

# Transformation of Vinyloxirane on Pt–SiO<sub>2</sub> and Pd–SiO<sub>2</sub>

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The transformation of vinyloxirane and ethyloxirane were studied on Pt–SiO<sub>2</sub> and Pd–SiO<sub>2</sub> catalysts at 273 and 301 K in a recirculation reactor, in the presence of hydrogen or deuterium. There are significant differences, not only in reaction rates, but also in reaction routes, depending upon the nature of the metal. The main reaction routes are: deoxygenation and hydrogen or deuterium addition on Pt–SiO<sub>2</sub>; isomerization and hydrogenolysis on Pd–SiO<sub>2</sub>. The reaction routes leading to the formation of the individual products are interpreted on the basis of the experimental results. In the case of the hydrogenolysis of oxiranes, Pd was shown to exhibit a special reactivity, unlike earlier observations described in the literature.

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**Key Words:** vinyl- and ethyloxirane; Pt–SiO<sub>2</sub> and Pd–SiO<sub>2</sub> catalysts; effects of hydrogen and deuterium; mechanism of ring opening; deoxygenation; hydrogenolysis; isomerization; hydrogenation; deuteration; isotope effect.

## INTRODUCTION

Hydrogenative ring opening of oxiranes has been studied extensively (see (1–3)). The reaction has both theoretical and practical significance, also proven by the reports published lately (e.g., (4–8)). 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 characterization of metal catalysts.

Studies on oxiranes, containing a C=C bond are of special importance, as the presence of two functional groups within a single molecule makes possible the investigation of the selectivity of catalytic hydrogenolysis or hydrogenation which is important from the point of view of synthesis, on the one hand, and for studies on the mechanism of metal catalytic reactions, on the other. For these two purposes a more detailed elucidation of the hydrogenation and hydrogenolysis of vinyloxirane was set as the aim of the present work.

Relatively little information has been published on the catalytic transformation of vinyloxirane in the presence of hydrogen. This is despite the huge interest for the use of

vinyloxirane in the chemical industry, because nowadays vinyloxirane can be prepared easily by the selective epoxidation of butadiene (9). The isomerization and hydrogenolysis of the oxirane ring are catalyzed by Rh-complexes (10, 11). In the case of Pd- and Ir-complexes, selective hydrogenation of the C=C bond has been observed (12). The utilization of metal catalysts (Rh, Pd, Pd–Au, Pd–Re) has been published in patents (13–15) reporting the selective hydrogenation of the C=C bond. Hydrogenolysis of the oxirane ring was observed during hydrogenation of steroid vinyloxiranes catalyzed by Raney and Ni (16).

According to earlier studies (17), the main products of the transformation of ethyloxirane on Pt and Pd catalysts at 300–400 K are 2-butanol and 2-butanone. In the course of the hydrogenative transformation of monosubstituted oxiranes the cleavage of the C–O bond near the substituent yields primary alcohol and aldehyde while the cleavage of the other C–O bond results in the formation of secondary alcohol and ketone. Regioselectivity depends primarily on the quality of the metal catalyst. While in the case of Pt and Pd, bond cleavage occurs from the sterically less hindered direction, on Ni and Cu it proceeds from the other, sterically more hindered direction (17). These reactions are also accompanied by deoxygenation, depending upon the catalyst.

## EXPERIMENTAL

### Materials

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

Three percent Pd–SiO<sub>2</sub> (D = 15%) and Pt–SiO<sub>2</sub> (D = 14%) were prepared by impregnation (18, 19). The catalysts were reduced in flowing hydrogen at 623 K. The dispersion of the catalysts was determined by H<sub>2</sub> and CO chemisorption and were checked by transmission electron microscopy. In the course of the pretreatment the catalyst was heated to 423 K at 26.6 kPa hydrogen or deuterium pressure, kept at this temperature for 1 h and cooled to the reaction temperature under continuous vacuum.

## Methods

Measurements were carried out in a circulation reactor (20). The volume of the reactor was 69 cm<sup>3</sup> and that of the entire system was 170 cm<sup>3</sup>. The reactor was heated by an air thermostat. Analysis was carried out in a gas chromatograph (HP 5890) with a quadrupole mass selective detector (HP 5970 MSD) attached to the system. Separation was done in a Carbowax 20M capillary column (HP-20M). 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 15 EHG generator (the purity of D<sub>2</sub>O was 99.8%). Deuterium was deoxygenated by a Model 1000 Oxygen Trap (CRS, USA).

## Procedure

Fresh catalyst (10 mg) and 1.33 kPa of vinyloxirane or ethyloxirane were added for each measurement. For competition studies a 1 : 1 mixture of the two oxiranes was added to a total pressure of 1.33 kPa. The pressure of hydrogen or deuterium was 20 kPa in all cases; reaction temperatures were 273 and 301 K in the case of both molecules.

