JOURNAL OF CATALYSIS 63, 364–371 (1980)

Stereochemistry of Heterogeneous Catalytic Hydrogenolysis and Isomerization of Oxiranes

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Received March 1, 1979; revised November 28, 1979

The hydrogenolysis and isomerization of methyloxirane and *cis*- and *trans*-2,3-dimethyloxirane were studied on Pt, Pd, and Ni catalysts in static and pulse microreactors. On Pt and Pd catalysts, considerable differences could be demonstrated between the rates of transformation of the *cis* and *trans* isomers, whereas on Ni catalyst there was scarcely any difference. It may be assumed that in the transformation of the *trans* isomer on Pt and Pd catalysts the rate-determining step is the formation of the 1,3-diadsorbed surface species; on the Ni catalyst, however, as in the case of 2-methyloxirane and the *cis* isomer on any of the three catalysts, the rate-determining step is the further reaction of the adsorbed surface species. The results obtained by the pulse reaction technique are indicative of the irreversible adsorption of the reactants. Besides contributing to the clarification of the mechanisms and stereochemistry of the reactions examined, the data obtained give a possibility for the explanation of the fundamental differences in regioselectivity on the Pt, Pd, and Ni catalysts. On Pt and Pd catalysts, the mechanism of formation of 1,3-diadsorbed surface species differs from the mechanism obtained on Ni catalyst.

INTRODUCTION

The mechanisms of isomerization and hydrogenolysis of oxiranes on metal catalysts have been studied by Sénéchal and Cornet (*1*). They found that hydrogenolysis accompanied by the formation of alcohols and isomerization resulting in the formation of the corresponding ketone are both primary processes; they occur via diadsorbed or triadsorbed species. It was assumed that both mechanisms involve the same precursor, a molecule bound to the surface via the oxygen. Isomerization to the aldehyde proceeds via a different mechanism (*2*). In the case of oxiranes with asymmetric structures, Pt and Pd catalysts favor the splitting of the less sterically hindered C–O bond, but a Ni catalyst that of the more sterically hindered C–O bond. Splitting in the more sterically hindered direction increases with the increase of the steric hindrance (*2*). The cause of the difference in the splitting directions was not given (*1*). In their view, the fundamental difference observed between Pd and Ni is not directly connected with the electronic structures of the metals. Ni and Cu exhibited similar selectivities, although their band structures differ, while at the same time Ni (3*d* 4*s*) and Pd (4*d* 5*s*) exhibited different selectivities, whereas their band structures are similar. Mitsui *et al.* (*3, 4*) also earlier observed the different behaviors of Ni and Pd, and to explain the phenomenon assumed the differing adsorptions of the starting substance.

Cornet *et al.* (*11*) gave the mechanism shown in Fig. 1 for the deuterolysis of *trans*-2,3-dimethyloxirane.

In the light of the above experimental data, we have made a study of the transformations of methyloxirane and the 2,3-dimethyloxiranes on Pt, Pd, and Ni catalysts, in order to obtain further data on the mechanism of the process and the role of adsorption in this.

EXPERIMENTAL

The apparatus (Fig. 2) consists essentially of two microreactors coupled in series, their construction being the same as described previously (*5*). In the static operation mode, only microreactor B is used. The microreactor is connected to the gas

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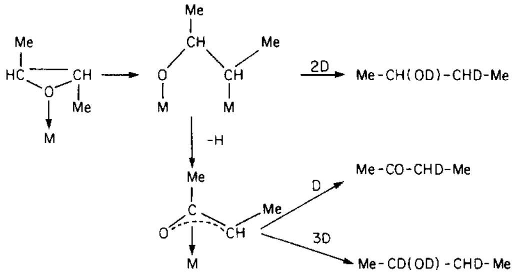


FIG. 1. Deuterolysis of *trans*-2,3-dimethyloxirane.

chromatograph via a six-port valve. In one position the valve permits the carrier gas to pass through the microreactor, while in the other position it closes both ends of the microreactor. The starting substances were injected into the closed microreactor with a Hamilton syringe and had an initial partial pressure of 55–60 mm Hg. After an optional reaction time we switched the valve and connected the microreactor to the chromatograph (*5*). In the pulse operation mode, microreactor B contains the catalyst, while microreactor A and a six-port valve are used to introduce the reactant pulse into the carrier gas stream.

