Stereochemistry of the Hydrogenolysis of Oxacycloalkanes on Metal Catalysts

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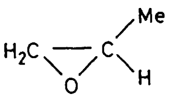
Summary On the basis of reaction kinetics, H–D exchange, and i.r. studies of the hydrogenolysis of oxirans and oxolans, the opposite regio- and stereo-selectivities of Pt and Ni are interpreted, a new reaction mechanism is proposed, and it is shown experimentally that the reaction mechanism depends *inter alia* on the steric structure of the molecule.



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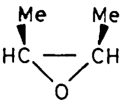

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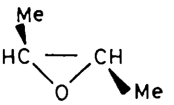

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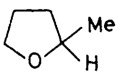

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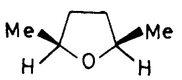

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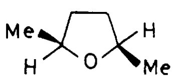

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Earlier extensive investigations of the hydrogenolysis of the C–O bond[1–5] have not permitted an interpretation of the different behaviour of Ni and Pt,[6] or an explanation of the influence of stereochemical factors on the mechanism of this reaction. Accordingly, we have now examined the reactions on Pt and Ni catalysts of certain strained and non-strained cyclic systems: the oxirans (**1**—**3**) and the oxolans (**4**—**6**). The results of the reaction kinetic measurements are in Table 1. On the basis of these data and the results of i.r.[9] and H–D exchange[10] investigations, the following reaction pathways are proposed to explain the observed differences in regio- and stereo-selectivities (see the Scheme). On Pt, the cleavage of the oxiran proceeds by insertion of the Pt,[11] which simultaneously affects the

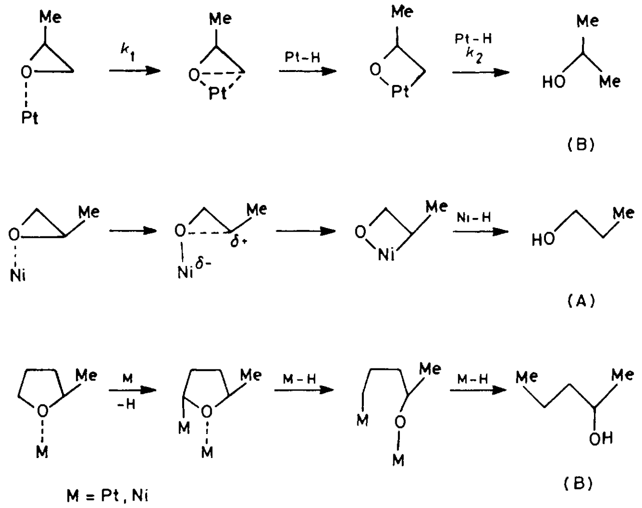
Table 1. Initial rates (mol m^{-2} min^{-1} $\times$ 10^5) of transformation of the oxacycloalkanes (**1**)—(**6**) on metal catalysts in a static micro-reactor system.[a]

		(**1**)		(**2**)		(**3**)		(**4**)		(**5**)	(**6**)
Products		Pt (100 °C)	Ni (150 °C)	Pt (100 °C)	Ni (150 °C)	Pt (100 °C)	Ni (150 °C)	Pt/S[b] (250 °C)	Ni/S[b] (200 °C)	Pt/C[b] (125 °C)	Pt/C[b] (125 °C)
1-Alcohol	(A)[c]	5	23	—	—	—	—	0	0	—	—
2-Alcohol	(B)[c]	33	3	72	25	6	23	1	9	1·8	2·0
Ketone[d]	(C)	1	0	4	5	0·5	6	8[g]	13[g]	0·2	0·2
Aldehyde[d]	(D)	0	10	—	—	—	—	0	0	—	—
Hydrocarbon[e]		4	8	8	28	2	22	1	10	1·5	1·5
x[f]		1	0·1	1	1	1	1	1	1	1	1

