JOURNAL OF CATALYSIS **100**, 39–44 (1986)

The Mechanism of Hydrogenolysis and Isomerization of Oxacycloalkanes on Metals

III. Effect of Partial Pressure of Hydrogen on the Selectivity of Hydrogenolysis of Oxacycloalkanes on Pt[1]

M. BARTÓK,[2] F. NOTHEISZ, Á. G. ZSIGMOND, AND G. V. SMITH[3]

Department of Organic Chemistry, József Attila University, Szeged, Hungary

Received February 26, 1985; revised January 14, 1986

The rates of hydrogenolysis and isomerization of methyloxirane, *cis*- and *trans*-2,3-dimethyloxirane and 2-methyloxetane were studied on a Pt/C catalyst, as functions of the hydrogen pressure and the temperature. A new phenomenon was observed in the case of 2-methyloxetane: the change in mechanism as the temperature was elevated led to a change in regioselectivity. There is no such effect for methyloxirane, for which the dissociative mechanism is not competitive at high hydrogen pressure. Likewise, the mechanisms of transformation of methyloxirane and the 2,3-dimethyloxiranes are not the same. Methyloxirane probably participated in edgewise adsorption on the surface of the catalyst, while *cis*-2,3-dimethyloxirane undergoes flat adsorption.

INTRODUCTION

During their reactions in the presence of hydrogen, the oxacycloalkanes undergo hydrogenolysis and isomerization simultaneously. We earlier reported that primarily the less sterically hindered bond is split on a Pt catalyst (*1*) and that hydrogen is also required for the occurrence of isomerization (*2, 3*).

In the literature the term hydroisomerization is defined to mean isomerization reactions that proceed only in the presence of hydrogen (*4–6*). Although the hydroisomerization of hydrocarbons has been investigated in detail (*7–13*) and the results have even been reviewed (*14–19*), scarcely any studies have been devoted to the mechanism of the hydroisomerization of organic compounds containing heteroatoms.

The experimental data (*20, 21*) indicate that the partial pressure of hydrogen on Pt influences the rates of hydrogenolysis and isomerization; further, secondary alcohols are primarily formed by an associative mechanism (*22, 23*), while the formation of ketones involves a dissociative mechanism. Accordingly, it may be presumed that a change in the hydrogen pressure will act on these two reactions in different ways, and that a study of this effect may well provide important data contributing to an understanding of the catalytic transformations of oxacycloalkanes.

EXPERIMENTAL

Most of the investigations were performed in a closed circulation reactor (Fig. 1).

The volume of the reactor was 54 cm^3, and the total volume of the system was 175 cm^3. The reactor was heated with an air thermostat. The volume of the sampling capillary was 0.05 cm^3, and the total sampling volume was 0.3 cm^3/ Analysis was performed with a gas chromatograph fitted with a flame ionization detector. The measurement conditions were as described previously (*24*).

The temperature-dependence of the re-

---

[1] Part II: Ref. (*24*).

[2] To whom all correspondence should be sent.

[3] Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Ill. 62901.

0021-9517/86 $3.00

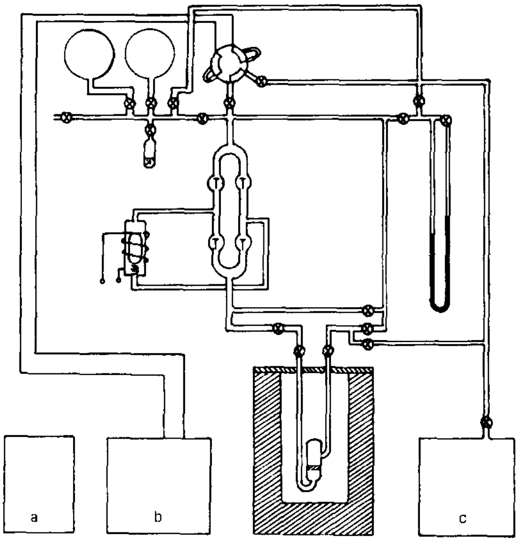


FIG. 1. The circulation reactor (a, integrator; b, GC; c, vacuum system).

gioselectivity was studied in a static microreactor. Hydrogen was used as carrier gas, and the hydrogen pressure in the microreactor was 130 kPa. The setup and the measurement conditions were as described earlier (*24, 25*).