In this case the initial concentration of the pulse is independent of the flow rate (*6*). Besides the measurements, the combined use of the system and the column switching valve built into the chromatograph also permits study of the form of the pulse at the inlet of the catalyst bed. Valve C is in the opposite situation compared to the other two and gives a possibility for freezing out (*7*).

Methyloxirane was a product of BDH, while *cis*- and *trans*-2,3-dimethyloxirane were prepared by the method of Wilson and Lucas (*8*). The products were separated at 60°C with two columns, each 1.5 m long, connected in series; in the first of these the liquid phase was 15% Reoplex-400, and in the second 20% β,β'-oxy-dipropionitrile ether on a kieselguhr support.

Measurements were made with a Carlo Erba Model C ATC/f gas chromatograph and an Autolab System I computing integrator. Catalytically purified gaseous hydrogen was used as carrier gas. The metal catalysts were prepared according to the methods described by Tétényi and Schächter (*9*). In the static measurements, 10 mg Pt, 5 mg Ni, and 2.5 mg Pd catalyst was employed, but in the pulse measurements 20 mg was employed. The specific surface areas of the catalysts were determined by nitrogen adsorption (*10*).

Since the catalysts were strongly deactivated in the course of the measurement, fresh catalyst was taken for every examination. By means of a Carlo Erba LT Programmer, the catalysts were heated in a current of air at 10°C min^{-1} to 300°C, maintained for 30 min at this temperature, and then cooled to room temperature in a stream of nitrogen. Prior to measurement, they were heated to 300°C at 10°C min^{-1} in a stream of hydrogen and then cooled to the reaction temperature. The following values were obtained for the specific surface areas of catalysts pretreated in this way: Pt 1.7; Pd 1.6; Ni 1.8 $\text{m}^2\,\text{g}^{-1}$. The reproducibility of the initial reaction rate on fresh, unused catalyst depends on the pretreatment. If this pretreatment is performed very carefully, the variation in the initial reaction rate values is ±5%. On catalysts that have already been employed, the reaction rate is roughly 30% lower and the reproducibility too is poorer than on unused catalyst.

The initial reaction rate values were determined from the constants of the function $y = A(1 - e^{-Bx})$, where y = percentage conversion of oxirane, x = reaction time, A = limiting value of y, and $A \cdot B = r_0$.

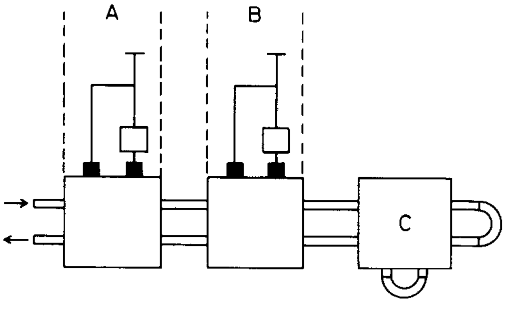


FIG. 2. Section of microreactor system.

Figures 3–5 demonstrate the time interval for which the rate equation was utilized. The constants were determined by an iterative method with a Texas Instruments SR-52 calculator.

RESULTS

The product compositions found in the transformations of the compounds examined correspond to those described in the literature. The static experimental data obtained with the Pt catalyst are presented in Figs. 3–5.

(The product compositions obtained with the pulse technique agree in general with the results obtained with the static microreactor. For attainment of nearly the same conversion, it was necessary to work at a higher temperature in the pulse microreactor, because of the shortness of the contact time, and under such conditions the quantity of oxo compounds increases.)

