

Transformation of *cis*- and *trans*-2,3-Dimethyloxiranes on a Cu/SiO₂ Catalyst

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Transformation of *cis*- and *trans*-2,3-dimethyloxiranes on a copper catalyst was studied at 363 K at various hydrogen pressures as well as in the presence of deuterium, in a recirculating reactor. The main reactions are hydrogenolysis, isomerization, and deoxygenation (2-butanol, 2-butanone, and 2-butenes are formed). In the course of transformation, the surface of the catalyst is oxidized via deoxygenation, leading to the generation of Lewis acid–base ion pairs. 2-Butanol and 2-butenes are formed on Cu(0) atoms while the formation of 2-butanone occurs mainly on copper ions. Differences between the reactivities of the oxirane isomers and the characteristic features of the mechanism of the three reactions observed are discussed in detail. Finally, experimental observations are compared with the transformation of *cis*- and *trans*-1,2-dimethylcyclopropanes under similar conditions. © 1997

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INTRODUCTION

Relatively few data are available in the literature regarding the transformation of oxiranes on Cu catalysts (1–5). No experimental observations have been published at all on transformations of dimethyloxiranes on copper catalysts. Therefore, it seemed an important task to study the transformation of *cis*- and *trans*-2,3-dimethyloxirane on a copper catalyst at various hydrogen pressures and in the presence of deuterium. These studies allow conclusions to be drawn regarding the stereochemistry of the reactions, the structure of the adsorbed form generated on the metal surface, and, consequently, the mechanism of the transformation.

EXPERIMENTAL

Materials

cis- and *trans*-2,3-Dimethyloxiranes were purchased from Aldrich. The purity of the isomers were 99 and 98%, respectively. The *trans*-isomer was shown to contain no detectable amount of the *cis*-isomer. Before the reaction, oxirane samples were subjected to several freeze–thaw cycles.

Cu/SiO₂ catalyst (6.36%) was prepared by ion exchange. Preparation and characterization of the catalyst have been described (6). Fresh catalyst (20 mg) was added for each measurement. Pretreatment was performed in a recirculating system; the catalyst was treated at 26.6 kPa hydrogen or deuterium for 1 h at 573 K.

Methods

Measurements were carried out in a recirculation reactor (7). The volume of the reactor was 69 ml and the total volume of the system was 170 ml. The reactor was heated by an air thermostat. The total sample volume was ca. 0.5 ml. 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 quadrupole mass selective detector was attached to the system. Separation was done in a Carbowax 20M capillary column (HP-20M, 25 mm × 0.2 mm × 0.2 μm film thickness). Calculations were made in a Data Apex Chromatography Station for Windows 1.5 using a HP 5970 chromatogram analysis program.

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 D₂O was 99.8%). Deuterium was deoxygenated by a Model 1000 oxygen trap (CRS, U.S.A.).

Procedure

cis- or *trans*-Oxirane (1.33 kPa) was added for each measurement. When the hydrogen pressure dependence was studied, hydrogen pressure was varied within the range of 0–101.3 kPa. Reaction temperature was 363 K for both isomers. The effect of temperature was studied at a hydrogen pressure of 20 kPa, at 353–403 K.

Initial rates (%/min) and turnover frequencies (min⁻¹) were calculated. Based on temperature dependence, apparent activation energies were also calculated.

Deuterolysis was performed at a deuterium pressure of 20 kPa and a reaction temperature of 363 K. The data were used for the calculation of deuterium distribution.

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The mass spectra were measured in hydrogen and deuterium, too. The measured deuterium spectra were corrected by the natural deuterium distribution. The molecular ion of 2-butanone at mass 72 was used for the calculation of deuterium distribution on the basis of the equation $I_x/\Sigma I_x \times 100$. Fragments at mass 43 and 58 are indicating that CHD group is present in the molecule. In the case of 2-butanol the peaks at mass 45 and 59 were selected for the calculation. The two peaks together contains the whole molecule and make it possible to calculate the deuterium distribution of the molecular ion. The mass spectra at mass 45 were almost identical in hydrogen and in deuterium, indicating that there is no deuterium in the CH₃ and CH groups. Because of the experimentally demonstrated OD–OH exchange during the chromatographic separation, the 2-butanol containing one C–D bond was considered as *d*₂, while the molecule containing two C–D bonds was considered as *d*₃, and so on.