Hydrogen was prepared with a Matheson 8326 electrolysis apparatus. These instruments produce ultrapure hydrogen by electrolytically dissociating water and then diffusing the hydrogen through a thin palladium membrane. The 18.5% Pt/C catalyst was prepared by the impregnation method (*26*). The support (Carbon fibers, Strem 06-0140) was impregnated with H_2PtCl_6 (Reanal 0593, Budapest) solution; after drying, reduction was carried out in a stream of hydrogen at 573 K for 6 h. In the pretreatment, the catalyst was heated in a stream of hydrogen up to 573 K at a rate of 10 K min^{-1}, kept at this temperature for 1 h, and then cooled to the temperature of the reaction during evacuation. The catalyst was characterized by hydrogen chemisorption and hydrogen–oxygen titration. The dispersion was 22%. Fresh catalyst was taken for each measurement; the quantity of catalyst was 5×10^{-3} g.

The methyloxirane was a BDH product, while the *cis*- and *trans*-dimethyloxiranes were prepared as described previously (*25*). 2-Methyloxetane was prepared as in (*27*).

The initial rate values were determined from the constants of the function $y = A(1 - e^{-Bx})$, where y = amount of product and x = reaction time. Correction factors were applied to convert the initial rates obtained to units of mol m^{-2} min^{-1}. The specific surface area was calculated from the dispersity on the basis of the surface atom density of 1.12×10^{15} Pt atom cm^{-2}.

RESULTS

The transformation of methyloxirane was studied in a circulation reactor at 373 K. Mainly 2-propanol and acetone were formed, with a smaller amount of 1-propanol (Fig. 2). The effect of the hydrogen pressure on the reaction rate was examined in the interval 0.65–48.7 kPa. At 373 K, the formation rates of all three products increased monotonically as the hydrogen pressure was elevated in this interval (Fig. 3). At the same time, at 473 K it could be observed that the rate of 1-propanol formation was maximum at a hydrogen pressure of 15 kPa (Fig. 4).

We also studied the rate of transformation of 2-methyloxetane as a function of the

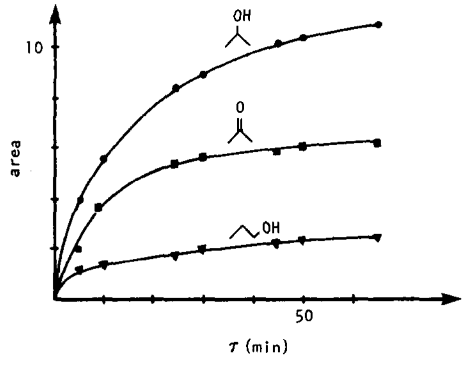


FIG. 2. Transformation of methyloxirane over Pt on carbon catalyst at 423 K (p_{oxirane} = 2.0 kPa, p_{H_2} = 2.1 kPa, catalyst = 5×10^{-3} g).

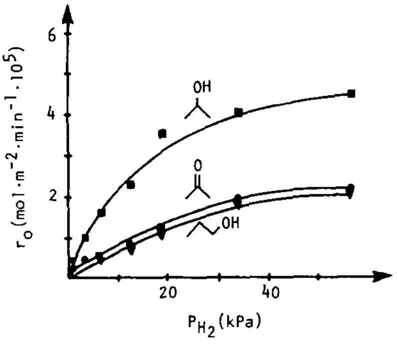


FIG. 3. Initial rates of appearance of products from methyloxirane at 373 K over Pt on carbon catalyst at different hydrogen pressures (p_{oxirane} = 2.0 kPa, catalyst = 5 × 10^{-3} g).

partial pressure of hydrogen (Fig. 5). For all three products, the formation rates gave a maximum as a function of the hydrogen pressure. For the two alcohols, the maxima coincided; they appeared at a higher hydrogen pressure than in the case of the ketone.