The initial rates calculated for the individual reaction directions for all three catalysts are listed in Table 1. (In addition to the products given in the table, a minimal amount of water too was formed.) It was not considered essential to perform a more accurate analysis of the hydrocarbon mixture. (According to the literature (*1*, *11*), an olefin is first formed, which is then hydrogenated to an extent depending on the conditions.)

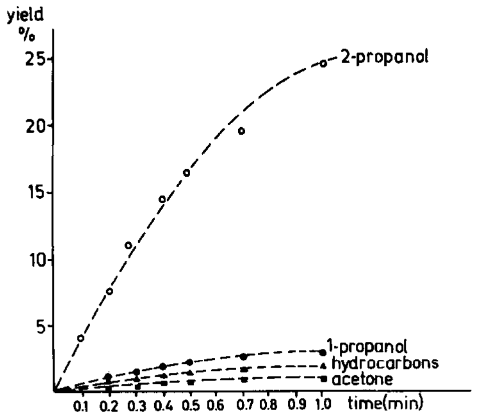


FIG. 3. Transformation of methyloxirane over Pt catalyst at 100°C (0.01 g catalyst; 1.4 · 10^{-5} mole reactant) in a static microreactor system.

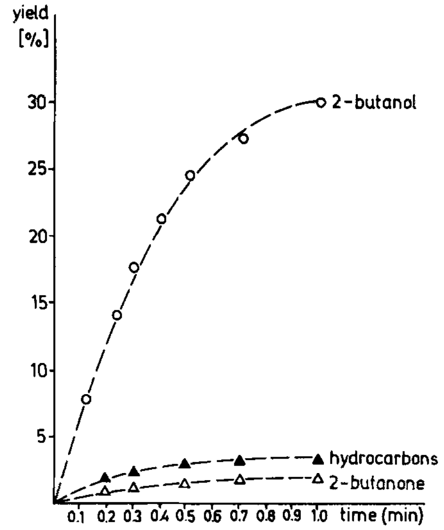


FIG. 4. Transformation of *cis*-2,3-dimethyloxirane over Pt catalyst at 100°C (0.01 g catalyst; 1.4 · 10^{-5} mole reactant) in a static microreactor system.

A comparison was made of the initial overall rates of transformation of methyloxirane and *cis*- and *trans*-2,3-dimethyloxirane on the three metal catalysts. The results are found in Table 2, where the overall reaction rates yield information on the rates of formation and further transformation of the diadsorbed species.

In this case we suppose that in such a strained ring the process begins with the splitting of the C–O and not the C–H bond.

Preliminary examinations in the static microreactor indicated that the hydrogenolysis of the oxiranes is a zero-order process in the range in question (Table 3).

The zero order of the reaction is supported by the fact that the conversion values obtained in the hydrogenolysis of methyloxirane as investigated by the pulse microreactor technique yielded a straight line when plotted as a function of the reciprocal space velocity, varied via the amount of catalyst (Fig. 6).

Our experimental data show that if the obtained conversions are plotted as a function of the reciprocal space velocity (the

TABLE 1

Initial Rates of Transformation of Oxiranes on Metal Catalysts (10^5 mole m^{-2} min^{-1}) in a Static Microreactor System

	Methyloxirane			*cis*-2,3-Dimethyloxirane			*trans*-2,3-Dimethyloxirane		
	Pt 100°C	Pd 100°C	Ni 150°C	Pt 100°C	Pd 100°C	Ni 150°C	Pt 100°C	Pd 100°C	Ni 150°C
1-Alcohol	5	37	23	—	—	—	—	—	—
2-Alcohol	33	138	3	72	369	25.5	6	13	23
Ketone	1	18	0	4	44	5	0.5	6	5.5
Aldehyde	0	4	10	—	—	—	—	—	—
Hydrocarbons	4	0.5	8	8	19	28	2	2.5	22
S[a]	0.88	0.79	0.11	—	—	—	—	—	—

[a] S = 2-alcohol/(1-alcohol + 2-alcohol).

space velocity was varied with the flow rate), a straight line results which cannot be extrapolated to the origin. The results are presented in Figs. 7 and 8.

