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Hydrogen pressure dependence in the ring opening of methyloxirane over silica-supported Pd and Rh catalysts: effect of high temperature on ring-opening routes

István Pálinkó *, József Ocskó

Department of Organic Chemistry, József Attila University, Dóm tér 8, Szeged, H-6720 Hungary

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Abstract

The high-temperature ring-opening reactions of methyloxirane were investigated with or without added hydrogen over silica-supported Pd and Rh catalysts. Without added hydrogen, mainly isomerization occurred, giving acetone through the rupture of the sterically less hindered C–O bond (*route b*). With added hydrogen, hydrogenative ring opening also took place and the sterically more hindered C–O bond was broken as well (*route a*). At 473 K allyl alcohol was formed too: a product not found at lower temperatures. Since *route a* was predominant over both catalysts, a bifunctional mechanism had to be considered. It is known that methyloxirane adsorbs irreversibly, therefore the shape of product formation rate vs. hydrogen pressure curves could be used for mechanistic considerations.

Keywords: Methyloxirane; Ring-opening reactions; Silica; Palladium; Rhodium; Hydrogen; Pressure dependence; High temperature effects; Supported catalysts

1. Introduction

Even catalytic systems selected for model studies in academic research are rather complex. Initially, they include the reactants and the catalyst, later on intermediates and products. Other modifying factors such as various kinds of coke deposits, oxidation of the surface etc. influence, quite often severely, the catalytic action. Temperature is also a crucial factor in determining selectivities, opening new reaction pathways, in many instances through helping the construction of the actual catalytic surface.

A rather complex system was chosen for this study: the ring opening of methyloxirane over supported transition metal catalysts in the absence or presence of added hydrogen. Since methyloxirane is an asymmetric molecule it provides with the opportunity of examining the effect of temperature and the presence or absence of added hydrogen on transformation pathways, the regioselectivity and mechanism(s) of the ring opening. At high temperature the contribution of the support or the support–metal interface further complicates the system.

It is well known that oxiranes start to adsorb at their oxygen atom [1] creating a metal–metal oxide surface even initially. This is an additional

* Corresponding author.

factor to be considered in rationalizing reaction mechanisms.

2. Experimental

Methyloxirane, from Fluka, proved to be gas chromatographically pure. Thus, it was used without purification. Oxygen-free hydrogen was prepared in a Matheson 8326 generator, operating with a palladium membrane.

The Pd/SiO₂ and Rh/SiO₂ catalysts were prepared by impregnating Cab-O-Sil M5 non-acidic support (BDH) with acidic solutions of PdCl₂ and RhCl₃, respectively, followed by reduction in flowing hydrogen at 773 K for 16 h. The high-temperature hydrogen treatment diminished the chlorine content of the catalysts as revealed by X-ray fluorescence spectroscopy [2]. The dispersion (number of exposed metal atoms/number of total metal atoms) was measured at room temperature in a flow system with CO for Pd/SiO₂ and H₂ for Rh/SiO₂, assuming 1:1 adsorption stoichiometry. The dispersion values obtained (3.0% Pd/SiO₂: 15.4%, 3.2% Rh/SiO₂: 27.0%) were verified by O₂-H₂ titration at 373 K and by electron microscopy with a Hitachi H500H transmission electron microscope. Dispersion values obtained by the various methods were in excellent agreement. After reduction the catalysts were stored in a vacuum desiccator. Fresh samples (usually 12.5 mg) were used for each run. They were activated before experiments by heating for 2 h at 473 K under flowing hydrogen.

The reactions were carried out in a conventional closed circulation reactor attached to a Carlo Erba Fractovap 2150 gas chromatograph where analysis of the withdrawn samples were performed [2]. Separation of products was accomplished on a combination of a 0.5 m long 20% Reoplex/Chromosorb W stainless steel column (kept at 293 K) and a 1.5 m long all-glass column packed with 20% 1:1 ODPN-Reoplex/Chromosorb W (kept at 313 K). The reactor was heated by an air thermostat. The reactants (1.33 kPa of methyloxirane and various amounts of hydrogen) were premixed

in the circulation part of the reactor before the reaction. Prior to mixing, the methyloxirane was subjected to several freeze–thaw–evacuate cycles.

Initial rates (5–10% conversion) were always determined and transformed to turnover frequencies (molecules exp.atom⁻¹ s⁻¹) on the basis of dispersion data determined by CO or H₂ chemisorption.

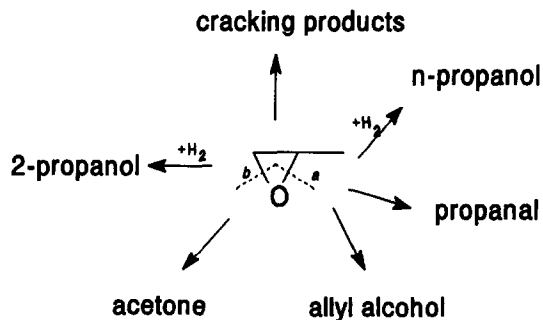
3. Results

In this part are reported observations concerning the ring-opening reactions of methyloxirane at relatively high temperature (473 K) in the absence and presence of added hydrogen.