The data in Figs. 4 and 5 and Table 1 reveal that in the case of 2-Me-oxetane at 473 K, in contrast with 2-Me-oxirane, the regioselectivity was changed. The study of *cis*- and *trans*-2,3-dimethyloxiranes as a function of hydrogen pressure permitted comparison of the behavior of the two stereoisomeric compounds. For *cis*-2,3-dimethyloxirane, the rate of ketone formation displayed a maximum as a function of the hydrogen pressure. In contrast, there was no such maximum in the alcohol formation rate (Fig. 6). The dependence on the hydrogen pressure was similar in character for *trans*-2,3-dimethyloxirane, but the maximum for the ketone was less sharp (Fig. 7).

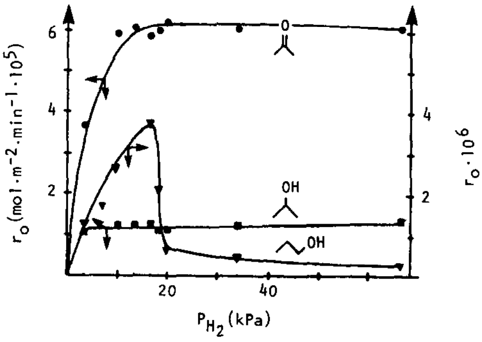


FIG. 4. Initial rates of appearance of products from methyloxirane at 473 K over Pt on carbon catalyst at different hydrogen pressures (p_{oxirane} = 2.0 kPa, catalyst = 5 × 10^{-3} g).

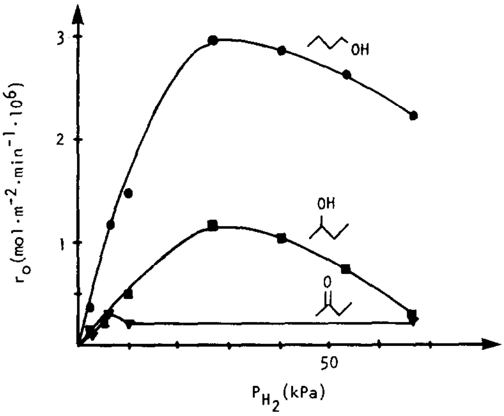


FIG. 5. Initial rates of appearance of products from 2-methyloxetane at 473 K over Pt on carbon catalyst (p_{oxetane} = 2.0 kPa, catalyst = 5 × 10^{-3} g).

DISCUSSION

The study of the rate of methyloxirane transformation as a function of hydrogen partial pressure showed that at 373 K the rate of 1-propanol formation increases monotonically as the hydrogen pressure is raised, whereas at 473 K it passes through a maximum.

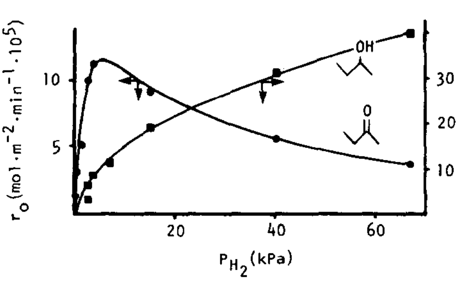


FIG. 6. Initial rates of appearance of products from *cis*-2,3-dimethyloxirane at 373 K over Pt on carbon catalyst (p_{oxirane} = 1.4 kPa, catalyst = 5 × 10^{-3} g).

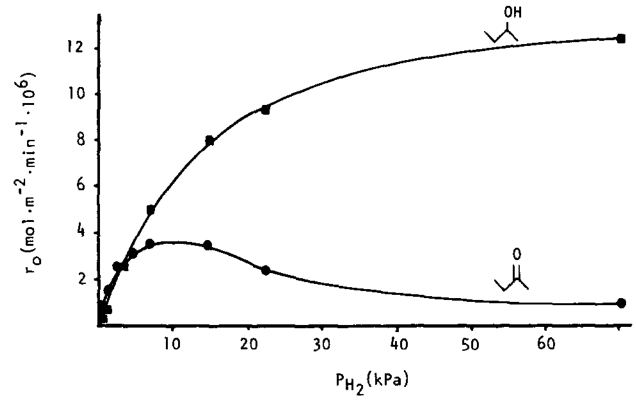
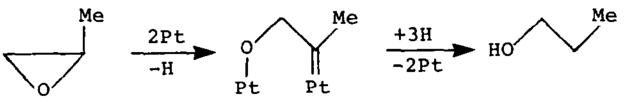


FIG. 7. Initial rates of appearance of products from *trans*-2,3-dimethyloxirane at 373 K over Pt on carbon catalyst ($p_{\text{oxirane}} = 1.4$ kPa, catalyst = 5×10^{-3} g).