(The statistical calculations performed on the basis of the experimental results confirmed the correctness of the linear fitting and also the fact that, when the scatter in the experimental results is taken into consideration, the intercepts of the straight lines on the axis differ significantly from zero.)

Behavior of such a nature was first experienced by Bett and Hall (*7*), and according to Hattori and Murakami (*12*) the phenomenon is caused by the irreversible adsorption of the starting compound. Although the reaction they studied was monomolecular ($A_{(g)} \longrightarrow A_{(ad)} \xrightarrow{\text{slow}} B_{(g)}$), while in our case the hydrogen too participates in the surface reaction, it is nevertheless probable that this does not appreciably influence the conclusions drawn because of the constant hydrogen coverage of the surface (*13*).

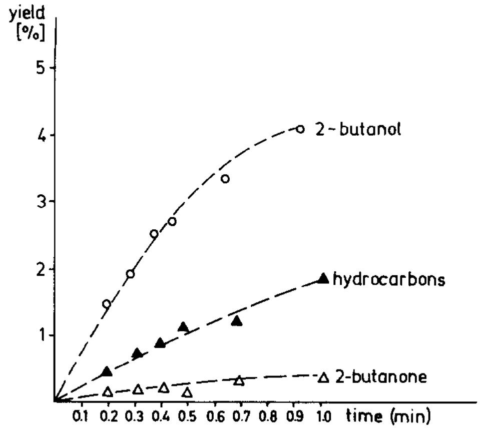


FIG. 5. Transformation of *trans*-2,3-dimethyloxirane over Pt catalyst at 100°C (0.01 g catalyst; 1.4 · 10^{-5} mole reactant) in a static microreactor system.

On the basis of our experimental results, the following are the main findings:

(1) The direction of splitting of methyloxirane is different on Ni from that on Pd or Pt catalyst.

(2) On Pt and Pd catalysts, *trans*-2,3-dimethyloxirane is transformed at a much lower rate than the two other compounds examined.

(3) On Pt and Pd catalysts, *cis*-2,3-dimethyloxirane is transformed at a higher rate than methyloxirane.

(4) On Ni catalyst, the rates of transfor-

TABLE 2

Initial Overall Rates of Transformation of Oxiranes to Alcohols and Ketone on Metal Catalysts (10^5 mole m^{-2} min^{-1}) in a Static Microreactor System

	Catalyst		
	Pt 100°C	Pd 100°C	Ni 150°C
Methyloxirane	39	193	26
cis-2,3-Dimethyloxirane	76	413	30.5
trans-2,3-Dimethyloxirane	6.5	19	28.5

TABLE 3

Rate of Hydrogenolysis of Methyloxirane with Changing Initial Oxirane Pressure at 100°C over a Pt Catalyst in a Static Microreactor System

Initial methyloxirane vapor pressure (mm HG)	Rate of hydrogenolysis, r_0 10^4 mole m^{-2} min^{-1}
234	3.3
280	4.0
339	3.1
363	3.8
387	2.9

mation of all three compounds are almost the same.

(5) The results obtained by the pulse reaction technique are indicative of the irreversible adsorption of the reactants.

In our view:

(1) The fact that the stereoisomeric compounds are transformed with different reaction rates can be explained by the difference in the rate-determining steps; this is either the formation of the diadsorbed species or its further transformation.

(2) The different selectivities of the individual metals can be interpreted by the different mechanisms of formation of the diadsorbed species.

Our conceptions of the mechanisms of the reactions and the natures of the rate-determining steps are shown in Figs. 9 and 10.

