JOURNAL OF CATALYSIS 95, 605–608 (1985)

New Stereoselective Isomerization and Hydrogenolysis of 1,3-Dioxanes on Platinum: Study of Molecular Conformation and Reactivity

The studies of the stereochemistry of heterogeneous catalytic processes provide data that are essential for the elucidation of the mechanisms of the reactions taking place on the catalysts, and hence for an even better understanding of the phenomenon of catalysis. The stereochemical investigations to date have helped clarify numerous experimental observations in the fields of both homogeneous and heterogeneous catalyses. Most studies have been carried out concerning hydrogenation, H–D exchange, dehydration, polymerization, certain isomerizations, and the synthesis and transformation of chiral systems (*1–8*).

In our view, the study of the stereochemistry of different chemical processes on metal catalysts, and within this the study in particular of the effects of the molecular conformation on the adsorption, the reaction rate, and the reaction directions, has not yet become widespread.

Since the study of isomerization and hydrogenolysis is one of the central problems in metal catalysis (*9*), we have examined the above transformations of various cyclic carbon compounds containing C—O bonds. Our previous experimental results showed that on a platinum catalyst the 1,3-dioxacycloalkanes undergo isomerization to esters and hydrogenolysis to alkoxyalcohols (*10*). Isomerizations to the esters can be observed only for the 5- and 6-member compound types. Under similar experimental conditions the 7-member homologs undergo hydrogenolysis to the corresponding alkoxyalcohols; open-chain acetals similarly do not isomerize to esters. It was proved experimentally that esters are not formed in the absence of hydrogen (*10*).

With the aim of elucidating the stereochemical course of these reactions, a GLC pulse-microreactor technique was employed to study the transformations on a 10% Pt–T (T = thermolite) catalyst at 150–250°C of geometrical isomers of 1,3-dioxanes **1–8**. Thermolite is a support of the diatomaceous earth type employed in gas chromatography; it is a fire-resistant clay, consisting predominantly of calcium magnesium silicate—number of acidic centers: 0.056 meq g^{-1} (titrated by *n*-butylamine), number of basic centers: 0.001 meq g^{-1} (titrated by benzoic acid). For comparison, similar data of Kieselguhr (Merck) are 0.1 and 0 meq g^{-1}, respectively.

References relating to the preparation and characterization of compounds **1–8**, together with the GLC data, are found in an earlier publication (*11*) and references therein. It should be noted that the configurations and probable conformations of the variously substituted 1,3-dioxane stereoisomers are well characterized, mainly by Eliel *et al.* (*12*), Anteunis *et al.* (*13*), and Pihlaja *et al.* (*14*). Methods used include NMR spectroscopy and the determination of equilibrium constants and conformational energies. The large differences in the conformations of the stereoisomer pairs are confirmed by the GLC retentions (*11*).

The preparation (*15*) and characterization of the catalyst and the experimental technique have been described (*16*). The specific surface of the catalyst determined via O_2–H_2 titration was 16 m^2 g^{-1} metal ±10%. The area-averaged diameter of the catalyst particles determined via electron micrographs (Tesla BS 500) was 47 nm.

A Rasotherm glass microreactor with an

0021-9517/85 $3.00

TABLE 1

Retention Times of Starting Materials and Products

Compound studied	Retention time (sec)					
	A	B	C	D	E	F
1, 2	516	420	—	—	348	654
3, 4	882	684	—	—	582	1020
5, 6	1200	1128	672	1084	—	1538
7, 8	1230	1170	684	1050	—	1490

internal diameter of 6 mm was incorporated with a Carlo Erba Model GV GLC instrument. The catalyst (0.5 g) was placed between layers of quartz sand—carrier gas: 60 ml H_2 min^{-1}; amount of substance injected: 4 μl; chromatography: column 2 m 15% Carbowax 20M/Kieselguhr + 2 m 15% Apiezon M/Kieselguhr, thermostat 200°C.