RESULTS AND DISCUSSION

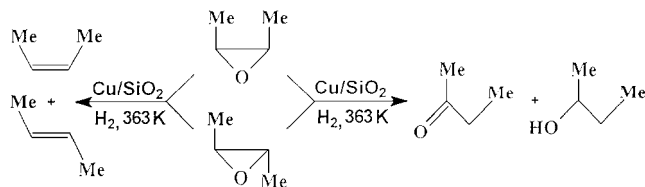
Activity and Selectivity of Transformations

Hydrogenolysis and isomerization lead to the formation of 2-butanol and 2-butanone, while deoxygenation produces *cis*- and *trans*-2-butene (Scheme 1).

The GC–MS recirculation system operating with a capillary column did not allow the simultaneous separation of volatile compounds and the components with higher boiling point. Conditions were therefore selected so that 2-butanol, 2-butanone, and oxiranes were separated from each other, while *cis*- and *trans*-2-butene were eluted in one peak.

Rates of formation of the products of the two isomeric dimethyloxiranes are shown in Figs. 1 and 2.

The transformation rate of *cis*-2,3-dimethyloxirane on a Cu/SiO₂ catalyst at 363 K was only 20% higher than that of the *trans*-isomer, unlike on a platinum or palladium catalyst (8, 9) where $k_{cis} \gg k_{trans}$; i.e., in the case of dimethyloxiranes experimental results obtained on copper resemble those measured on nickel. The difference between reaction rates on Cu/SiO₂ may be accounted for by the difference between the rates of the deoxygenation reactions of the two oxirane isomers.



SCHEME 1. Reaction pathways in the transformations of *cis*- and *trans*-2,3-dimethyloxiranes.

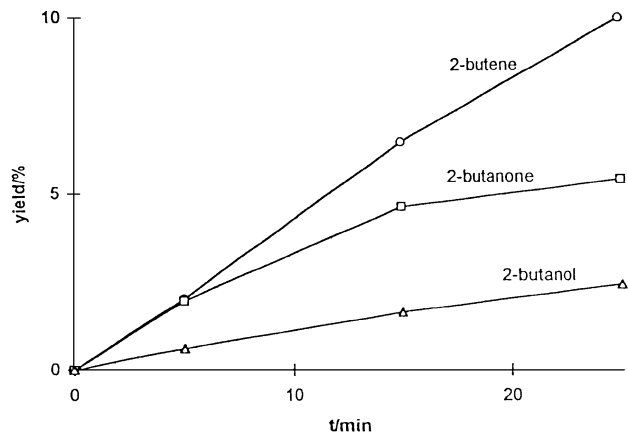


FIG. 1. Transformation of *cis*-2,3-dimethyloxirane over Cu/SiO₂ catalyst (363 K; $p_{\text{hydrogen}} = 20$ kPa; $p_{\text{oxirane}} = 1.33$ kPa; catalyst = 20 mg).

As a result of measurements of temperature dependence, apparent activation energies were determined (Table 1). These were nearly identical for the two isomers and higher than on Pd catalyst (10). The low activation energy on Pd indicates that oxirane is adsorbed on the surface of the metal at very low temperatures already and covers it completely. Temperature plays a role in the hydrogenolysis of C–Pd bond and this process is rate-limiting step at low temperatures. Conversely, the surface of copper is probably not fully covered by oxirane and—in contrast to the process on palladium—the rate limiting step is the cleavage of the C–O bond.

