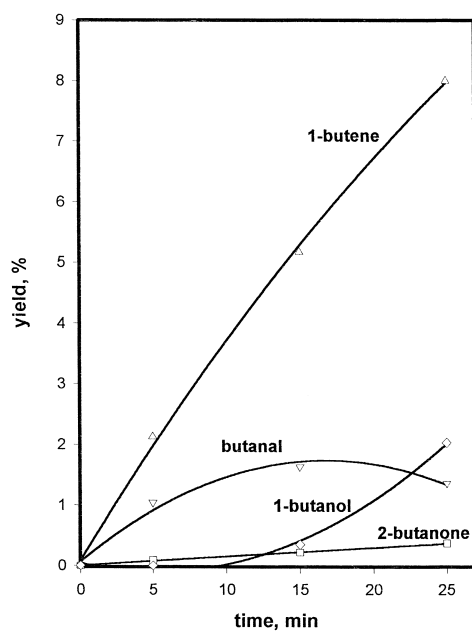


Fig. 2. Transformation of ethyloxirane on Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg, 373 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 20$  kPa).

Cleavage of the sterically less hindered bond also takes place but to a lesser extent, resulting in the formation of 2-butanone (under the given experimental conditions, detectable amounts of 2-butanone appeared only at very high hydrogen pressures (66.7 kPa) and after a very long reaction time). The formation of 1-butanol has an induction period which is detectable at all hydrogen pressures but is especially marked in the low hydrogen pressure range. It is most probable that the fresh surface is initially very rapidly oxidized but subsequently, the reduction of the oxidized surface also starts up and a stationary, partially oxidized copper surface is created. We have earlier proposed [7] that alcohol formation occurs on the Cu(0) atoms of this surface while isomerization takes place on the copper-copper oxide interface. The induction period may thus, be correlated with the formation of the surface with optimal composition. This assumption is in good agreement with the observation that at low hydrogen pressures, a sufficient degree of reduction requires a longer time. The concept presented above is also supported by the fact

that in the case of butanal formation, an induction period was detectable only at a low hydrogen pressure since at higher hydrogen pressures, reduction prevents the excessive oxidation of the surface and, consequently, of the copper-copper oxide interface diminishes to a suboptimal value. It was also verified by our measurements that the reduction of butanal takes place only at high hydrogen pressures.

Based on measurements carried out at various temperatures, apparent activation energies were determined (Table 1). The values listed in Table 1 very closely approximate those obtained for *cis*-2,3-dimethyloxirane [7], in very good accordance with the fact that ethyloxirane and *cis*-2,3-dimethyloxirane are adsorbed on the surface in a very similar way.

When transformations are studied as a function of hydrogen pressure (Fig. 3), it may be established that the rate of deoxygenation monotonously increases up to ca. 46 kPa and then decreases slightly. This slight decrease indicates that at high hydrogen pressures, the adsorption of the oxirane on the surface is inhibited, although only slightly. The rates of formation of butanal and 2-butanone are much more sensitive to changes in hydrogen pressure both exhibiting a marked maximum. The location of the maximum is around 33 kPa in both cases. The first part of the curve (increasing rate with increasing hydrogen pressure) may indicate that the transformation is hydroisomerization. The second part where the further increase in hydrogen pressure results in decreasing rate, in turn, may suggest that the mechanism is dissociative. Increasing hydrogen pressure enhances the rate of the hydroisomerization step and reduces that

Table 1  
Apparent activation energies ( $E_a$ ) of the transformation of ethyloxirane

Products	$E_a$ (kJ/mol)
1-Butene	60 ± 4
Butanal	58 ± 4
2-Butanone	82 ± 5
Total	61 ± 4