Samples taken at various times were used for the calculation of molar percentage values which served for the basis of comparison. Deuterium distribution was calculated from the data obtained in measurements with deuterium.

## RESULTS AND DISCUSSION

### Activity of Catalysts

Changes in the conversion of the two oxiranes studied as a function of reaction time in the presence of hydrogen or deuterium at 273 and 301 K are shown in Figs. 1 and 2.

According to these data, under identical experimental conditions the activity of Pt is higher than that of Pd in the hydrogenolysis of ethyloxirane (the conversion of ethyloxirane is minimal at 273 K on Pd). This is probably caused by the presence of the Pd- $\beta$ -hydride, which is inactive in C-O hydrogenolysis. As regards the rate of conversion, the situation is the same for vinyloxirane at 273 K because the  $\beta$ -hydride is inactive in hydrogenation of C=C bond (21). At 301 K, however, the transformation of vinyloxirane is faster on Pd than on Pt. This is likely explained by the instability of the  $\beta$ -hydride in the presence of oxygen, since trace amounts of oxygen can destroy this phase (22). The vinyloxirane can be deoxygenated at 301 K, producing a surface oxide layer. The formation of ionic type active sites is also manifested in the reaction routes because the main products on Pd-SiO<sub>2</sub> originate from the cleavage of the more hindered C-O bond of vinyloxirane. It is an important

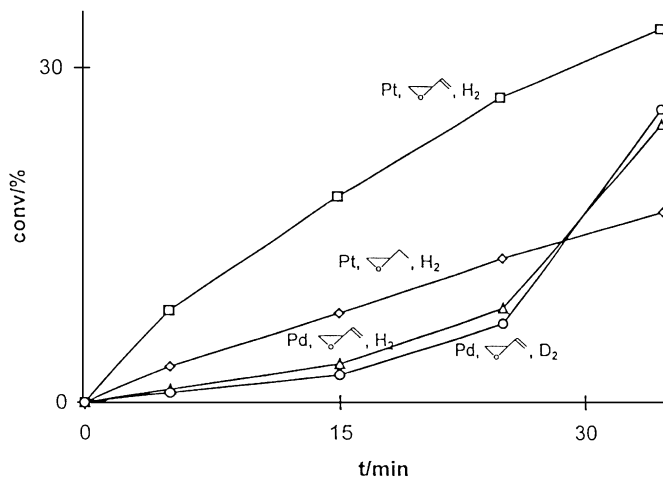


FIG. 1. Transformation of ethyloxirane and vinyloxirane on Pt-SiO<sub>2</sub> and Pd-SiO<sub>2</sub> catalysts (catalyst = 10 mg, 273 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium or hydrogen}} = 20$  kPa).

experimental observation that the conversion of vinyloxirane on Pd is nearly identical in hydrogen and in deuterium. This means that at 301 K, under the given conditions the  $\beta$ -hydride phase no more plays a determinative role.

Since on well-hydrogenating catalysts (Pt, Pd) vinyloxirane also gives rise to ethyloxirane, hydrogenolysis and isomerization of ethyloxirane were first examined.

### Transformation of Ethyloxirane on Pt-SiO<sub>2</sub>

After deoxygenation and hydrogenation of the surface intermediate, ethyloxirane is selectively converted into butane on Pt catalysts at temperatures as low as 273 K at the experimental conditions outlined in Fig. 1. According to the evidence of the measurements in deuterium, simultaneously with deoxygenation the C-H bonds are also cleaved

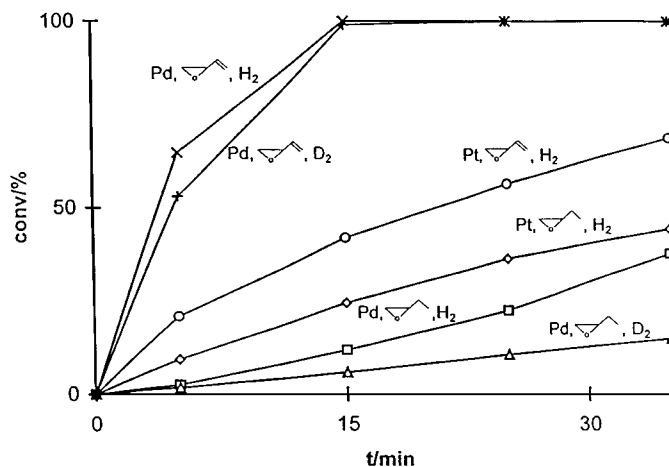


FIG. 2. Transformation of ethyloxirane and vinyloxirane on Pt-SiO<sub>2</sub> and Pd-SiO<sub>2</sub> catalysts (catalyst = 10 mg, 301 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium or hydrogen}} = 20$  kPa).