HYDROGEN PRESSURE DEPENDENCE OF RING-OPENING REACTIONS

Dependence of the transformations upon hydrogen pressure (Figs. 3 and 4) reveals that the rates of hydrogenolysis and deoxygenation increase virtually linearly with

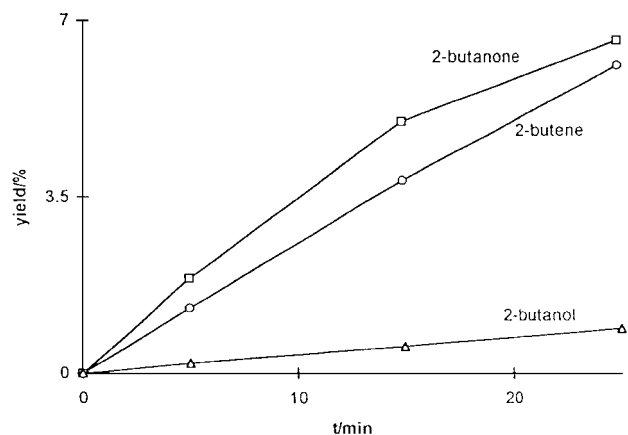




FIG. 2. Transformation of *trans*-2,3-dimethyloxirane over Cu/SiO₂ catalyst (363 K; $p_{\text{hydrogen}} = 20$ kPa; $p_{\text{oxirane}} = 1.33$ kPa; catalyst = 20 mg).

TABLE 1
Comparison of Activation Energies (E_a)

Products	E_a (kJ/mol)	
		
2-Butene	64.3	77.1
2-Butanone	60.7	77.7
2-Butanol	36.9	47.1
Total	60.0	76.3

Note. 353–403 K; $p_{\text{hydrogen}} = 20$ kPa; $p_{\text{oxirane}} = 1.33$ kPa; catalyst = 20 mg Cu/SiO₂.

increasing hydrogen pressure in the case of both isomers, while the rate of isomerization displays a maximum (see below). The increase is especially pronounced in the case of deoxygenation; therefore, while at low and medium hydrogen pressures the main products are 2-butanone and 2-butene, at high hydrogen pressures it is unambiguously deoxygenation that becomes predominant. In contrast to platinum, palladium and nickel, hydrogenation of 2-butene to yield butane is not observed. (Due to the significantly higher adsorptivity of oxirane, the olefin is not hydrogenated on Cu under these conditions, in the presence of oxirane.)

It should be noted that the effect of hydrogen pressure has an identical tendency in the case of both 2-butene and 2-butanol and the formation of these products is not repressed even at high hydrogen pressures, suggesting that they are most probably formed on active sites of similar structure.

Oxiranes oxidize the surface of the copper catalyst via deoxygenation (5). Due to the presence of hydrogen, however, the oxidized surface is reduced, leading to the formation of a partially oxidized metal surface (11). As hydrogen pressure is increased, the rate of the reduction and consequently the ratio of Cu(0) atoms relative to Cu ions increases. At

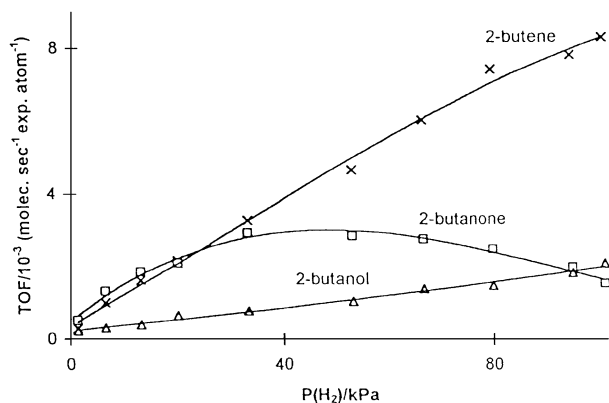


FIG. 3. Turnover frequency of product formation vs hydrogen pressure at *cis*-2,3-dimethyloxirane (catalyst = 20 mg Cu/SiO₂; 363 K).

