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The Mechanisms of Hydrogenolysis and Isomerization of Oxacycloalkanes on Metals

II. New Results on the Transformations of 2-Methyloxacycloalkanes on Metals

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The hydrogenolysis and isomerization of 2-methyloxacycloalkanes were studied on Pt, Pd, and Ni catalysts in a static microreactor system. The experimental data permitted investigation of the relations between the reaction rate, the regioselectivity, the number of ring atoms, and the nature of the metal catalyst, as well as the postulation of the most probable reaction routes, and a comparison with the patterns of hydrogenolysis of cycloalkanes. The mechanisms of hydrogenolysis of the 2-methyloxacycloalkanes depend on the metal, the number of ring atoms, and the experimental conditions.

INTRODUCTION

In recent decades the investigation of the various reactions of the alkanes and cycloalkanes has been one of the central questions of catalysis research (*1–3*). Study of the hydrogenolysis of the cycloalkanes still remains a task of particular importance, for the ring-opening ability depends not only on the catalyst, but also on the geometry of the reactant. Use has been made of the methylcycloalkanes (**I**) (see Fig. 1) as the most convenient model compounds for this research. The results recently achieved from examinations on methylcyclopropane (*4–9*), methylcyclobutane (*10–12*), and methylcyclopentane (*12–22*) have led to the establishment of essential regularities. Methylcyclopropane has also served as a good model for the study of the isomerizing character of catalysts containing acidic centers (e.g., (*23*)). It is difficult to study the hydrogenolysis of the compounds with cyclohexane and cycloheptane skeletons, because of the dominant nature of the concurrent aromatization (*24–26*).

During investigations into the hydrogenolysis of methylcycloalkanes, it has been found that the ring opens mainly at position *b*, to an extent depending on the number of ring atoms, the catalyst, and the experimental conditions. From the pattern of the ring opening, useful conclusions have been reached with regard to the mechanism of the hydrogenolysis.

Since the investigation of systems involving various numbers of ring atoms has already led to a substantial enrichment of the knowledge of metal catalysis, we set out to study certain 2-methyloxacycloalkanes (**1, 2, 3, 4**) on M/CS catalysts (M = Ni, Pd, Pt; CS = Cab-O-Sil). The metals employed were chosen on the basis of the following aspects. It is known that, of the three parameters (activity, deepness, pattern) typifying the hydrogenating properties of metals (*2*), deepness has proved the most characteristic for the individual metals. In the case of the hydrocarbons, single rupture is characteristic of Pd and Pt, and multiple rupture typifies Ni.

In earlier studies connected with this theme, we found that for the 2-methyloxacycloalkanes on thermolite-supported metal catalysts the ring-opening ratio *b*/*a* varies considerably with the number of ring atoms (*27*).

Since our earlier investigations (*28, 29*)

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provided experimental evidence that the three- and four-membered cyclic ethers (i.e., oxiranes and oxetanes) undergo isomerization to aldehydes (ring opening *a*) on the action of the acidic centers of the supported catalysts, it appeared necessary to carry out examinations on metal catalysts not containing acidic centers as well. Realization of this aim was facilitated by the development of a new technique for the determination of the rates of heterogeneous catalytic reactions (*30*).

This topic is of added importance from the aspect that, based on a comparison with the results for cycloalkanes, study of the catalytic properties of the metals may be extended to organic compound types containing heteroatoms. By this means a possibility arises for generalization of the catalytic properties, while study of the new reactions allows an improved understanding of the nature of metal catalysis. Finally, over and above these general aims, the experimental results may yield new indirect evidence on the mechanisms of hydrogenolysis and isomerization of the oxacycloalkanes (*31, 32*), and will pave the way for the study of the stereochemistry of metal-catalyzed transformations of oxacycloalkanes containing rings of various sizes.

EXPERIMENTAL

Details of the preparation and characterization of the 2-methyloxacycloalkanes [2-methyloxirane (epoxypropane) (**1**), 2-methyloxetane (2-methyloxacyclobutane) (**2**), 2-methyloxolane (2-methyltetrahydrofurane) (**3**), 2-methyloxane (2-methyltetrahydropyrane) (**4**)] are to be found in earlier publications (see references in (*28*)). Figure 1 shows the most probable conformations suggested by the various physical methods.