TABLE 1  
Transformation of Ethyloxirane in Deuterium over Pt-SiO<sub>2</sub> Catalyst

t (min)	conv. (%)	S <sub>butane</sub>	S <sub>2-butanol</sub>	S <sub>2-butanone</sub> <sup>a</sup>	Distribution of deuterium (%)							
					In butane						In 2-butanol	
					d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	d <sub>6</sub>	d <sub>7</sub>	d <sub>2</sub>	d <sub>3</sub>
5	9	0.75	0.21	0.04	69.6	26.2	4.2	0	0	0	100	0
15	24	0.76	0.22	0.02	57.7	26.7	12.0	3.5	0	0	100	0
25	34	0.76	0.22	0.02	52.9	25.7	12.7	5.9	2.8	0	95.0	5.0
35	44	0.75	0.23	0.02	50.4	24.2	13.2	7.4	3.7	1.1	92.2	7.8

Note. Catalyst = 10 mg, 301 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium}} = 20$  kPa.

<sup>a</sup> Only 2-butane-*d*<sub>1</sub> formed.

(e.g., 75% butane-*d*<sub>2</sub>, 21% butane-*d*<sub>3</sub>, and 4% butane-*d*<sub>4</sub> were formed at the conversion of 3%). At 301 K the main product is still butane (S<sub>butane</sub> = 77%) but, as a results of the cleavage of the sterically less hindered bond, 2-butanol (S<sub>2-butanol</sub> = 22%) and small amounts of 2-butanone (less than 1%) also appear. This suggests that the first event is the formation of PtO sites on the surface and the active sites for isomerization are formed in the course of this process.

Deoxygenation of oxiranes under relatively mild experimental conditions is a well-known reaction (23). The driving force to the reaction is the strain energy of the three-membered ring. Due to its stereospecific character, this reaction is used in the synthetic organic chemistry for the stereoselective formation of C=C bonds. The process takes place at room temperature on the surface of Pt and leads to the formation of PtO. Under the given experimental conditions, PtO is readily converted back to Pt by hydrogen which makes deoxygenation continuous. The latter, well-known reaction is used frequently for the characterization of Pt catalysts (hydrogen-oxygen titration method to measure the surface area of supported platinum catalysts (24, 25)).

Measurements in the presence of deuterium (Table 1) showed that hydrogenolysis and isomerization give rise to 2-butanol-*d*<sub>2</sub> and 2-butanone-*d*<sub>1</sub>, respectively.

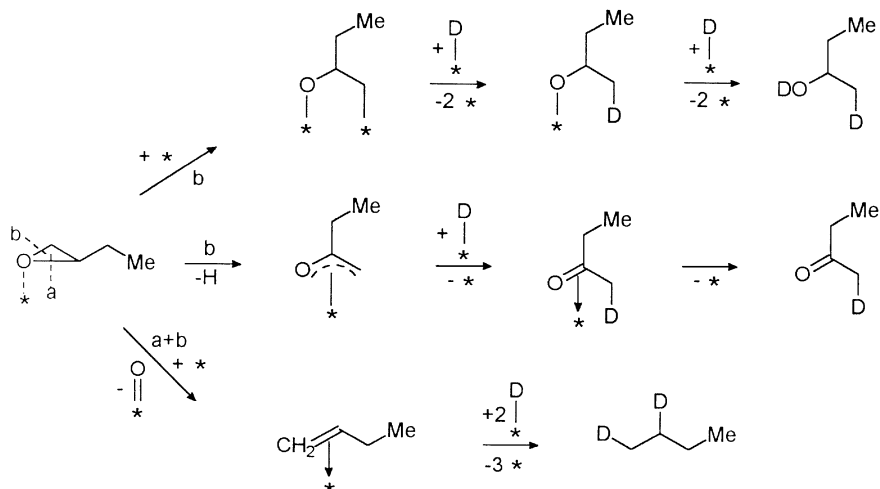
In the case of the products containing oxygen, the place of the incorporation of deuterium may also be determined on the basis of the evaluation of mass spectra. Deuterium is located on the methyl group and the oxygen in 2-butanol-*d*<sub>2</sub> and on the methyl group in 2-butanone-*d*<sub>1</sub> (Scheme 1). (It has to be noted that the deuterium in the O-D group is exchanged for hydrogen in the capillary glass column; therefore this D is not detected in the mass spectrum. The occurrence of the exchange on the column was verified by our measurements with perdeuterated methanol.) The scarcity of multiple exchange events in the case of 2-butanone and 2-butanol allows us to conclude that the intermediate formed after ring opening spends very little time on the surface; i.e., the oxygen-containing products are very rapidly desorbed from the surface of the catalyst and the proba-

bility of readsorption in the presence of oxiranes is very low. It should be noted that conversions on the Pt catalyst recorded in the measurements of hydrogen are in good agreement with those of deuterium at both temperatures, which means that there is no isotope effect.