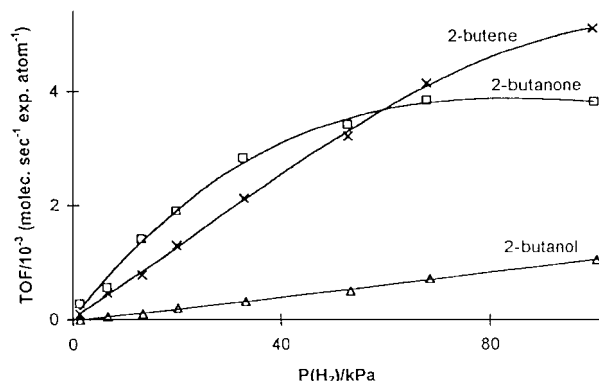


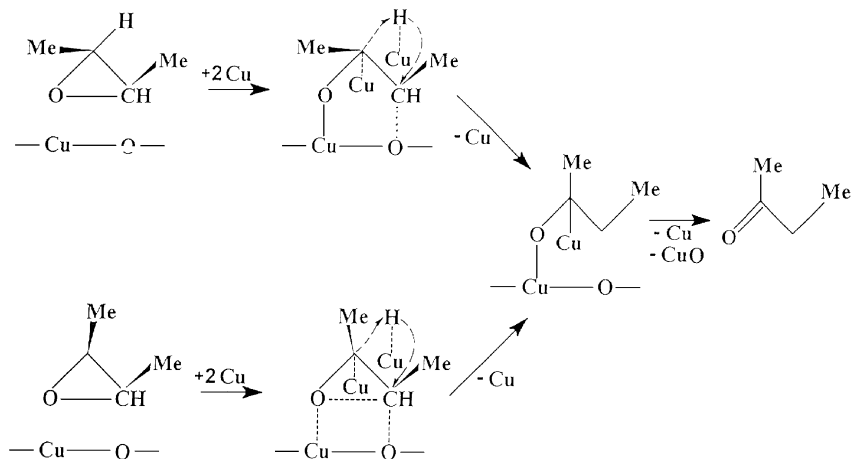
FIG. 4. Turnover frequency of product formation vs hydrogen pressure at *trans*-2,3-dimethyloxirane (catalyst = 20 mg Cu/SiO₂; 363 K).

high hydrogen pressures, therefore, reactions proceeding on Cu(0) atoms may become dominant and those take place on copper ions may be limited. Deoxygenation evidently proceeds on Cu(0) atoms; therefore, it is to be expected that the amount of 2-butene will increase with increasing hydrogen pressure. Considering the similarity of hydrogen dependences, the formation of 2-butanol is most probably also associated with the presence of Cu(0) atoms (in other words, Cu(0) atoms are necessary for the formation of 2-butanol).

Regarding isomerization, in the case of the *cis*-isomer the process displays a slight maximum while the isomerization of the *trans*-oxirane is more like a saturation curve in the pressure range studied. Naturally, it cannot be excluded that above 100 kPa a decrease in rate may occur also in the case of the *trans*-isomer. The effect of hydrogen pressure on reaction rate suggests that it is not electrophilic catalysis alone that brings about the formation of 2-butanone.

It is a well-known fact that zero-valent copper has a low affinity to alcohols (12). However, insertion of oxygen into a copper surface generates positively charged active sites that promote the adsorption of alcohols. For example, the amount of methanol adsorbed on a partially oxidized copper surface displays a maximum at 20% oxygen coverage. Active centers are made up by Lewis acid–base ion pairs. The alkoxide ion is adsorbed on the metal ion while the hydrogen of the hydroxyl group is attached to the oxygen (13). By analogy, adsorption of oxiranes and cleavage of their C–O bonds may proceed along similar lines. Cu(0) atoms surrounding the active sites may play an important role in hydrogen supply (5). Since isomerization necessitates the presence of Cu–O ion pairs, maximal rate may be expected at a hydrogen pressure which allows a maximal surface concentration of these active sites.

The maximum observed around 40 kPa in the case of the *cis*-isomer indicates a higher sensitivity to hydrogen than that of the *trans*-isomer. This difference supports the assumption that the decrease in the rate of isomerization



SCHEME 2. Mechanisms of 2-butanone formation.

observed is associated not only with a decrease in the surface concentration of copper ions but also with the dissociative character of the mechanism. The lower sensitivity of the *trans*-isomer to hydrogen pressure suggests that in this case the dissociation step plays a less significant role in the mechanism. It seems highly probable that cleavage of the C-O bond necessary for ring opening proceeds with an identical rate whether adsorption is planar or edgewise. In the case of the *cis*-isomer, facial adsorption is possible, while steric hindrance in the case of the *trans*-isomer favors edge adsorption. It is therefore probable that cleavage of the C-O and C-H bonds of the *cis*-isomer is simultaneous, while cleavage of the C-O bonds of the *trans*-isomer precedes that of its C-H bond, rendering this isomer less sensitive to the effect of hydrogen (Scheme 2).