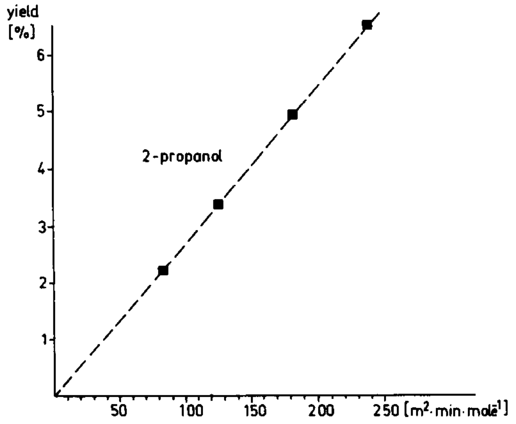


FIG. 6. Hydrogenolysis of methyloxirane at 100°C over Pt using the pulse microreactor technique. Space velocity was varied by catalyst weight; $r \cdot 10^4 = 2.71$ mole m^{-2} min^{-1}; R (correlation coefficient) = 0.996; a (intercept) = -0.17 ± 1.5; P (probability level) = 5%.

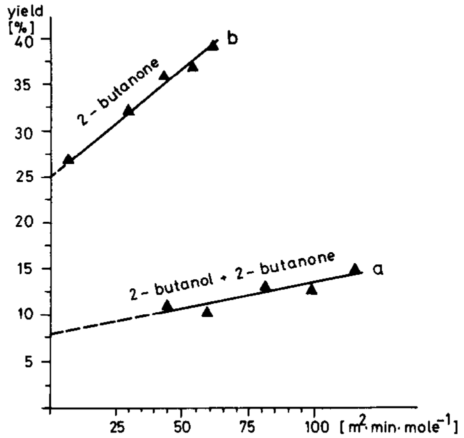


FIG. 7. (a) Isomerization and hydrogenolysis of *trans*-2,3-dimethyloxirane at 175°C over Pt using the pulse microreactor technique. $r \cdot 10^4 = 3.1$ mole m^{-2} min^{-1}; $R = 0.928$; $a = 8 \pm 2$; $P = 5\%$. (b) Isomerization of *cis*-2,3-dimethyloxirane at 150°C over Pt using the pulse microreactor technique. $r \cdot 10^4 = 19{,}8$ mole min^{-2} min^{-1}; $R = 0.977$; $a = 25 \pm 3$; $P = 5\%$.

DISCUSSION

Mitsui and Nagahisa (*3*) too found a fundamental difference between the behaviors of Ni and Pd in the hydrogenolysis of the stereoisomeric oxiranes. On the former catalyst the process is accompanied by retention, and on the latter by inversion. They assumed that on the Ni catalyst the oxygen is bound to the surface, and on the Pd catalyst the carbon (*4*). In their view, the reason for this is that Pd has a lower affinity than Ni for negative elements. More recent examinations, however, indicate that binding of the cyclic ethers to the surface of the catalyst begins via the oxygen on the platinum metals too (*1, 11, 14*). Formation of the diadsorbed species demands the simultaneous chemisorption of the α-carbon atom. If the adsorption is the rate-determining step it is obvious that the *cis* isomer and the methyloxirane are in an essentially more favorable situation than the *trans* isomer. But on the basis of experimental data we suppose that, on Pt and Pd