#### Transformation of Ethyloxirane on Pd-SiO<sub>2</sub>

The extent of the conversion of ethyloxirane on the Pd catalyst at 273 K in the presence of hydrogen or deuterium is very small, only traces are converted to 2-butanol. At 301 K it is mainly the sterically less hindered C-O bond that is cleaved and 2-butanol is formed (even in the 35th minute, conversion to butane, butanal, and 2-butanone is only 2.9%). Thus, under identical conditions the amount of butane formed on Pd is two orders of magnitude less than on Pt and the main product is 2-butanol. Consequently, on Pd the main reaction route is not deoxygenation but hydrogenolysis of the C-O bond. The repression of deoxygenation may be explained by the presence of surface PdO which is generated at the beginning of the reaction and is less readily reduced than PtO under the given conditions. According to the new literature data (26) (XPS analysis of palladium oxide layers and particles): "The reduction rate of the surface oxide is ~8 times lower than the reduction rate of the bulk oxide."

Conversion was considerably higher in the measurements using hydrogen than in those with deuterium (Fig. 2), indicating the operation of the isotope effect. Our earlier data (7) indicated that at a higher temperature (363 K) there was no significant difference in the behaviour between the two isotopes in the case of 2,3-dimethyloxirane. No isotope effect was observed by other authors in the course of the hydrogenolysis and deuterolysis of oxiranes either (17, 27-32). The evidence for the isotope effect in the course of the hydrogenolysis of ethyloxirane at a relatively low temperature on Pd allows a very important conclusion to be drawn regarding the reaction mechanism, namely, that hydrogen or deuterium adsorbed on the surface plays a role in the rate-limiting step of the reaction, i.e. ring-opening. At



SCHEME 1. Mechanism of ethyloxirane transformation on Pt-SiO<sub>2</sub> and Pd-SiO<sub>2</sub> catalysts.

higher temperatures, where no isotope effect is observed, the reaction of the hydrogen atom with the oxirane ring is preceded by the dissociation of the C-O bond on the surface. At lower temperatures, however, the three-membered ring is opened by hydrogen or deuterium chemisorbed on the surface.

The entry of deuterium into the oxygen-containing products is similar to the process described for Pt. There is no detectable level of multiple exchanges; therefore the presence of 2-butanol-*d*<sub>2</sub> and 2-butanone-*d*<sub>1</sub> again indicates fast desorption into the gas phase and the absence of readsorption. In the case of butanol-*d*<sub>1</sub> formed via cleavage of the sterically more hindered bond, the situation is similar.

On the basis of our experimental results, the isomerization and hydrogenolysis of ethyloxirane may be interpreted as shown in Scheme 1.

According to the reaction pathway outlined in Scheme 1, 2-butanol and 2-butanone are formed on reduced metal clusters by associative and dissociative mechanisms, respectively. In this case the isomerization takes place on metal atoms where the molecule is bound to the surface by  $\pi$ -allyl

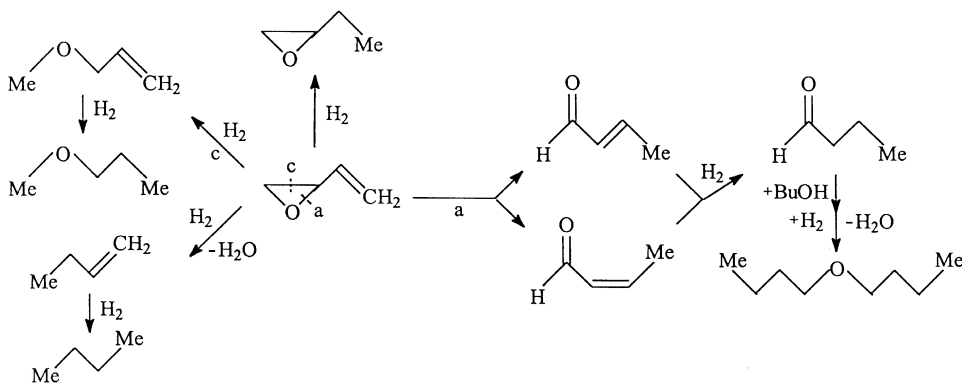
adsorption (27). Pd also tends to form such electrophilic centers by the surface oxidation, while Pt—due to the rapid reduction of PtO—is less prone to this course of events.

It is important to mention that no deuterium was found in unconverted ethyloxirane on either catalyst studied. This observation again supports the earlier notion that oxirane is irreversibly bound to the surface of Pt and Pd catalysts and is desorbed only as a product.

#### Transformation of Vinyloxirane on Pt-SiO<sub>2</sub>

Reaction routes of the transformations of vinyloxirane on Pt and Pd catalysts in the presence of hydrogen or deuterium are demonstrated on Scheme 2. The extent of the participation of the individual processes depends on the experimental conditions and, naturally, on the quality of the catalyst. In the absence of hydrogen (mixed with 67 kPa of He), vinyloxirane is not transformed either on reduced Pt, or on reduced Pd, at 273 or 301 K.