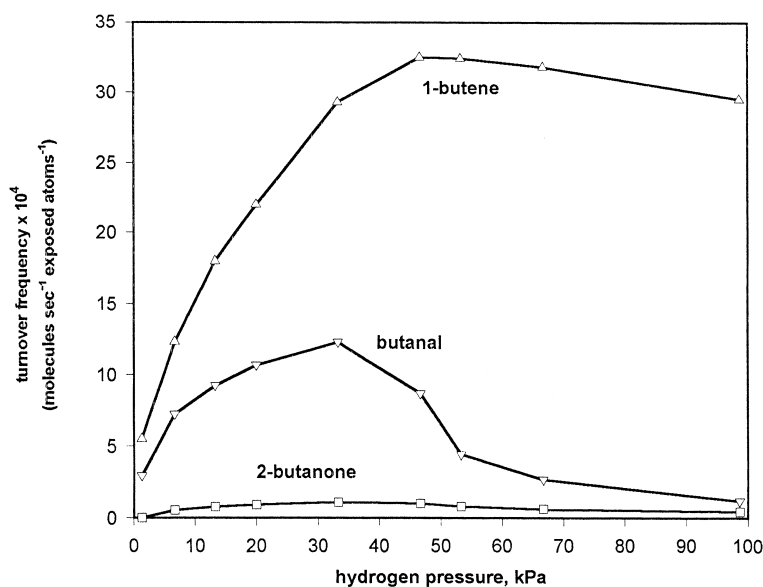


Fig. 3. Initial turnover frequency of product formation vs. hydrogen pressure at ethyloxirane on Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg,  $p_{\text{oxirane}} = 1.33$  kPa, 373 K).

of the dissociation step. Thus, as a result of two opposing effects, the rate of isomerization will reach a maximum at an optimal surface concentration of hydrogen. The identical courses indicate that butanal and 2-butanone are produced by similar mechanisms. The effect of hydrogen pressure suggests that the common mechanism is a conversion of a dissociative character.

It may not be excluded, however, that the decrease in transformation rate with increasing hydrogen pressure is due to changes in the surface. The oxirane can oxidize the surface of the Cu catalyst by deoxygenation. Due to the presence of hydrogen, the oxide being produced is continuously reduced, resulting in the forma-

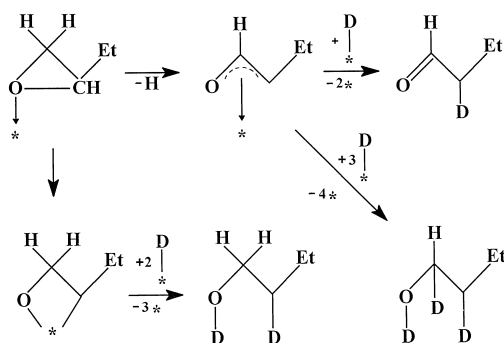
tion of a partially oxidized metal surface ensuring maximal catalytic activity. The ratio of Cu(0) to Cu(I) on the surface is affected by hydrogen pressure, so when the latter is increased, reactions taking place on Cu(0) are accelerated and those dependent on Cu(I) are decelerated. This may be one of the reasons why the rate of formation of 1-butene is only very slightly reduced and isomerization is repressed at high hydrogen pressures.

It has been pointed out already by Wachs and Madix [23,24] on the example of methanol that active centers are made up by Lewis acid–basic ion pairs. The alkoxide ion is adsorbed on the metal ion and the hydrogen of the hydroxyl

Table 2

Transformation of ethyloxirane in deuterium over Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg, 373 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium}} = 20$  kPa)

$t$ (min)	Conversion (%)	$S_{\text{butanal}}$	$S_{1\text{-butanol}}$	$S_{2\text{-butanone}}$	$S_{1\text{-butene}}$	Distribution of deuterium (%)								
						In butanal			In 1-butanol			In 2-butanone		
						$d_0$	$d_1$	$d_2$	$d_2$	$d_3$	$d_4$	$d_0$	$d_1$	$d_2$
5	3	0.32	0	0.03	0.65	12.6	87.4	0	52.4	47.6	0	27.8	72.2	0
15	7	0.23	0.05	0.03	0.69	12.6	83.5	3.9	52.1	44.7	3.2	23.7	76.3	0
25	12	0.12	0.17	0.03	0.68	12.6	81.3	6.1	51.1	42.1	6.8	19.6	80.3	0.1



Scheme 2. Mechanism of ethyloxirane transformation on Cu-SiO<sub>2</sub> catalyst (butanal and 1-butanol formation).

group on the oxygen. By this analogy, the adsorption of oxiranes and the cleavage of their C–O bonds may take a similar course. The zero-valent Cu atoms surrounding the active centers play an important role in hydrogen supply [6].

In the course of the measurements in deuterium, no deuterium was found in unreacted ethyloxirane. This corresponds to our earlier observation on oxiranes [7], i.e., that oxiranes are irreversibly adsorbed on the copper surface and only their products are desorbed. No deuterium was detectable in 1-butene either, indicating that deoxygenation proceeds without the cleavage of the C–H bonds.