It has been reported (*28*) that the maximum observed as a function of the hydrogen pressure occurs at an ever lower hydrogen pressure, the more unsaturated the surface species. In the hydrogenolysis of oxiranes (*22, 23*), the simultaneous occurrence of an associative and a dissociative mechanism is assumed. It appears obvious to ascribe the curve with the maximum to the dissociative mechanism. This indicates that at 373 K the mechanism is associative, while at 473 K it is dissociative. In the case of the associative mechanism, the regioselectivity is governed by the stereochemical factors, and splitting of the less sterically hindered bond is favored. In contrast, at higher temperatures a dissociative mechanism occurs. In this case the transformation begins with splitting of a C—H bond, and the higher reactivity of the secondary C—H bond will be the factor determining the selectivity.



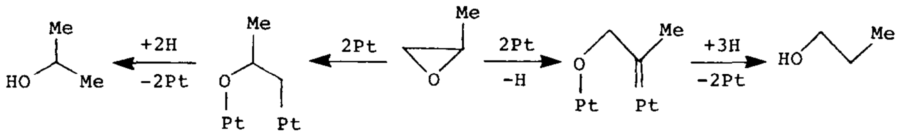
However, the dissociative mechanism is competitive only at low hydrogen pressure; above a hydrogen pressure of 20 kPa, the dissociative mechanism is suppressed and

TABLE 1

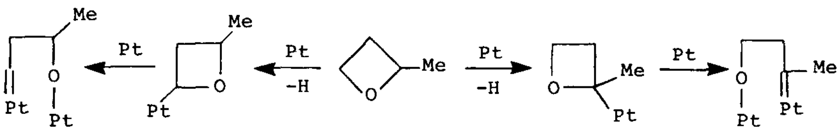
Initial Distribution of Products over Pt on Carbon Catalyst in a Static Microreactor System

Compound	Temperature (K)	Initial distribution of products (mol%)				b/a
		Aldehyde (a)	1-Alcohol (a)	Ketone (b)	2-Alcohol (b)	
Methyloxirane	373	0	13	3	84	6.7
	473	0	11	3	86	8.0
2-Methyloxetane	373	0	13	1	86	6.7
	473	0	75	5	20	0.33

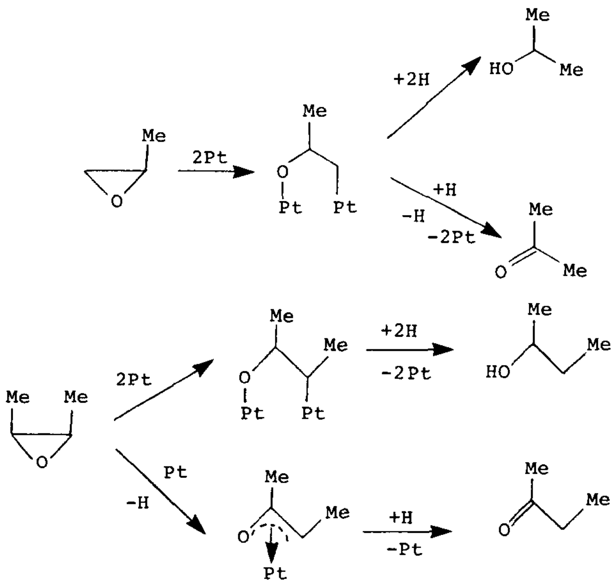
the associative mechanism predominates. This is the reason why 1-propanol is barely formed in the microreactor.



For 2-methyloxetane at 373 K, the less sterically hindered bond is split. At 473 K, the dissociative mechanism predominates. In this case, the dissociative mechanism is suppressed to a much lower extent by an increase in the hydrogen pressure than it is in the case of methyloxirane; thus, at a higher temperature the associative mechanism is no longer competitive.



