

The Mechanism of Hydrogenolysis and Isomerization of Oxacycloalkanes on Metals

IX. Structure Sensitive Hydrogenolysis and Isomerization of Methyloxirane over Well-Characterized Pt/SiO₂ Catalysts¹

D. OSTGARD,² F. NOTHEISZ, Á. G. ZSIGMOND, G. V. SMITH,² AND M. BARTÓK³

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

Received March 6, 1990; revised August 30, 1990

The hydrogenolysis of methyloxirane (propylene oxide) was investigated over five Pt/SiO₂ catalysts with different degrees of dispersion (7–100%), at 393 K, with a pulse technique coupled with GC. The number of turnovers per surface atom per pulse (turnover yield) was found to depend on the degree of dispersion. The rate of the ring-opening reaction passed through a maximum at approximately 60% D, which corresponds to a maximum in edge sites on fcc octahedra, or to ²M sites. The regioselectivity of the ring opening did not depend upon the degree of dispersion, but the formation of the two main products (acetone and 2-propanol) displayed some structure sensitivity. The paper also deals with the interpretation of a recently observed example of structure sensitivity. © 1991 Academic Press, Inc.

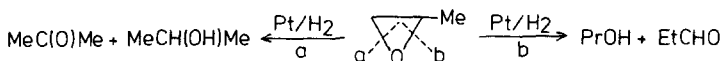
INTRODUCTION

Our results on the transformations, mechanisms, and stereochemistry of oxiranes (epoxides) were reported earlier (1–10). The transformations took place on Pt, in the presence of hydrogen; they are outlined in

the scheme in the case of methyloxirane (propylene oxide).

The findings based on the earlier experiments were in agreement with the literature observations (11, 12).

Accordingly, the transformation of methyloxirane on Pt catalysts is characterized by



splitting of the sterically less hindered bond (splitting in direction *a*); i.e., the two main products are acetone and 2-propanol.

We now report results on the hydrogenolysis and isomerization of methyloxirane on a set of Pt/SiO₂ catalysts with different degrees of dispersion. A study was made of the structure sensitivity via the ring-opening

transformation of methyloxirane on Pt, and also of the nature of the active sites responsible for the transformation. The new data obtained permit a better understanding of the mechanism of Pt-catalyzed reactions.

EXPERIMENTAL

Methods

The investigations were performed in a glass microreactor connected to a gas chromatograph (pulse technique). Details on this experimental procedure were reported earlier (2).

¹ Part VIII: Ref. (10).

² Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901.

³ To whom correspondence should be addressed.

The carrier gas used here was hydrogen, prepared in a Matheson 8326 electrolysis apparatus equipped with a Pd diffusion cell. The H_2 flow rate was 20 ml/min. The reaction temperature was 393 K. In the measurement, 5- or 10-mg catalyst samples were used.

The top of the microreactor was closed by a rubber septum. Pulses of reactant (1 μ l) were injected through the septum into the stream of hydrogen by a microsyringe. The shape of the pulse was a triangle. The time between pulses depended on the GC analysis time. The catalyst was usually more active for the first few injections, and with each additional pulse the activity dropped until a steady-state activity (SSA) was reached. All the turnover yields were calculated for the first three pulses and for the average activity of the catalyst after it had reached the steady state. Pulse microreactor experiments were also run on the silica support, which proved to be inactive for methyloxirane reactions.

Material

Methyloxirane was a product of BDH (GC purity: 99%). Prior to use, it was double distilled and further purified by percolation through a Camag alumina column in an inert atmosphere.

Catalyst

Three types of Pt/SiO₂ catalyst were used. The 1.91, 1.17, 0.48, and 0.83% Pt/SiO₂ catalysts originated in the laboratories of Burwell and Butt (13). They were prepared either by impregnation with chloroplatinic acid (1.91 and 1.17% Pt/SiO₂) or by ion-exchange of Pt(NH₃)₄Cl₂ on Davison grade silica gel (0.48 and 0.83% Pt/SiO₂). The 1.91% Pt/SiO₂ catalyst was calcined at 552 K for 4 h in flowing air. The catalysts were reduced as in (13).

The third type of catalyst, 0.13% Pt/SiO₂, was prepared by using platinum acetylacetonate (14). The percentage of exposed Pt atoms was determined by H₂ or CO chemisorption and H₂-O₂ titration; other details can be found in the original papers (13, 14).

The catalyst pretreatment consisted in heating the catalyst to 473 K for $\frac{1}{2}$ h in flowing hydrogen (flow rate: 20 ml/min), maintaining that temperature for $\frac{1}{2}$ h, and cooling the catalyst down to the reaction temperature (393 K).