In the presence of hydrogen, on Pt catalyst at 273 K 1-butene, butane, and ethyloxirane are formed (Fig. 3). The hydrogenation and deoxygenation of vinyloxirane take



SCHEME 2. Reaction pathways in the transformation of vinyloxirane on Pt-SiO<sub>2</sub> and Pd-SiO<sub>2</sub> catalysts.

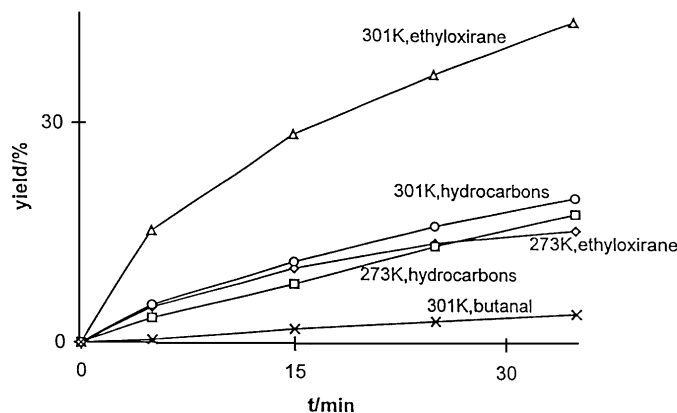


FIG. 3. Transformation of vinyloxirane on Pt-SiO<sub>2</sub> catalyst (catalyst = 10 mg,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 20$  kPa).

place simultaneously. As long as vinyloxirane molecules are present in the system, the methyloxirane and butene molecules cannot adsorb on the surface; therefore their transformation cannot occur. This is supported by the fact that the 1-butene/butane ratio is more or less constant in the course of the reaction and 1-butene is predominant all along (Table 2).

Under the given chromatographic conditions, butane and butene are eluted in one peak; therefore they were quantified on the basis of the characteristic  $m/e$  values (56, 58). Formation of butane mainly from ethyloxirane is also supported in an indirect way by the near identity of the amount of hydrocarbon formed in the ethyloxirane/Pt and vinyloxirane/Pt systems which, on the other hand, allows one to conclude that the effect of the substituent on deoxygenation is not the determinant.

At 301 K, the main product is ethyloxirane but the amount of 1-butene and butane is still significant (Fig. 3); moreover, cleavage in the sterically more hindered direction also takes place, giving rise to butanal. Since in the ethyloxirane/Pt system it is the cleavage of the sterically less

TABLE 2

Distribution of 1-Butene and Butane in the Transformation of Vinyloxirane over Pt-SiO<sub>2</sub>

t (min)	Distribution of 1-butene and butane (%)					
	Pt/SiO <sub>2</sub>				Pd/SiO <sub>2</sub>	
	273 K		301 K		301 K	
	$m/e = 56^*$	$m/e = 58^*$	$m/e = 56^*$	$m/e = 58^*$	$m/e = 56^*$	$m/e = 58^*$
5	75	25	73	27	100	0
15	75	25	76	24	88	12
25	77	23	75	25	62	38
35	77	23	73	27	37	63

Note. Catalyst = 10 mg,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 20$  kPa.

hindered bond that is typical, it is improbable that butanal originates from ethyloxirane. It is more probable that butanal is formed in the course of the hydrogenation of the intermediate product originating from vinyloxirane. Just like in the ethyloxirane/Pt system, there is no significant difference between the measurements carried out in hydrogen and in deuterium (the differences are within 10%).

Deuterium distribution in ethyloxirane formed in the course of deuterium addition is presented in Table 3. Besides the expected maximum in  $d_2$  and further H-D exchange in the ethyl group, the amounts of  $d_0$  and  $d_1$  are relatively high, which is attributable to the fast dissociation of the vinylic and allylic hydrogens in vinyloxirane.

The reaction route of the transformation of vinyloxirane on a Pt-SiO<sub>2</sub> catalyst, in the presence of hydrogen, at 273–301 K is shown in Scheme 3.

Transformation of Vinyloxirane on Pd-SiO<sub>2</sub>

On a Pd catalyst in the presence of hydrogen at 273 K, hydrogenation of vinyloxirane yields mostly ethyloxirane (Fig. 4); some 3-methoxypropene is also formed via C-C bond cleavage, but traces of 1-butene are detectable as well. On the basis of the product composition it appears unambiguous that the geometry of the adsorption of vinyloxirane on Pd is different from that on Pt.

The representation of conversion versus time (Figs. 4 and 5) reveals that products formation has an induction period. This may be caused by the presence of the  $\beta$ -hydride at this temperature which is well known to be inactive in hydrogenation of alkenes (21). Vinyloxirane, however, destroys the hydride phase by its adsorption.