[a] Examinations were made in a static microreactor (ref. 7) with a Carlo Erba ATC/f g.l.c. and an Autolab System I computing integrator. The preparation and characterization of the catalysts have been described (refs. 7, 8). Catalyst quantities (in mg) Pt 10, Ni 5, Pt/S 32, Ni/S 54, and Pt/C 16. [b] S = Cab-O-Sil, C = active carbon support. [c] See the Scheme. [d] Isomers of corresponding oxacycloalkanes (acetone, butan-2-one, pentan-2-one, hexan-2-one, or propionaldehyde). [e] Unidentified saturated hydrocarbons containing the same number of or fewer carbon atoms than the oxacycloalkanes. [f] $x = [(B) + (C)]/[(A) + (B) + (C) + (D)]$. [g] Owing to the higher temperature, the equilibrium reaction 2-alcohol $\rightleftharpoons$ ketone + H_2 is shifted towards dehydrogenation.

TABLE 2. Experimental observations.

	Oxirans	Oxolans
Regioselectivity	Opposite on Ni and on Pt	Same on Pt and on Ni
Reaction rate	On Pt (**2**) $\gg$ (**3**); on Ni (**2**) = *ca.* (**3**)	On Pt and Ni (**5**) = *ca.* (**6**)
Adsorption (ref. 7)	Irreversible	Reversible
Reaction with D_2 on Pt (refs. 4, 10)	No H–D exchange; $H_2DC–CH(OD)Me$ formed from (**1**)	No H–D exchange at C(2); $HD_2C[CH_2]_2C(:O)Me$ formed from (**4**)
I.r. studies (ref. 9)	The adsorption begins at oxygen for both metals	



SCHEME

O and C atoms. Complete splitting of the C–O bond occurs through the action of chemisorbed hydrogen. Formation of the surface species is controlled by steric factors. The considerably different rates of transformation of the stereoisomers (**2**) and (**3**) on a Pt catalyst may be explained by the rate-determining step for the reactions.† For (**3**) this is the formation of the diadsorbed species (k_1), and for (**2**) its further reaction (k_2). Because of the higher electron affinity of Ni, its insertion becomes ionic, formation of the surface species is controlled by electronic factors, and rupture of the C–O bond precedes formation of the Ni–C bond. On both catalysts, the oxolan ring is split only through the action of the chemisorbed hydrogen; the non-strained oxolan ring does not split during adsorption. Dissociative chemisorption of the C(5) atom of the ring is necessary for bond rupture. Then, owing to the action of the chemisorbed hydrogen and to the more favourable stereoelectronic factors, the C(5)–O bond undergoes rupture instead of the C(5)–M bond.

The above mechanism is supported by the following experimental observations summarised in Table 2. The reaction route given for the oxolans is the general mechanism for hydrogenolysis of the C–O bond. The insertion mechanism is shown only in the case of compounds containing weak C–O bonds (oxirans, oxetans, R_3C–O, allyl–O, and benzyl–O).

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[1] S. Mitsui, Y. Senda, and K. Konno, *Chem. Ind.* (*London*), 1963, 1354.
[2] S. Mitsui and Y. Nagahisa, *Chem. Ind.* (*London*), 1965, 1975.
[3] S. Mitsui, Y. Kudo, and M. Kobayashi, *Tetrahedron*, 1969, **25**, 1921.
[4] G. Sénéchal and D. Cornet, *Bull. Soc. Chim. Fr.*, 1971, 773.
[5] G. Sénéchal, J. C. Duchet, and D. Cornet, *Bull. Soc. Chim. Fr.*, 1971, 783.
[6] R. L. Augustine, *Catal. Rev.*, 1976, **13**, 285.
[7] M. Bartók, F. Notheisz, and A. G. Zsigmond, *J. Catal.*, in the press.
[8] M. Bartók and F. Notheisz, *J. Chem. Soc., Chem. Commun.*, 1979, 744.
[9] J. Apjok, L. I. Lafer, M. Bartók, and V. I. Yakerson, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1977, 24.
[10] J. C. Duchet and D. Cornet, *J. Catal.*, 1976, **44**, 57.
[11] M. N. Akhtar, W. R. Jackson, and J. J. Rooney, *J. Am. Chem. Soc.*, 1976, **96**, 276.