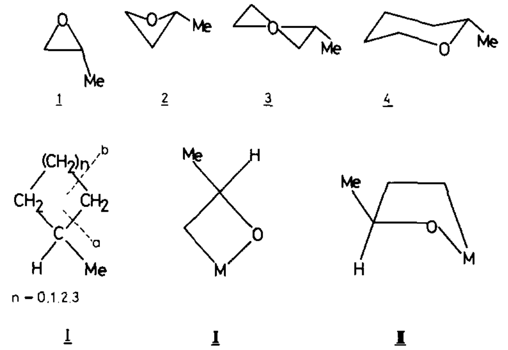

FIG. 1. Most probable conformations of the 2-methyloxacycloalkanes (**1**, **2**, **3**, **4**) and **I**, **II**, **III**.

The preparation, pretreatment, and detailed characterization of the unsupported metal catalysts have similarly been published (*31*), as has the new method for the study of catalytic transformations (a microreactor coupled to a gas chromatograph, in the static operation mode) (*30, 31*).

Preparation of the M/CS (CS = Cab-O-Sil) catalysts. Ten grams of CS was moistened with ion-free water, and an aqueous solution (0.3 g metal/20 ml) of the appropriate metal salt (H_2PtCl_6, $PdCl_2$, or $Ni(NO_3)_2$) was added under intensive stirring. After

TABLE 1

Chromatographic Conditions and Retention Times (min) of Products Formed in the Transformations of 2-Methyloxacycloalkanes

Compound:	1	2	3	4
Carrier gas (ml H_2/min):	50	40	50	50
Temp. (°C):	60	70	80	80
Products[a]				
Aldehyde (**5**)	3.06	8.7	1.73	2.37
1-Alcohol (**6**)	9.61	45.0	7.41	12.30
Ketone (**7**)	3.99	11.2	2.54	3.94
2-Alcohol (**8**)	4.80	20.4	4.49	7.58
1, **2**, **3**, **4**	2.22	6.9	1.56	1.99

Note. Chromatographic columns: For **1**: 1.5 m 20% ODPN on Chromosorb W + 1.5 m 15% Reoplex 400 on Kieselguhr. For **2**: 1.5 m 10% Carbowax 20 *M* on Kieselguhr + 1.5 m 15% Fractonitril III on Kieselguhr. For **3**: 1.5 m 15% Reoplex on Kieselguhr. For **4**: 1.5 m 15% Reoplex on Kieselguhr.

[a] CO and hydrocarbons were also formed. Gas analysis conditions: 1.5-m column containing BDH silica gel for chromatographic adsorption; thermostate, 100°C; carrier gas, 10 ml H_2/min. Retention times (min): CO + methane, 1.84; ethane, 2.24; propane, 3.05; butane, 4.66; pentane, 7.98; hexane, 12.85. Carlo Erba MS5A molecular sieve (2 m), 25°C; carrier gas, 40 ml H_2/min, retention times (min): methane, 6.3; CO, 7.5.

the mixture had stood for 1 day, the water was removed by film evaporation and the mass was then dried for 16 h at 130°C. Reduction was carried out in a current of hydrogen, for 1 h at 210°C, and subsequently for 2 h at 350°C. Before use, the catalysts were pretreated according to (*31*). After this pretreatment, the catalyst surface can be regarded as oxygen free under the reaction conditions employed (in the presence of hydrogen). The specific surfaces were Pt/CS 38, Pd/CS 72, Ni/CS 45 m^2/g metal (± 10%).

A Carlo Erba ATC/f chromatograph was used for the measurements (chromatography conditions and retention times are given in Table 1). The experimental data were evaluated with a Perkin-Elmer Sigma 10 integrator. The initial reaction rates were obtained from the constants of a saturation function, the latter being determined by an iterative method with the aid of a Texas Instrument SR-52 calculator. Details of the measurement and calculation method were likewise described earlier (*31*).