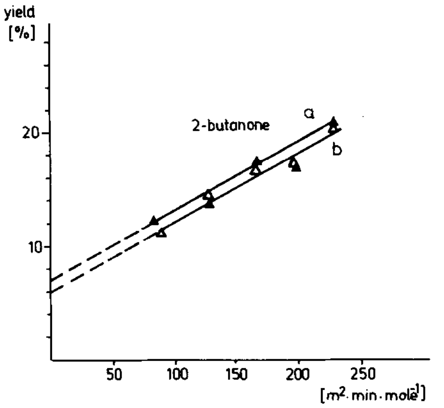


FIG. 8. (a) Isomerization of *trans*-2,3-dimethyloxirane at 150°C over Ni using the pulse microreactor technique. $r \cdot 10^4 = 6.3$ mole in m^{-2} min^{-1}; $R = 0.941$; $a = 7 \pm 4$; $P = 5\%$. (b) Isomerization of *cis*-2,3-dimethyloxirane at 150°C over Ni using the pulse microreactor technique. $r \cdot 10^4 = 6.1$ mole m^{-2} min^{-1}; $R = 0.979$; $a = 6.0 \pm 2.4$; $P = 5\%$.

catalysts, the rate-determining step for the *trans* isomer is the formation of the 1,3-diadsorbed surface species, while for the *cis* isomer and for the methyloxirane it is the further transformation of this species (to a triadsorbed species or, by hydrogenolysis, to an alcohol).

Our proposal relating to the reaction mechanism is supported by the following observations:

(1) From a study of the kinetics of oxirane hydrogenolysis on a Pt catalyst, it was concluded (*15*) that the hydrogen atom takes part in the rate-determining step ($r = k \cdot H_2^{1/2} \cdot P_O^0$; O = oxirane). At the same time, in the hydrogenolysis of *trans*-2,3-dimethyloxirane on Pd the order obtained for the hydrogen was −0.4 (*1*), which indicates that in this case the rate-determining step is the adsorption of the oxirane.

(2) In the hydrogenolysis of *cis*- and *trans*-1,2-dimethylcyclopropane on metal films (Pd, Pt, Ni) and on supported Pt, it was proved experimentally (*16*) that the stereostructure of the molecule determines the regioselectivity of the reaction and hence has a considerable influence on the mechanism of the reaction. (The hydrogenolysis gave rise to *n*-pentane from the *cis* compound and to i-pentane from the *trans* compound, as a consequence of the different adsorptions of the reactants.)

(3) Our investigations indicate that at higher temperatures on a Pt catalyst the difference between the rates of transformation of *trans*- and *cis*-2,3-dimethyloxirane also becomes progressively lower, and at around 300°C the rates become almost identical. This fact can be explained in that the adsorption of the *trans* isomer accelerates at the higher temperatures, and the transformation of the 1,3-diadsorbed species be-

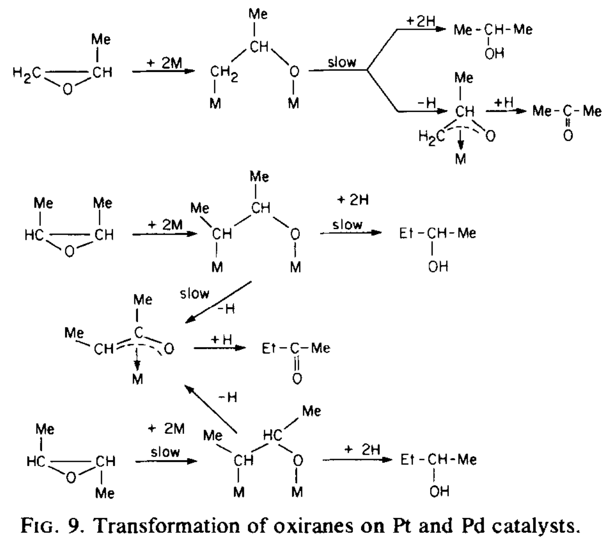


FIG. 9. Transformation of oxiranes on Pt and Pd catalysts.