Isomerization in the course of cleavage of the sterically more hindered bond yields mostly butanal-*d*<sub>1</sub>, as expected from the dissociative mechanism, while the main products of deuterolysis are 1-butanol-*d*<sub>2</sub> and 1-butanol-*d*<sub>3</sub> in roughly equal amounts (Table 2). The latter observation supports the notion that 1-butanol is not formed by hydrogenation of butanal but the two compounds are derived from a common surface species. This also means that 1-butanol may be produced by two mechanisms, one associative and one dissociative. The former most probably is hydrogenolysis on the Cu(0) surface while the latter is the complete hydrogenation of the surface complex leading to butanal. Isomerization in the course of cleavage in the sterically less hindered direction led mainly to the forma-

tion of 2-butanone-*d*<sub>1</sub>, in agreement with the dissociative mechanism.

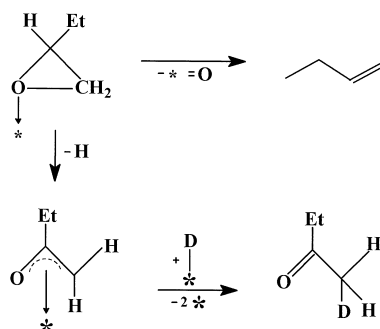
Based on our experimental results, isomerization and hydrogenolysis described above are interpreted according to Schemes 2 and 3.

As shown by the mechanism outlined in Scheme 2, 1-butanol is formed on Cu(0) atoms. The copper atom is inserted into the C–O bond, yielding metalla-oxacyclobutane. The driving force of the reaction is the strain energy of the three-membered ring which is significantly decreased upon the formation of the four-membered ring. Butanal-*d*<sub>1</sub> and 1-butanol-*d*<sub>3</sub> are generated by the dissociative mechanism.

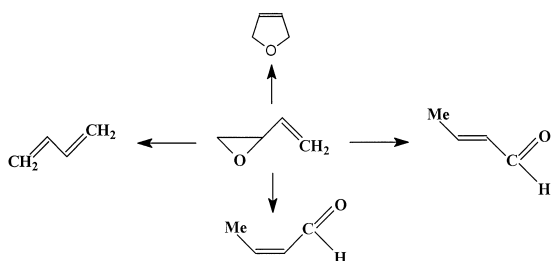
The formation of 2-butanone-*d*<sub>1</sub> takes place on the electrophilic Cu(I) atoms. Active centers for the above reactions are supplied by the partially oxidized copper surface generated by the opposing processes of oxidation and reduction. The highest catalytic activity is realized when the optimal copper–copper oxide surface structure is established. Thus, in the case of isomerization, it is the presence of copper ions while for hydrogenolysis and deoxygenation, it is that of Cu(0) that is essential.

### 3.2. Vinyloxirane

Vinyloxirane is transformed even in the absence of hydrogen: both the removal of oxygen and isomerization take place on the reduced catalyst (Scheme 4 and Fig. 4) and the oxirane ring is also enlarged to a five-membered ring.



Scheme 3. Mechanism of ethyloxirane transformation on Cu-SiO<sub>2</sub> catalyst (1-butene and 2-butanone formation).



Scheme 4. Reaction pathways in the transformation of vinyloxirane on Cu-SiO<sub>2</sub> catalyst.

The main product is *trans*-2-butenal formed via isomerization. Its formation is due to the presence of surface copper ions produced in the course of the deoxygenation of vinyloxirane, therefore, the formation of *trans*-2-butenal exhibits an induction period. Thus, the process taking place is electrophilic catalysis, since in the absence of hydrogen, it is impossible for the surface copper ions to be reverted to Cu(0). As

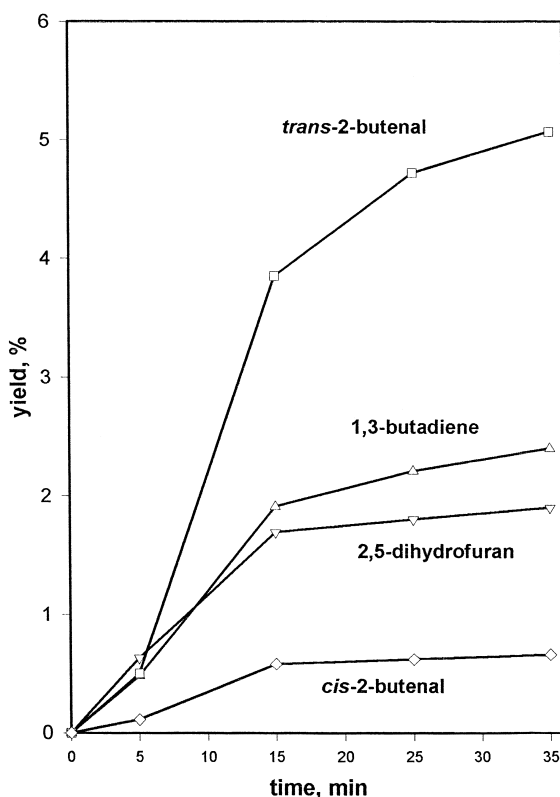


Fig. 4. Transformation of vinyloxirane on Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 40$  kPa, 373 K).