The results obtained in measurements with deuterium (Fig. 5) are slightly different from those with hydrogen as novel products appear: *trans*-2-butenal, *cis*-2-butenal, and, via their hydrogenation after an extended reaction time, butanal (the combined amount of the latter two products is below 1%).

The experimental data of the transformation of vinyloxirane at a higher temperature (301 K) show that the induction periods observed at 273 K are absent at this temperature. (As temperature increases, the  $\beta$ -hydride phase is most probably transformed faster by the oxirane adsorbed; therefore the induction period is not detected.)

The primary products are further converted: hydrogenation of 3-methoxypropene yields methoxypropane; and the hydrogenations of *trans*- and *cis*-butenal lead to butanal. Their connection is indicated by the decrease of concentration of the unsaturated molecules after a maximum and the increase of the saturated molecules after an induction period. 1-Butene formed by deoxygenation is gradually reduced to butane (Table 2). These statements hold true both in hydrogen and in deuterium. The main difference between the two systems is the operation of the isotope effect during hydrogenation of the C=C bond. Secondary

TABLE 3  
Transformation of Vinyloxirane in Deuterium over Pt-SiO<sub>2</sub><sup>a</sup> and Pd-SiO<sub>2</sub><sup>b</sup> Catalysts

t (min)	Distribution of deuterium in (%)																											
	ethyloxirane (a)					ethyloxirane (b)				3-methoxypropene (b)				methoxypropene (b)				trans-2-butenal (b)				butanal (b)						
	d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	d <sub>6</sub>
5	27	39	29	6	0	46	39	15	0	59	39	3	0	—	—	—	—	70	29	1	0	23	33	27	14	3	0	0
15	26	36	29	7	1	28	42	21	9	27	33	33	7	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	51	34	13	2	16	30	27	16	8	3	0
25	24	37	29	8	2	33	39	19	9	10	39	52	0	50	24	26	0	32	40	25	4	12	25	29	20	10	4	0
35	24	37	29	8	2	31	41	20	9	—	—	—	—	9	24	35	33	—	—	—	—	9	23	27	22	12	6	1

Note. Catalysts = 10 mg, 301 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium}} = 20$  kPa.

<sup>a</sup> Traces.

processes are, therefore, easier to follow using deuterium. Comparison of the results obtained at 273 and 301 K reveals that on increasing the temperature, cleavage in the sterically more hindered direction is significantly enhanced and becomes dominant. Cleavage in the sterically more hindered direction has already been observed in the case of 2,2-dimethyloxirane (28). In the present case the driving force of ring opening in the sterically hindered direction is the heterolysis of the weak allylic C–O bond which is at the same time part of the strained three-membered ring.

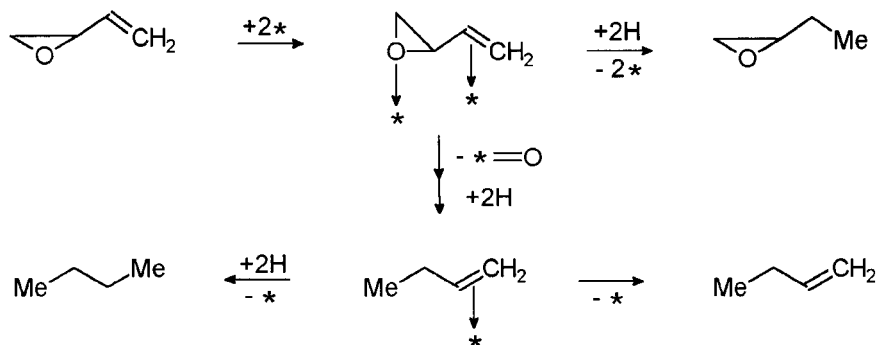
Since reaction routes operative on a Pd catalyst are different from those on Pt, measurements were also carried out in hydrogen at 363 K (Fig. 6). The main products are butanal, methoxypropane, and dibutyl ether, as secondary products (Scheme 4). Dibutylether is derived from butanal by the reaction verified earlier (semiacetal formation between adsorbed butanal and adsorbed butanol on the surface, followed by hydrogenolysis (33)). The hydrocarbon formed is mainly butane, but small amounts of methane and ethylene are also detectable. CO produced by the cleavage of butanal is most certainly retained on the surface of the catalyst and poisons part of the active centers.

In the course of the experiments in deuterium, untransformed vinyloxirane was shown to contain no deuterium

on either catalyst. The conclusions drawn from this fact are identical with those in the case of ethyloxirane. Deuterium distributions determined in the products of vinyloxirane (Table 3) exhibit interesting anomalies. The statements regarding the ethyloxirane formed on Pt also hold true in the case of Pd. The situation is similar also in the case of the other products (methoxypropane, butanal); the deuterium content of the molecules is lower than expected.