The possible transformation pathways of methyloxirane are depicted in Scheme 1. Ring opening may occur through isomerization as well as hydrogenation. Cracking products are usually observed, the extent of which very much depends on the temperature of the reaction. Rupture of the sterically more hindered C–O bond (*route a*) may give propanal, allyl alcohol (isomerization), n-propanol (hydrogenation), while the cleavage of the sterically less hindered C–O bond (*route b*) may result with acetone (isomerization) and 2-propanol (hydrogenation).

The initial rates of product accumulation in the function of hydrogen pressure for Pd/SiO₂ are displayed in Fig. 1.

In accordance with previous studies (for a review, see [3]), both isomerization and hydrogenation occur in the presence of hydrogen. However, a new isomerization product, allyl alcohol



Scheme 1. Ring-opening routes of methyloxirane.

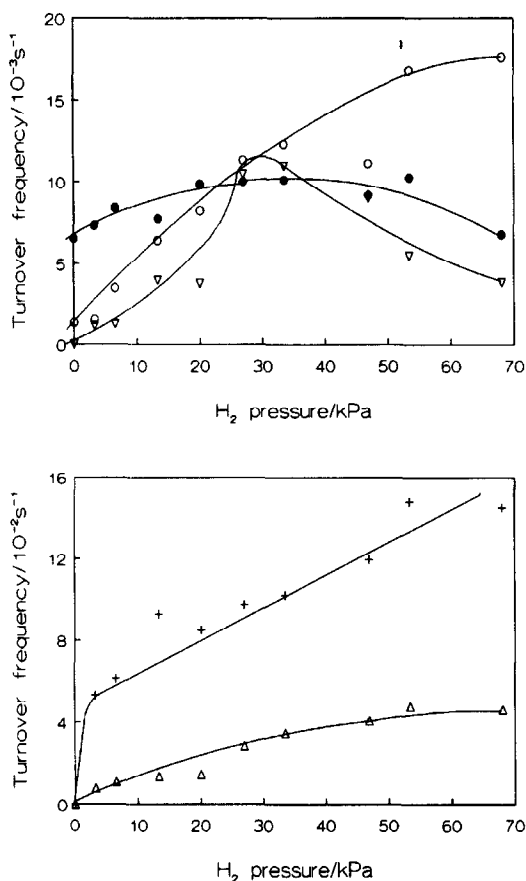


Fig. 1. Initial rates for the ring opening of methyloxirane at 473 K over Pd/SiO₂: (●) acetone, (○) 2-propanol, (▽) allyl alcohol, (+) propanal, (Δ) n-propanol.

appears at 473 K (over Rh/SiO₂ as well). The formation of allyl alcohol and acetone is suppressed by increasing hydrogen pressure. The formation of other products are described by saturation curves.

As far as the hydrogen dependence is concerned over Rh/SiO₂, the increase in hydrogen pressure accelerates the formation of each product up to about 40 kPa H₂ pressure, then the curves approach saturation (Fig. 2).

The rate of ring opening in the sterically hindered direction (1,2 C–O bond scission: *route a*) exceeds that of the sterically less hindered direction (1,3 C–O bond scission: *route b*) over both catalysts (Table 1). Regioselectivity towards *route a* is more pronounced for Pd/SiO₂.

When hydrogen is not present, acetone forms over Rh/SiO₂ as well as over Pd/SiO₂. However,

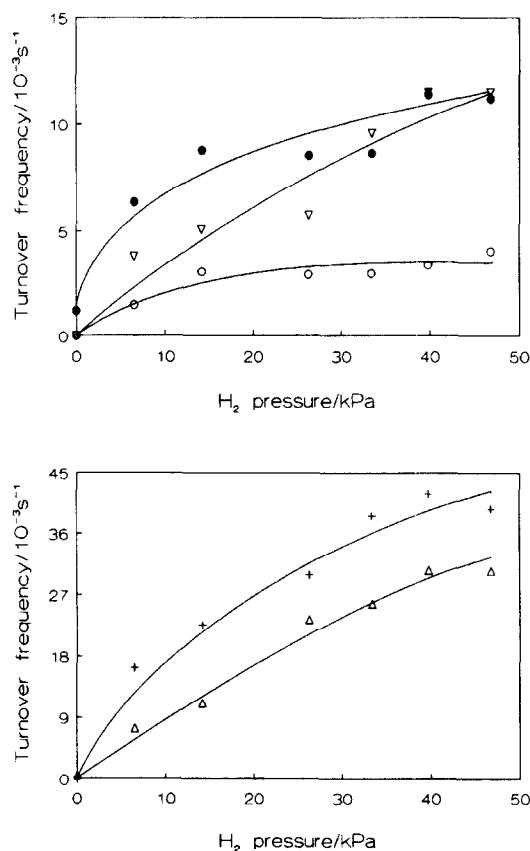


Fig. 2. Initial rates for the ring opening of methyloxirane at 473 K over Rh/SiO₂: (●) acetone, (○) 2-propanol, (▽) allyl alcohol, (+) propanal, (Δ) n-propanol.