Transformation Mechanisms: Nature of Active Sites

In the course of experiments in deuterium, no deuterium was found in unreacted oxirane irrespective of the kind of isomer studied, indicating that oxirane is irreversibly adsorbed on the Cu surface and is desorbed only as a product. There was no traceable amount of deuterium in 2-butenes either, evidence that deoxygenation proceeds without cleavage of the C-H bond.

Isomerization resulted in the formation of mainly 2-butanone- d_0 ; however, a small amount of 2-butanone- d_1 was also detected. The observed predominance of 2-butanone- d_0 indicates that it is essentially intramolecular hydrogen migration that happens.

Comparison of the data in Tables 2 and 3 with those published regarding nickel (14) reveals that while on copper the product is mainly 2-butanone- d_0 , on nickel mostly 2-butanone- d_1 is formed in the course of isomerization. This allows to conclude that, in contrast to copper, on nickel 2-butanone is formed mostly via the triadsorbed (or π -allyl) form.

There is a significant difference between the deuterium distributions of deuterated 2-butanol samples obtained from *cis*- and *trans*-2,3-dimethyloxirane. Namely, the *cis*-compound yielded more 2-butanol- d_3 , while the *trans*-isomer gave rise to more 2-butanol- d_2 . The reason for this is that planar adsorption of *cis*-oxirane allows a more rapid formation of the transitional π -allyl species which is adsorbed form of 2-butanol- d_3 . The mechanism represented in Scheme 3 well demonstrates the formation of the two types of deuterated butanol.

In *trans*-oxirane, however, the formation of the above species is inhibited, since only one of the two hydrogen atoms, C(2)-H or C(3)-H, is situated close to the surface of the catalyst. Consequently, due to planar adsorption, the formation of the diadsorbed surface species is preferential, resulting in a higher reaction rate for 2-butanol- d_2 .

Based on our experimental results, isomerization, hydrogenolysis, and deoxygenation may be interpreted as shown in Schemes 2 and 3.

According to the hypothetical mechanism outlined here, in the course of isomerization the ring is opened on

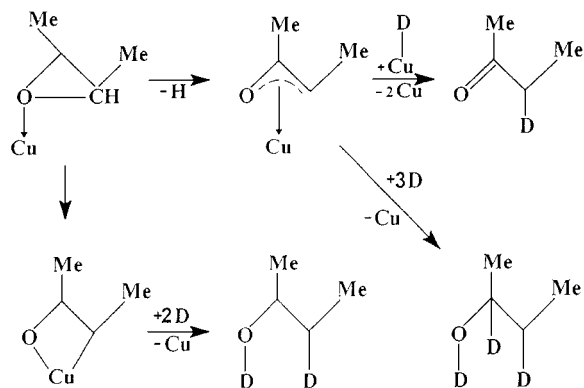
SCHEME 3. Mechanisms of 2-butanone- d_1 , 2-butanol- d_2 , and 2-butanol- d_3 formations.

TABLE 2
Transformation of *cis*-2,3-Dimethyloxirane in Deuterium

<i>t</i> (min)	Conv. (%)	<i>S</i> ₂ -butanone	<i>S</i> ₂ -butanol	<i>S</i> ₂ -butene	Distribution of deuterium (%)							
					In 2-butanone					In 2-butanol		
					<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄
5	4.6	0.43	0.13	0.44	70.9	26.0	3.1	0	0	91.6	8.4	0
15	12.7	0.36	0.13	0.51	55.2	37.8	6.1	0.9	0	82.5	17.5	0
50	23.1	0.30	0.14	0.56	37.2	45.2	13.9	3.3	0.4	66.8	24.7	8.5

Note. Catalyst = 20 mg Cu/SiO₂; *p*_{deuterium} = 20 kPa; *p*_{oxirane} = 1.33 kPa; 363 K.

neighboring surface -Cu-O- atoms. The reaction itself is intramolecular migration of hydrogen, which proceeds in an essentially similar way in both the *cis*- and the *trans*-isomer. In the case of the *cis*-isomer, however, cleavage of C-O and C-H bonds may occur simultaneously due to planar adsorption, while steric hindrance makes adsorption of the *trans*-isomer edgewise and therefore cleavage of C-O precedes that of C-H.