It is highly probable that the formation of dehydrogenated carbonaceous residue from the oxirane leads to a pool of surface hydrogen atoms and the  $d_0$  in oxirane. However, the tendency of deuterium incorporation to increase with the progress of reaction time is quite obvious. The formation of *trans*-2-butenal is the result of a hydrosomerization reaction involving the incorporation of a deuterium atom. H–D exchange in the primary product naturally yields  $d_2$  and  $d_3$  compounds.

The reaction of vinyloxirane on a Pd-SiO<sub>2</sub> catalyst, in the presence of hydrogen or deuterium at 273–301 K may be interpreted on the basis of Scheme 4. The considerable differences, as compared to Pt, may be attributed to the different affinities of the two metals toward oxygen, since the competition between the two reactive parts of the molecule (strained oxirane ring and C=C bond) is determined by this characteristic. The formation of 3-methoxypropane and,



SCHEME 3. Mechanism of vinyloxirane transformation on Pt-SiO<sub>2</sub> catalyst.

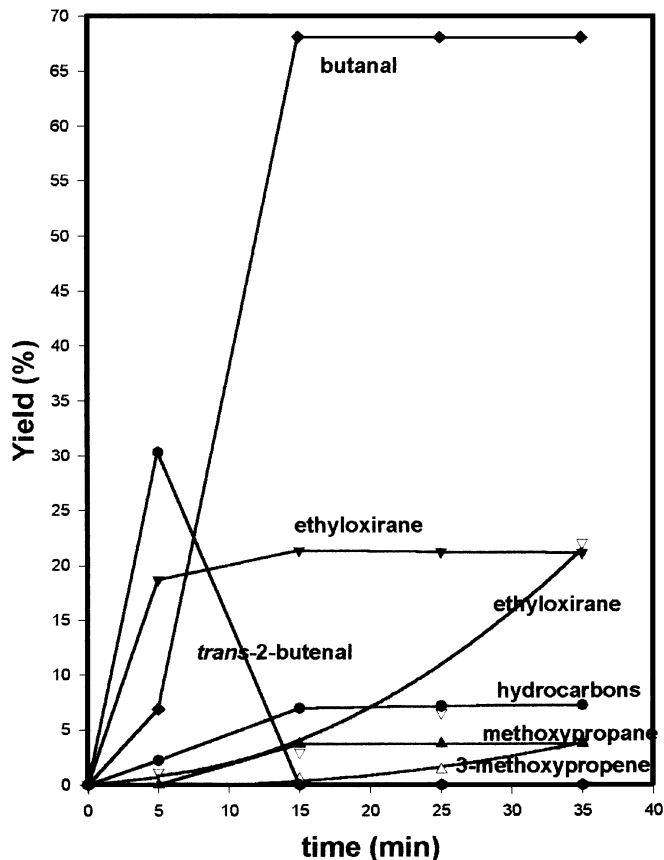


FIG. 4. Transformation of vinyloxirane on Pd-SiO<sub>2</sub> catalyst (catalyst = 10 mg, 273 K, empty symbols, and 301 K; black symbols,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{hydrogen}} = 20$  kPa).

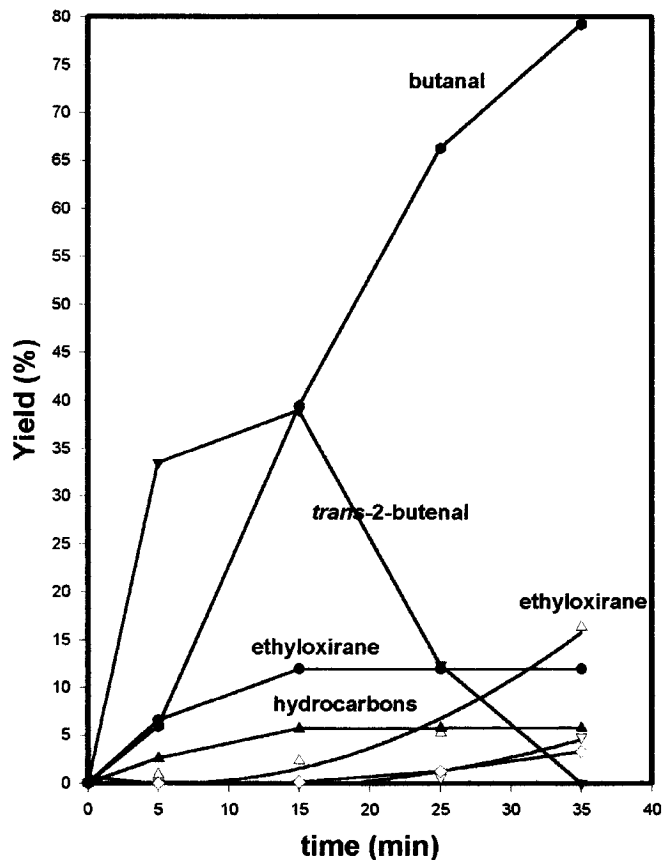


FIG. 5. Transformation of vinyloxirane on Pd-SiO<sub>2</sub> catalyst (catalyst = 10 mg, 273 K, empty symbols,  $\nabla$ , *trans*-2-butenal;  $\diamond$ , 3-methoxypropene, and 301 K, black symbols,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium}} = 20$  kPa).

furthermore, the decrease in the rate of deoxygenation show that vinyloxirane is able to be adsorbed on Pd without the formation of a metal–oxygen bond. It is well known, for example, that hydrogenation of aliphatic ketones usually does not happen on Pd (34, 35). There is also a significant difference between the reactions of the two metals and their oxides in the presence of oxygen and hydrogen (24, 25, 36).