Studies of the transformations of the 2,3-dimethyloxirane isomers demonstrates that the rate of ethyl methyl ketone formation gives a maximum as a function of the hydrogen pressure. This maximum is particularly sharp for the *cis* isomer. This maximum reveals that a relatively narrow range of surface hydrogen coverage is optimum for ketone formation. Since this maximum is not observed for methyloxirane, the mechanisms of transformation of methyloxirane and the 2,3-dimethyloxiranes are not completely identical.



Our earlier investigations (*25*) indicated that the 2,3-dimethyloxiranes adsorb flat on a Pt catalyst. This type of adsorption allows synchronous bond splitting. Since synchronous bond splitting does not occur for mthyloxirane, we concluded that it adsorbs edgewise on the catalyst surface. In such a case, the methyl group is the most distant from the catalyst surface. Because of the steric hindrance between the methyl group and the catalyst surface only a primary carbon atom can adsorb on the surface in this way.

ACKNOWLEDGMENTS

We gratefully acknowledge MTA and NSF support for the US/Hungarian collaboration. The financial support for this work by the Hungarian Ministry of Education (Grant 40/1981) and the Hungarian Academy of Sciences (Grant 319/82/1.3) is also acknowledged.

REFERENCES

1. Bartók, M., Notheisz, F., and Kiss, J. T., *J. Catal.* **68,** 249 (1981).
2. Bartók, M., *Acta Phys. Chem.* **21,** 79 (1975).
3. Bartók, M., *React. Kinet. Catal. Lett.* **3,** 115 (1975).
4. Ciapetta, F. G., and Hunter, J. B., *Ind. Eng. Chem.* **45,** 147 (1953).
5. Pines, H., and Shaw, A. W., "Advances in Catalysis," Vol. 9, p. 569. Academic Press, 1957.
6. Wells, P. B., and Wilson, G. R., *J. Catal.* **90,** 70 (1967).
7. Barron, Y., Cornet, D., Maire, G., and Gault, F. G., *J. Catal.* **2,** 152 (1963).
8. Anderson, J. R., and Avery, N. R., *J. Catal.* **2,** 542 (1963).
9. Boudart, M., and Ptak, L. D., *J. Catal.* **16,** 90 (1970).
10. Mc Kervey, M. A., Rooney, J. J., and Samman, N. G., *J. Catal.* **30,** 330 (1973).
11. Páal, Z., and Tétényi, P., *J. Catal.* **29,** 176 (1973).
12. Burwell, R. L., and Briggs, W. S., *J. Amer. Chem. Soc.* **74,** 5096 (1952).
13. Bragin, O. V., and Liberman, A. I., *Usp. Khim.* **39,** 2122 (1970).
14. Bond, G. C., and Wells, P. B., "Advances in Catalysis," Vol. 15, p. 92. Academic Press, New York, 1964.
15. Siegel, S., "Advances in Catalysis," Vol. 16, p. 124. Academic Press, New York, 1964.
16. Boudart, M., "Advances in Catalysis," Vol. 20, p. 153. Academic Press, New York, 1969.
17. Anderson, J. R., "Advances in Catalysis," Vol. 23, p. 1. Academic Press, New York, 1973.
18. Sinfelt, J. H., "Advances in Catalysis," Vol. 23, p. 91. Academic Press, New York, 1973.
19. Clarke, J. K. A., and Rooney, J. J., "Advances in Catalysis," Vol. 25, p. 125. Academic Press, New York, 1976.
20. Bartók, M., and Notheisz, F., *J. Catal.* **68,** 209 (1981).
21. Davidova, G., and Kraus, M., *J. Catal.* **61,** 1 (1980).
22. Senechal, G., and Cornet, D., *Bull. Soc. Chim. Fr.*, 773 (1971).
23. Senechal, G., Duchet, J. C., and Cornet, D., *Bull. Soc. Chim. Fr.*, 783 (1971).
24. Notheisz, F., and Bartók, M., *J. Catal.* **71,** 331 (1981).
25. Bartók, M., Notheisz, F., and Zsigmond, Á. G., *J. Catal.* **63,** 364 (1980).
26. Bartók, M., and Fényi, Sz., *Acta Phys. Chem.* **12,** 157 (1966).
27. Bartók, M., and Gilde, A. S., *Acta Phys. Chem.* **9,** 25 (1963).
28. Paál, Z., and Menon, P. G., *Catal. Rev.-Sci. Eng.* **25,** 229 (1983).