Analysis and Calculations

Chromatography (Carlo Erba FRAC-TOVAP model 1400 with a thermal conductivity detector) was conducted with $\frac{3}{4}$ -m column containing 20% ODPN/Kieselguhr + 1.5-m column containing 15% REOPLEX 400/Kieselguhr, at 328 K. The compounds formed were identified on the basis of the retention times of authentic compounds. Retention times were (in minutes): methyloxirane, 4.2; propanal, 6.2; acetone, 8.3; 2-propanol, 12.74; 1-propanol, 24.83. The GC data were processed with a Perkin-Elmer Sigma 10 integrator.

From the GC data, the number of turnovers per surface atom per pulse (turnover yields) was calculated. The turnover yield does not involve a unit of time, since the contact time of the pulse is not exactly known. This contact time, however, was the same in every experiment since the rate of flow of the carrier gas was constant. These turnover yields were calculated for each product with the help of detector response correction factors. The turnover yields of all the products were then summed to obtain the total turnover yield of the reaction. The reaction selectivities for the methyloxirane reaction were also calculated (Table 1).




RESULTS AND DISCUSSION

Experimental data on the hydrogenolysis and isomerization of methyloxirane, in a pulse microreactor, can be seen in Table 1.

The major products in this series of Pt/SiO₂ catalysts were acetone and 2-propanol. The results revealed that the regioselectivity does not depend on the degree of dispersion. On all of the catalysts, the sterically less hindered bond breaks. This observation is in good agreement with our earlier results

TABLE 1

Experimental Data on the Hydrogenolysis and Isomerization of Methyloxirane

Catalyst and dispersion	Pulse No.	Conversion (%)	Turnover yields ^a /selectivities ^b (mol%)								
			LP ^c a		 b		 c		 d		^d Σ T a
0.13% Pt/SiO ₂	1	2.3	0.51	63	0.21	26	0.09	11	0	0	0.81
	2	1.2	0.30	70	0.08	19	0.05	11	0	0	0.43
	3	1.1	0.30	81	0.07	19	0	0	0	0	0.37
100% D	SSA ^d	1.0	0.31	89	0.04	11	0	0	0	0	0.35
0.83% Pt/SiO ₂	1	59	0.53	6	2.07	25	5.16	63	0.46	6	8.22
	2	26	0.29	8	1.23	34	2.05	56	0.07	2	3.64
	3	25	0.29	8	1.18	34	1.90	53	0.19	5	3.56
80.9% D	SSA	25	0.29	8	1.17	34	1.91	55	0.12	3	3.49
0.48% Pt/SiO ₂	1	53	0.85	5	3.52	21	12.25	71	0.58	3	17.2
	2	40	0.92	8	3.48	28	7.63	62	0.27	2	12.3
	3	38	0.90	8	3.28	25	7.36	62	0.36	5	11.9
62.1% D	SSA	39	0.96	8	3.40	28	7.25	61	0.39	3	12.0
1.17% Pt/SiO ₂	1	65	0.47	4	2.20	17	9.35	74	0.68	5	12.7
	2	51	0.41	4	2.26	22	6.85	68	0.48	6	10.0
	3	46	0.39	4	2.01	22	6.24	69	0.36	5	9.0
40.7% D	SSA	44	0.45	5	2.27	26	5.56	65	0.32	4	8.6
1.91% Pt/SiO ₂	1 ^e	—									
	2	9	1.64	26	1.03	17	3.50	57	0	0	6.17
	3	9	1.44	23	0.96	15	3.66	59	0.15	3	6.21
7.1% D	SSA	6	1.12	28	0.66	17	2.14	54	0.06	1	3.98

^a Turnover yield (*T*) = number of turnovers per surface atom per pulse.^b Selectivity (*S*), $S = 100 T/\Sigma T$.^c LP (light products) = the mixture of hydrocarbons and carbon monoxide coming off the column before methyloxirane.^d SSA = steady state activity.^e The repeated experiments led to contradictory results. In some cases propanal was detected in the product mixture, but in other cases aldehyde was not found. This contradiction may be an indication of the heterogeneity of the catalyst particles. On the basis of our earlier results (3), the propanal formation is due to the electrophilic centers on the catalyst surface.

that in the absence of acidic sites, the regioselectivity is determined by the nature of the metal, and not by its structure (6).