## CONCLUSION

Our measurements at low temperatures allowed the identification of new phenomena in metal catalyzed hydrogenolysis of oxiranes. Under identical experimental conditions, ethyloxirane undergoes hydrogenolysis on Pd and deoxygenation on Pt.

The difference in reaction routes is even larger when the conversion of vinyloxirane is studied in the presence of hydrogen and/or deuterium, on a Pt- or Pd-SiO<sub>2</sub> catalyst. On Pt-SiO<sub>2</sub>, in addition to the hydrogenation of vinyloxirane to yield ethyloxirane, the dominant reaction is deoxygenation. On a Pd-SiO<sub>2</sub> catalyst, the main reaction route is the formation of products derived by the cleavage of the sterically hin-

dered bond (2-butenal and butanal). The difference in reaction routes between the two catalysts may be interpreted by the different structures of the surface species comprising the reactant, on the one hand, and the catalyst surface developing in the course of the reaction, on the other. In

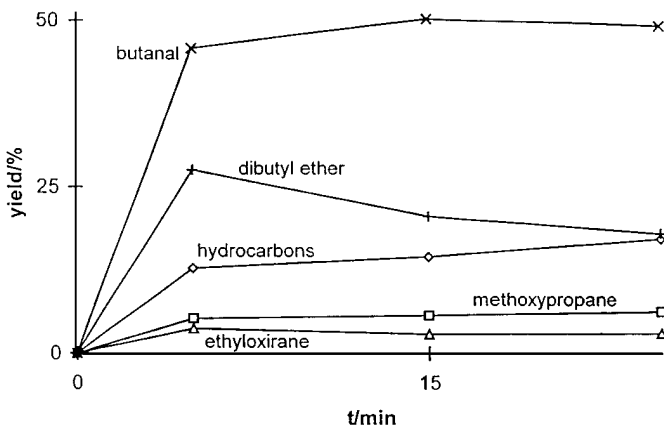
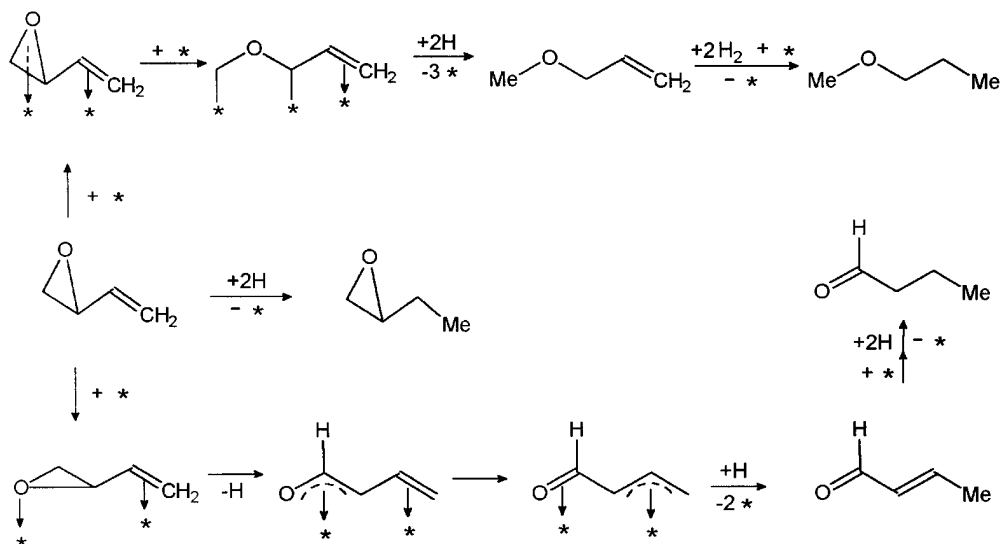


FIG. 6. Transformation of vinyloxirane on Pd-SiO<sub>2</sub> catalyst (catalyst = 10 mg, 363 K,  $p_{\text{oxirane}} = 1.33$  kPa,  $p_{\text{deuterium}} = 20$  kPa).

SCHEME 4. Mechanism of vinyloxirane transformation on Pd-SiO<sub>2</sub> catalyst.

the case of the isomerization reactions it is the presence of metal ions while in hydrogenolysis and deoxygenation it is the presence of metal clusters that is determinant.

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