Table 1
Regioselectivities of ring opening at selected hydrogen pressures

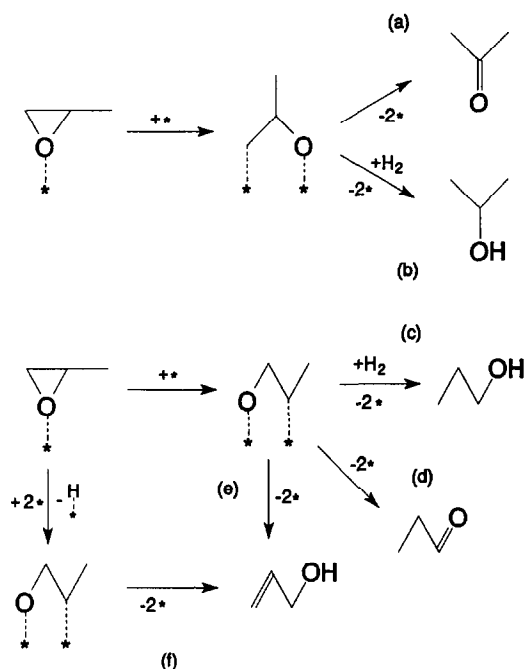
Catalyst	Hydrogen pressure/kPa				
Pd/SiO ₂	6.5	13.3	27.0	33.5	46.9
	<i>a/b</i>	7.4	7.8	6.4	6.6
Rh/SiO ₂	6.5	14.2	26.3	33.4	46.8
	<i>a/b</i>	3.5	3.3	5.2	6.4

on the latter catalyst 2-propanol, the hydrogenated product can also be detected. Hydrogen, necessary for this compound, possibly comes from degradation products.

Remarkably the overall rate of ring opening is higher over Pd/SiO₂ than over Rh/SiO₂.

4. Discussion

As already described and depicted in Scheme 1, methyloxirane is able to undergo several type of



Scheme 2. The mechanism of the ring-opening reactions of methyloxirane in the presence of H_2 over Pd/SiO_2 : (a), (b), (c), (d) and (e) or over Rh/SiO_2 : (a), (b), (c), (d) and (f).

transformations. The isomerization products usually observed are acetone, while hydrogenation gives 2-propanol and n-propanol. When non-acidic support was applied and the temperature was relatively low (e.g., 393 K [4]) or support-free catalysts [5] were used, the main products were acetone and 2-propanol. Propanal was not formed and the amount of the corresponding alcohol was also very low. Cracking producing CO and saturated and unsaturated lower weight hydrocarbons always accompanies ring opening of any kind.

We found, however, that the unusual *route a* was the predominant ring-opening direction. Moreover, beside propanal and n-propanol, allyl alcohol is also formed. It is surprising since the Cab-O-Sil support is used mostly when inertness is a requirement. Its non-acidic character is generally accepted, however, the high reaction temperature may strengthen very weak acid sites (not observable at lower temperatures). It is indicated by the formation of allyl alcohol, which is known to be produced over acidic metal oxides [6] while it is not reported either over support-free metals

[5] or silica-supported Pt at lower temperature (393 K) [4]. The appearance of metal ions on the metal surface and the metal support interface due to the partial oxidation of the metal surface by the adsorbed oxirane may also contribute to surface acidity. Since Pd has higher tendency to contain metal ions [7] than Rh, it is understandable that *route a* is more pronounced here than over the other catalyst.

Since methyloxirane adsorbs over the surface irreversibly (the ring opens upon adsorption) the form of hydrogen pressure dependence curves and experimental results in hydrogen-free environment allow mechanistic considerations.

It is clear that acetone can form without hydrogen, nevertheless hydrogen accelerates its formation over Rh/SiO_2 appreciably. Over Pd/SiO_2 , however, the hydrogen independent route has predominance. Over Rh/SiO_2 each product forms via an associative mechanism, hydrogen only helps desorption of adsorbed species either in the form of oxo compounds or alcohols. Over Pd/SiO_2 the mechanism is more complicated since acetone and allyl alcohol formation is suppressed by increasing hydrogen pressure suggesting dissociatively adsorbed surface intermediates.

The above detailed mechanistic considerations are summarized in Scheme 2.

5. Conclusions

In the hydrogenative ring-opening reaction of methyloxirane over Pd/SiO_2 or Rh/SiO_2 , the adsorption induced metal ion formation together with the high-temperature activated weak acid sites of the support result in the predominance of the sterically more hindered C–O bond scission producing propanal, allyl alcohol and n-propanol. The rupture of the sterically less hindered C–O bond proceeds over surface metal atoms with the formation of acetone and 2-propanol. Product distribution emerging from methyloxirane ring opening is a sensitive test of surface acidity.

Acknowledgements

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