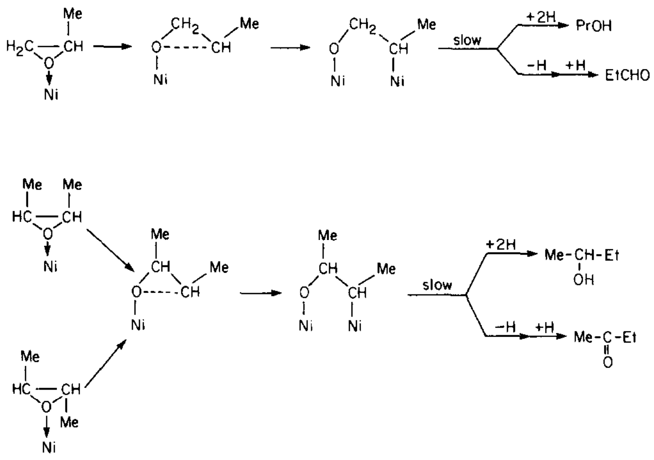
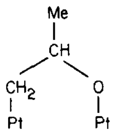


FIG. 10. Transformation of oxiranes on Ni catalyst.

comes the rate-determining process for the *trans* compound as well.

Since our experimental results confirm the irreversible adsorption of the starting material even in the case of the *trans*-2,3-dimethyloxirane, it must be assumed that the first step of the adsorption of the *trans* isomer is the cleavage of the O–C bond.

There is a stereochemical reason for the splitting direction observed in the case of methyloxirane on Pt and Pd catalysts.



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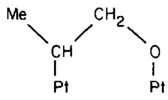
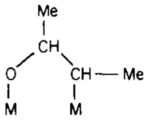


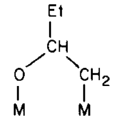
II

Because of the repulsion between the methyl group and the catalyst surface, the probability of the formation of the transition state leading to the diadsorbed surface species of type II is less than that for type I. This gives the explanation for the fact that, in the cases of Pt and Pd, the splitting proceeds mainly at the bond between the oxygen and the carbon not linked to the methyl group.

The conception we have given for the stereochemistry of the process is well supported by the observation by Sénéchal and Cornet (*1*) that the 2-butanol formed on Pd in the course of deuterolysis gives d_2 and d_5 maxima in the case of 2,3-butylene oxide, but only a d_2 maximum in the case of 1,2-butylene oxide.



III



IV

On the basis of our conception for the alcohol formation, it can readily be seen that, as regards the methyl groups of species III, it may be expected that one will participate in the H–D exchange reaction which lies closer to the surface of the metal, whereas the more distant methyl group and also the ethyl group of species IV will not; this is in full agreement with the experimental data.

In the case of the Ni catalyst, where mainly 1-propanol was formed from methyloxirane and there was hardly any difference between the *cis* and *trans* isomers, it seems acceptable to assume that splitting of the ring is fast in every case and that the further transformation of the 1,3-diadsorbed surface species becomes the rate-determining step. Binding to the catalyst begins on the oxygen, and chemisorption of the α-carbon atom is preceded by heterolysis of the C–O bond. This permits deformation of the ring in such a direction that the *trans* isomer avoids the repulsion between the methyl group and the catalyst surface. Clearly then, a difference cannot be expected between the *cis* and *trans* isomers. (Since formation of the secondary carbonium ion-like transition state is more probable than that of the primary one, mainly 1-propanol is formed from methyloxirane.) It must be noted that Pines and Nogueira (*17*) similarly explained the hydrogenolysis of cyclopropane on a Ni catalyst by means of an ionic mechanism. The above conception is in excellent agreement with those we have put forward for the mechanism. The different splitting direction oberved on Ni and Cu catalysts (*1*), therefore, is connected with the electrophilic character of the catalyst. This explanation is based on the view (*18*) that, even in the case of the metal catalysts, it is necessary to assume the presence always of the semiconducting oxide of the metal.

The finding that, on the Ni catalyst, an appreciable difference could not be observed between the reaction rates of the individual reactants draws attention to the fact that the rates of hydrogenolysis of the diadsorbed surface species are almost the same. This can presumably be explained in that, on the Ni catalyst, the hydrogenolysis of the Ni–O bonds will be the rate-determining step.

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