Figure 1 shows the correlation between the selectivities of acetone and 2-propanol formation and the degree of dispersion. For the Pt/SiO₂ catalyst originating from Burwell and Butt (13), 2-propanol is preferentially formed. The selectivity of acetone formation increases with the degree of dispersion, while that of 2-propanol formation decreases. The selectivity of the isomerization varies in direct proportion to the

degree of dispersion, whereas that of the hydrogenolysis exhibits a maximum curve (the maximum being situated at a degree of dispersion of 40–60%). The isomerization and hydrogenolysis of oxiranes are known to be parallel reactions (15) and there are essential differences in the structures of the active sites on catalysts with different degrees of dispersion (13, 14). The above experimental data permit a study of the nature of the active sites responsible for the courses of the two reactions. The experimental data show (Fig. 1) that the methods

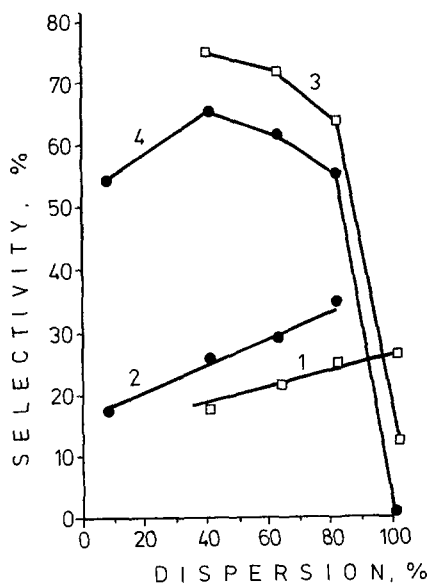


FIG. 1. Acetone (1, 2) and 2-propanol (3, 4) selectivities vs percentage dispersion for the methyloxirane reaction via the pulse microreactor technique. (curve 1 and 3: first pulse; curves 2 and 4: SSA).

of preparation of the catalysts (impregnation, ion exchange, AcAc method) do not influence the selectivity of the ring-opening reaction of oxiranes.

The table lists the total turnover yields of the methyloxirane reaction in the pulse microreactor system, and Fig. 2 shows that the transformation of methyloxirane is a structure sensitive reaction. The correlation between the turnover yield and the degree of dispersion passes through a maximum at about 63% D. Such maximum curves may be an indication that the reaction occurs predominantly on 2M sites (edge sites) (14, 16, 17) in Siegel's nomenclature (18–21).

Figure 3 in (14) shows the variation in the percentage of 2M sites with respect to particle dispersion for fcc octahedra and fcc truncated octahedra with complete and incomplete (max. B_5 structure) outer shells. In these graphs, the percentage of 2M sites passes through a maximum for each of the crystal models considered. This maximum varies, depending on the crystal model.

Maximum curves for these catalysts have

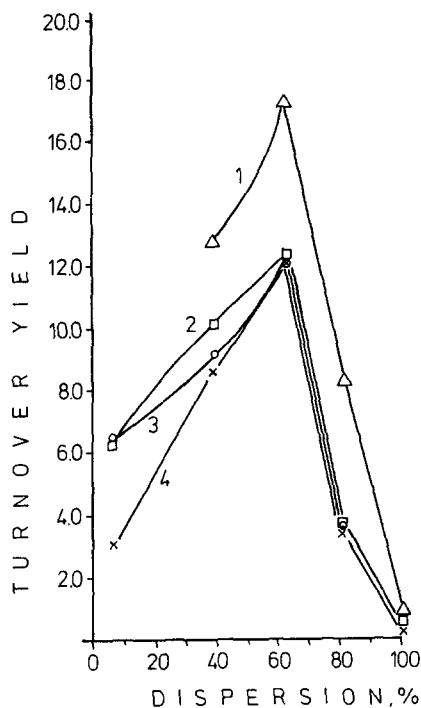


FIG. 2. The correlation between methyloxirane turnover yields to the percent dispersion. (curves 1, 2, 3: first, second, third pulse; curve 4: SSA).

also been reported for the ratio k_i/k_a for the hydrogenations of apopinene (17) and propene on Pd/SiO_2 (16). These authors also used crystal models in establishing that the 2M sites are the most active in these reactions. However, their maximum curves

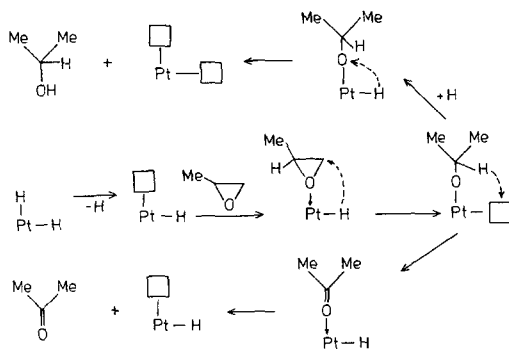


FIG. 3. The mechanism of isomerization and hydrogenation on 2Pt sites.

were much less pronounced than the one observed here. This could be due to the higher structure sensitivity of oxygen-containing compounds (22). As the particle size decreases, the affinity for oxygen increases, as does the degree of coordinative unsaturation for the particle (23). This behavior can be explained in terms of 3M , 2M , and 1M sites (18–21). 1M sites do not form oxides at all, 3M sites form strong oxide complexes quickly, and 2M sites form oxide complexes, but not to the extent of 3M sites. These ideas can also be related to the methyloxirane reaction, because the oxygen adsorbs first on the metal surface (11, 12, 24, 25) and the affinity of the metal for oxygen will strongly affect its reaction rate.