C, **D**, and **F** compounds in Table 1 were identified on the basis of their IR (Unicam SP 1000) and ^{1}H NMR spectra (JEOL C-60-HL) after separation of several recovered 20-μl pulses (Carlo Erba Fractovap Mod. P automatic preparative GLC).

TABLE 2

Experimental Data on Transformations of Compounds **1–8** at 200°C on Pt–T

Compound studied	Product composition[a] (mol%)						Decomp.[b]
	A	B	C	D	E	F	
1	5	13	0	0	10	62	10
2	11	3	0	0	9	6	11
3	10	2	0	0	10	65	13
4	8	2	0	0	12	68	10
5	1	7	41	23	0	8	20
6	2	6	44	22	0	9	17
7	0	0	53	21	0	5	21
8	0	0	56	15	0	6	23

[a] For symbols see Figs. 1 and 2; E = unknown substance.

[b] Various volatile cracking products with low GLC retentions, which were not identified. Their quantities were estimated from the mass balance calculated via the determination of **A–F**.

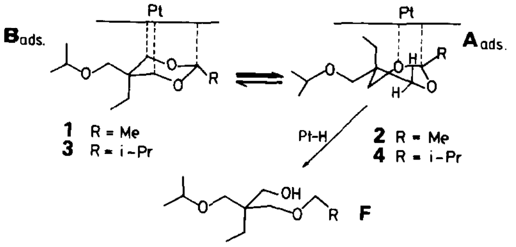

FIGURE 1

The experimental data in Table 2 reveal very considerable differences in reaction directions, depending on the molecular conformation.

Hydrogenolysis is observed in the transformation of stereoisomer pairs with different conformations (Fig. 1).

In contrast, in the case of stereoisomer pairs with the same (chair) conformation, isomerization is observed, again with high selectivity (Fig. 2).

The different behaviors can be attributed to stereochemical reasons, i.e., as a consequence of their different conformations. The molecules are adsorbed in completely different geometrical arrangements (flat-laying or two-point adsorption) on the surface of the catalyst (see Figs. 1 and 2). Reactions may occur via dissociative or associative mechanisms, depending on the temperature and other factors.

In the case of the dissociative mechanism, **5** and **6** may bind to the surface from the side of the axial hydrogens of the dioxane ring (flat-laying adsorption). In the case of **5**, this disposition of the molecule may be promoted by the 5-(2-methoxyethyl) group,

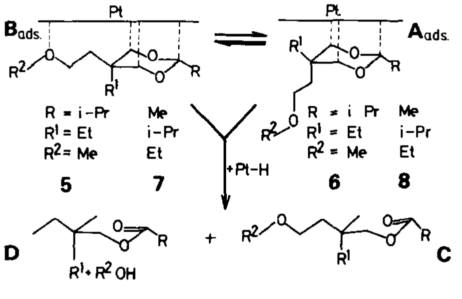

FIGURE 2

via the nonbonded electron pair of the oxygen atom. Adsorption of the molecule in such an arrangement decreases the probability of hydrogenolysis by keeping atoms C(2), O(1), and O(3) of the dioxane ring away from the surface of the catalyst. At the same time it promotes isomerization to the ester via splitting of the C(2)—H bond. The above-mentioned oriented adsorption of **5** is also strongly suggested by the experimental fact that the formation of products associated with hydrogenolysis of the methoxy group could also be observed (Fig. 2).

The adsorption of **3** in a manner analogous to that of **5** is inhibited by its configurational isomerization to **4** in a twist-boat conformation (this was shown by our experiments to be a very fast process) and further by the lack of surface-binding effect of the *trans* side chain. (In the stereoisomer pair containing an α-alkoxyalkyl group on C(5), in the case of **B** the oxygen of the alkoxyalkyl group is more distant from the surface, while in the case of **A** the C(5) Et inhibits binding to the surface.) The molecule probably adsorbs on atoms C(2)—O, a result of which is its hydrogenolysis (Fig. 1).