2-Butanol is formed on Cu(0) atoms. The copper atom is inserted into the C-O bond, leading to the formation of metalla-oxacyclobutane. The driving force of the reaction is the strain energy of the three-member ring which is markedly reduced upon formation of the four-member ring. Insertion does not require planar adsorption; therefore, there is no significant difference between the transformation rates of the two isomers.

The active centers for the above reactions are supplied by the partially oxidized copper surface generated by the opposed processes of oxidation and reduction. Maximal catalytic activity is realized when an optimal copper/copper oxide surface structure is formed. The determinant factor for isomerization is the presence of copper ions, while for hydrogenolysis and deoxygenation it is that of Cu(0).

Comparison of Transformation of Cyclopropanes and Oxiranes

The results of experiments on oxirane stereoisomers described above allow a comparison with data on the cor-

responding cyclopropane stereoisomers, published earlier (6). Namely, what is the effect of the presence of the heteroatom in the three-member ring on transformation rate, on selectivities, and, last but not least, on stereochemical characteristics in the case of stereoisomers of similar geometry?

Owing to significant differences between the electronegativities of C and O atoms, oxiranes are more readily adsorbed on copper than are cyclopropanes. Consequently, the rate of hydrogenative ring opening is considerably higher in the case of oxiranes.

For both types of compounds, transformation of the *cis*-stereoisomer proceeds at a higher rate. This observation as well as other experimental data (dependence on hydrogen pressure, effect of temperature) yield information regarding the geometry and structure of the adsorbed surface species, namely, that the *cis*-compounds are adsorbed in a planar and the *trans*-isomers in an edgewise manner.

Naturally, there is a large difference between the directions of the reactions as well. In the case of cyclopropanes only C-C cleavage occur, in the case of oxiranes both C-O and C-C cleavage may theoretically happen. However—also as a consequence of what was stated above—the latter fails to come about. In the case of cyclopropanes there is two-way hydrogenolysis (pentane and isopentane are formed), while oxiranes undergo deoxygenation, isomerization, and hydrogenolysis. The selectivity of the transformation is affected by differences due to the geometry of the stereoisomers.

TABLE 3
Transformation of *trans*-2,3-Dimethyloxirane in Deuterium

<i>t</i> (min)	Conv. (%)	<i>S</i> ₂ -butanone	<i>S</i> ₂ -butanol	<i>S</i> ₂ -butene	Distribution of deuterium (%)							
					In 2-butanone					In 2-butanol		
					<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄
5	3.4	0.56	0.06	0.38	72.1	25.4	2.5	0	0	95.8	4.2	0
15	9.4	0.53	0.06	0.41	55.0	38.1	6.0	1.0	0	92.5	7.5	0
50	17.6	0.49	0.06	0.45	35.9	44.3	15.1	4.2	0.6	88.3	9.7	2.1

Note. Catalyst = 20 mg Cu/SiO₂; *p*_{deuterium} = 20 kPa; *p*_{oxirane} = 1.33 kPa; 363 K.

Finally it must be noted that the catalytic reactions take place on surface active sites of different types. In the case of cyclopropanes it is mainly Cu(0) atoms that dominate; in the case of oxiranes, in addition to Cu(0) atoms copper ions also play a significant role (5).

CONCLUSIONS

In order to elucidate the stereochemistry of the transformation of oxiranes on copper under hydrogenative conditions, *cis*- and *trans*-dimethyloxirane were studied. The following results were obtained:

1. The *cis*-isomer has a slightly higher reactivity than the *trans*-isomer;

2. In the case of the *cis*-isomer, the rates of the three reactions studied decrease in the order deoxygenation > isomerization > hydrogenolysis, while the order for the *trans*-isomer is isomerization > deoxygenation > hydrogenolysis;

3. Increasing hydrogen pressure has a more significant effect on the pattern of transformations of the *cis*-isomer than on that of the *trans*-compound;

4. The above results are interpreted by the different geometry of the adsorption of the two compounds: the *cis*-isomer is adsorbed on the surface in a planar manner, while adsorption of the *trans*-isomer is edgewise.

ACKNOWLEDGMENTS

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