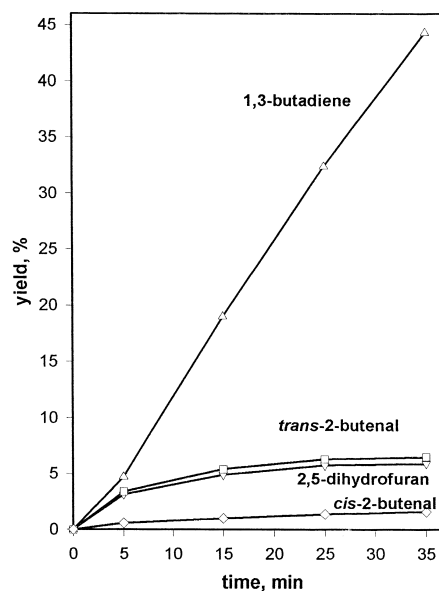


Fig. 5. Transformation of vinyloxirane on Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg, 373 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 20$  kPa).

a consequence, the amount of *trans*-2-butenal gradually increases with time.

These isomerizations (i.e., the formation of *trans*-2-butenal and 2,5-dihydrofuran) are not unknown in the literature. Vinyloxirane may be isomerized—in some cases in a highly selective manner—to *trans*-2-butenal [9,25–28], furthermore to 2,5-dihydrofuran [29–36] under a great variety of experimental conditions.

Similar reactions, i.e., isomerization, deoxygenation and ring enlargement take place also in the presence of hydrogen (Fig. 5). Both the reaction rate and the distribution of products are markedly different from those in the absence of hydrogen. The main reaction pathway in the presence of hydrogen is deoxygenation since

Table 3  
Apparent activation energies ( $E_a$ ) of the transformation of vinyloxirane

Products	$E_a$ (kJ/mol)
1,3-Butadiene	$54 \pm 4$
2,5-Dihydrofuran	$41 \pm 3$
<i>trans</i> -2-Butenal	$39 \pm 3$
<i>cis</i> -2-Butenal	$39 \pm 3$
Total	$50 \pm 4$

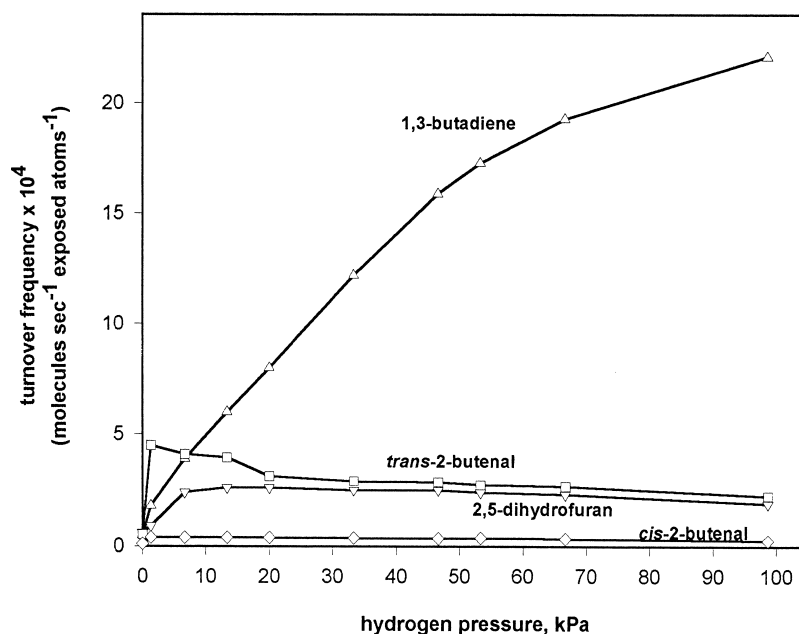


Fig. 6. Initial turnover frequency of product formation vs. hydrogen pressure at vinyloxirane on Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg,  $p_{\text{oxirane}} = 1.33$  kPa, 373 K).

Cu(0) surface sites on which deoxygenation takes place are continuously generated by the hydrogen.

A 1,3-butadiene produced by deoxygenation is not converted further to butene and butane (under the given experimental conditions) which is in good agreement with our observations on ethyloxirane. In the course of the cleavage of the C–O bond only isomerization takes place and no hydrogenolysis occurs. The products are 2,5-dihydrofuran, *trans*-2-butenal and *cis*-2-butenal. The apparent activation energies (Table 3) in the case of vinyloxirane are somewhat lower than those for ethyloxirane, pointing to

the difference in adsorption geometry between the two compounds.