According to this model two vacant coordination sites are required to adsorb H_2 and the model assumes that this occurs most rapidly when a single atom provides both. An H atom can migrate from one atom to an adjacent one if the later has a vacant site. Isomerization of the methyloxirane can occur on an 2M site after H migrates from an adjacent site to form 2MH . The elementary steps are analogous to those involved in the isomerization of an olefin according to an associative mechanism. Hydrogenation of the alkoxy intermediate requires a hydrogen atom attached to the same metal atom to permit the reductive elimination to an alcohol (Fig. 3).

The similar maximum curves show that both reactions occur on 2M sites.

Future work including the analysis of cracking products and investigations in a static circulation system, will supply new data for the more detailed interpretation of the reaction mechanism.

ACKNOWLEDGMENTS

We acknowledge support for this research provided by the National Science Foundation (Grant INT-8403357) and the Hungarian Academy of Sciences (Grant 320/1986).

REFERENCES

1. Bartók, M., and Notheisz, F., *J. Chem. Soc., Chem. Commun.*, 667 (1980).
2. Bartók, M., Notheisz, F., and Zsigmond, Á. G., *J. Catal.* **63**, 364 (1980).
3. Bartók, M., Notheisz, F., and Kiss, J. T., *J. Catal.* **68**, 249 (1981).
4. Bartók, M., and Notheisz, F., *J. Catal.* **68**, 209 (1981).
5. Notheisz, F., and Bartók, M., *J. Catal.* **71**, 331 (1981).
6. Notheisz, F., Bartók, M., and Zsigmond, Á. G., *React. Kinet. Catal. Lett.* **29**, 339 (1985).
7. Bartók, M., Notheisz, F., Zsigmond, Á. G., and Smith, G. V., *J. Catal.* **100**, 39 (1986).
8. Bartók, M., Notheisz, F., Zsigmond, Á. G., and Smith, G. V., *J. Catal.* **102**, 471 (1986).
9. Bartók, M., Notheisz, F., Zsigmond, Á. G., Smith, G. V., *J. Mol. Catal.* **44**, 337 (1988).
10. Notheisz, F., Zsigmond, Á. G., Bartók, M., and Smith, G. V., *J. Chem. Soc. Faraday Trans.* **83**, 2359 (1987).
11. Senechal, G., and Cornet, D., *Bull. Soc. Chim. France*, 773 (1971).
12. Senechal, G., Duchet, J. C., and Cornet, D., *Bull. Soc. Chim. France*, 783 (1971).
13. Uchijima, T., Hermann, J. M., Inoue, Y., Burwell, R. L. Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50**, 464 (1977).
14. Notheisz, F., Bartók, M., Ostgard, D., and Smith, G. V., *J. Catal.* **101**, 212 (1986).
15. Cornet, D., Gault, Y., and Gault, F. G., in "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 1184, Wiley, New York, 1965.
16. Rorris, E., Butt, J. B., Burwell, R. L. Jr., and Cohen, J. B., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 4, p. 321. Dechema, Frankfurt-am-Main, 1984.
17. Smith, G. V., Bartók, M., Ostgard, D., and Notheisz, F., *J. Catal.* **101**, 212 (1986).
18. Siegel, S., *J. Catal.* **30**, 139 (1973).
19. Siegel, S., Outlaw, J. Jr., and Garti, N., *J. Catal.* **52**, 102 (1978).
20. Augustine, R. L., and Warner, R. W., *J. Catal.* **80**, 358 (1983).
21. Augustine, R. L., and O'Hagan, P. J., in "Catalysis of Organic Reactions," (D. W. Blackburn, Ed.), p. 111. Dekker, New York, 1990.
22. Cinneide, A. D. O., and Clarke, J. K. A., *Catal. Rev.* **7**, 213 (1972).
23. Nandi, R. K., Molinaro, F., Tang, C., Cohen, J. B., Butt, J. B., and Burwell, R. L., Jr., *J. Catal.* **78**, 289 (1982).
24. Apjok, J., Lafer, L. I., Bartók, M., and Yakerson, V. I., *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 24 (1977).
25. Blyholder, G., and Neff, L. D., *J. Phys. Chem.*, **70**, 893 (1966).