For both reactant types the associative mechanism essentially means hydrogenolysis (Fig. 3). For one isomer pair the stereochemical conditions favor hydrogenolysis of the C(2)—O bond, while for the other pair they favor hydrogenolysis of the C(4)—O bond.

The knowledge of the main reaction kinetic parameters of the processes, together with other experimental data (investigations in the absence of hydrogen, selective poisoning studies, IR examination of the structures developing on the catalyst surface, H–D exchange reaction studies), will provide an insight into the mechanisms of the above processes.

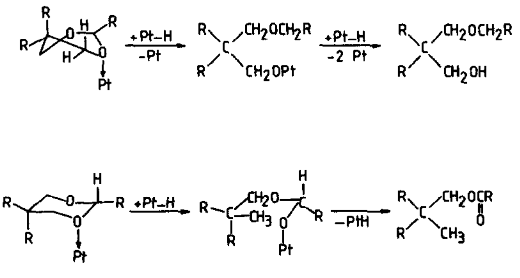

FIGURE 3

The results thus allowed recognition of new stereoselective heterogeneous catalytic processes, and provided the first experimental proof that the conformation of the reactant molecule plays a determining role regarding the direction of a heterogeneous catalytic reaction. It was also found that the more important precepts to date of modern conformational theory can be applied effectively in the study of the stereochemical course and mechanism of heterogeneous catalytic reactions.

ACKNOWLEDGMENTS

We acknowledge support for this research provided by the Ministry of Culture (Grants 40/1981 and P-167/1984) and the Hungarian Academy of Sciences (Grant 319/82/1.3).

REFERENCES

1. Burwell, R. L., Jr., *Chem. Rev.* **57,** 895 (1957).
2. Natta, G., and Pasquon, I., "Advances in Catalysis," Vol. 11, p. 1. Academic Press, New York, 1959.
3. Bond, G. C., and Wells, P. B., "Advances in Catalysis," Vol. 15, p. 91. Academic Press, New York, 1964.
4. Pines, H., and Manassen, J., "Advances in Catalysis," Vol. 16, p. 49. Academic Press, New York, 1966.
5. Siegel, S., "Advances in Catalysis," Vol. 16, p. 123. Academic Press, New York, 1966.
6. Weitkamp, A. W., "Advances in Catalysis," Vol. 18, p. 1. Academic Press, New York, 1968.
7. Morrison, J. D., and Mosher, H. S., "Asymmetric Organic Reactions." Prentice-Hall, Englewood Cliffs, N.J., 1971.
8. Kemball, C., *Catal. Rev.* **5,** 33 (1971).
9. Clarke, J. K. A., and Rooney, J. J., "Advances in Catalysis," Vol. 25, p. 125. Academic Press, New York, 1976; Dowden, D. A., *in* "Catalysis" (Specialist Periodical Report), (D. A. Dowden and C. Kemball, Eds.), Vol. 2, p. 1. The Chemical Society, London, 1978.

10. Bartók, M., and Czombos, J., *J. Chem. Soc., Chem. Commun.*, 106, 978 (1981).

11. Bartók, M., *J. Chromatogr.* **172,** 371 (1979).

12. Eliel, E. L., Powers, J. R., and Nader, F. W., *Tetrahedron* **30,** 515 (1974).

13. Anteunis, M., Tavernier, D., and Borremans, F., *Heterocycles* **4,** 293 (1976).

14. Pihlaja, K., Kivimäki, M., Myllyniemi, A., and Nurmi, T., *J. Org. Chem.* **47,** 4688 (1982).

15. Bartók, M., Apjok, J., Karakhanov, R. A., and Kovács, K., *Acta Chim. Acad. Sci. Hung.* **61,** 315 (1969).

16. Bartók, M., and Notheisz, F., *J. Chem. Soc., Chem. Commun.*, 139, 744 (1979).

M. BARTÓK
Á. MOLNÁR
J. APJOK

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

Received September 17, 1984