In accordance with what has been said above, the rate of deoxygenation monotonously increases with increasing hydrogen pressure (Fig. 6). As regards isomerization, a significant effect is observed only in the low hydrogen pressure range (0–13.3 kPa). Similarly to the case of ethyloxirane, these experimental data are assumed to reflect the development of the active sites responsible for the individual reactions.

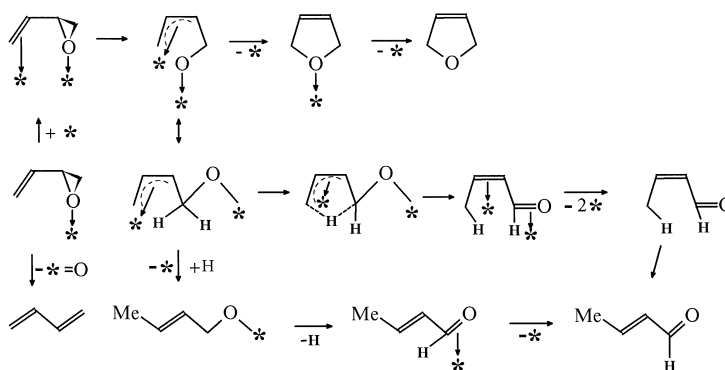
An interesting difference is observed between the formation rates of *trans*-2-butenal and 2,5-dihydrofuran at a low hydrogen pressure. The

Table 4

Transformation of vinyloxirane in deuterium over Cu-SiO<sub>2</sub> catalyst (catalyst = 20 mg, 373 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium}} = 33$  kPa)

$t$ (min)	Conversion (%)	$S_{2,5\text{-dihydrofuran}}$	$S_{\text{trans-2-butenal}}$	$S_{\text{cis-2-butenal}}$	Distribution of deuterium (%)								
					In 2,5-dihydrofuran			In <i>trans</i> -2-butenal			In <i>cis</i> -2-butenal		
					$d_0$	$d_1$	$d_2$	$d_0$	$d_1$	$d_2$	$d_0$	$d_1$	$d_2$
5	17	0.14	0.16	0.02	65.4	31.8	2.8	67.6	32.4	0	87.2	12.8	
15	42	0.11	0.09	0.01	48.6	38.2	13.2	56.3	43.0	0.7	63.1	36.9	
25	64	0.09	0.08	0.01	46.9	37.1	16.0	55.3	41.8	2.9	63.4	36.6	
35	82	0.07	0.07	0.01	43.0	39.4	17.6	54.2	41.0	4.8	60.0	40.0	



Scheme 5. Mechanism of vinyloxirane transformation on Cu-SiO<sub>2</sub> catalyst.

rate of formation of *trans*-2-butenal is much more enhanced by increases in hydrogen pressure than that of 2,5-dihydrofuran. This difference disappears at higher hydrogen pressures. These data suggest that the two compounds are formed on similar but not identical active centers.

In the course of the measurements in deuterium, unreacted vinyloxirane was found to contain no deuterium. No deuterium was detected in 1,3-butadiene either. The conclusions drawn from these data are identical with those reached in the case of ethyloxirane. The main products of isomerization were 2,5-dihydrofuran-*d*<sub>0</sub>, *trans*-2-butenal-*d*<sub>0</sub> and *cis*-2-butenal-*d*<sub>0</sub> (Table 4).

The amount of *d*<sub>1</sub>, however, may not be disregarded in the case of any of the products, since the compounds containing *d*<sub>1</sub> are formed either by hydroisomerization or by the H–D exchange reaction of *d*<sub>0</sub>-compounds, i.e., via secondary processes. A 2-butenal-*d*<sub>0</sub> may be a product of intramolecular hydrogen migration. At the same time—because of the relatively large amount of 2-butenal-*d*<sub>1</sub>—due to the presence of deuterium adsorbed on the surface of the catalyst, hydrogen transfer may not be excluded either. The proposed reaction pathway of the formation of the three isomers of vinyloxirane based on our experimental results is outlined in Scheme 5. The driving force of the isomerization reactions is the heterolysis of the

allylic C–O bond included in a strained three-membered ring.

Deoxygenation resulting in the formation of butadiene takes place on Cu(0) surface sites. Isomerization reactions necessitate the presence of active sites of electrophilic character, available in the form of copper ions generated by deoxygenation.

## Acknowledgements

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