RESULTS AND DISCUSSION

The experimental data are listed in Table 2. Investigations with the three-membered cyclic ether (**1**) were begun with an unsupported catalyst prepared by alkaline reduction. Since the transformations of the five- and six-membered cyclic ethers (**3** and **4**) required a higher temperature because of

TABLE 2

Initial Rates of Disappearance of **1**, **2**, **3**, and **4** (mole m^{-2} min^{-1} × 10^5) and Initial Distributions of Products on Metal Catalysts in a Static Microreactor System

Compound	Catalyst	Temperature (°C)	Initial distribution of products (mole%)[a]						*b*/*a*[c]
			5	**6**	**7**	**8**	**9**	*b*	
1	Ni	150	22	52	0	7	19	44	0.1
	Ni/CS	250	10	10.5	5.5	1.2	72.8	723[d]	*e*
	Pd	100	2	14	9.5	73	1.5	189	5
	Pd/CS	250	60	6.5	7.8	6	19.7	331[d]	*e*
	Pt	100	0	11.5	2.5	76.5	9.5	43	7
	Pt/CS	250	24	8.5	26.5	13	28	258[d]	*e*
2	Ni	150	0	4	70	2	24	4.6	10
	Ni/CS	250	12	13	32	3	40	401[d]	*e*
	Pd/CS	250	17	15	25	2	41	480[d]	*e*
	Pt	100	0	10	52	24	14	21	8
	Pt/CS	250	19	8	40	5	28	492[d]	*e*
3	Ni/CS	200	0	0	43	30	27	30	10
	Ni/CS	250	0	0	51	10	39	99	*e*
	Pd/CS	250	0	0	77	4	19	22	10
	Pt/CS	250	0	0	83	10	7	9.6	10
4	Ni/CS	250	0	0	13	0	87	24	*e*
	Pd/CS	250	0	0	50	0	50	10	*e*
	Pt/CS	250	0	0	18	0	82	1.1	*e*
	Pt/CS	300	0	0	36	0	64	19	*e*

[a] For the notations **5**–**8** see Fig. 2. **9** gives the amount of the gases the compositions of which are detailed in Table 3.

[b] Initial rates of disappearance of cyclic ethers (mole m^{-2} min^{-1} × 10^5).

[c] Products of *a*-type rupture: **5** and **6**. Products of *b*-type rupture: **7** and **8**.

[d] At 250°C the reaction rate is too high for the measurement technique employed to give reaction rate data of the same accuracy as for **3** and **4**; these data are therefore merely of an informatory nature.

[e] The ratio *b*/*a* is not characteristic, for the main transformation is accompanied by formation of **9**.

TABLE 3

Compositions (mole%) of 9[a] Formed in the Transformations of 1, 2, 3, and 4

Compound	Catalyst	Temperature (°C)	CH_4	CO	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
1	Pt	100	0	1	2	97[b]	0	0	0
1	Pt/CS	250	0	38	40	22	0	0	0
1	Ni	150	0	1	3	96[b]	0	0	0
1	Ni/CS	250	3	25	30	42	0	0	0
2	Ni/CS	250	5	42	0	51	2	0	0
2	Pt/CS	250	2	40	6[c]	48[b]	4	0	0
3	Ni/CS	250	42	20	0	7	20	11	0
3	Pt/CS	250	1	39	0	2	35	25	0
4	Ni/CS	250	18	40	0	11	5	13	13
4	Pt/CS	250	10	43	2	11	16	8	10

[a] The composition of 9 refers to the extent of the ruptures $a + b$, $a + c$, $b + d$, and certain secondary processes.

[b] Contains 4% propene.

[c] An approximately 1 : 1 ethane–ethylene mixture.

their lower reactivities, the investigations were subsequently performed on supported catalysts. With a view to a more basic understanding of the processes, the hydrocarbons formed were also analyzed in separate measurements (Table 3).

The experimental data in Tables 2 and 3, in combination with Fig. 2 and Table 4 (compiled on the basis of the earlier tables), permit numerous new conclusions to be drawn.

Treatment of 2-methyloxacycloalkanes with hydrogen in the presence of metals supported on silica leads to products of isomerization as well as of hydrogenolysis. The bond to oxygen which is broken preferentially in the ring-opening reaction depends upon the metal and the ring size.

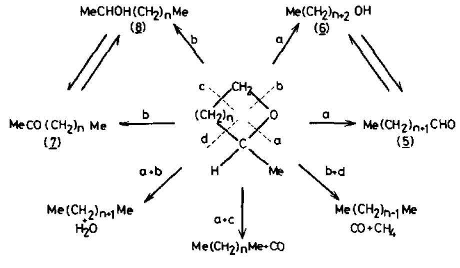

FIG. 2. Reaction directions of transformations of 2-methyloxacycloalkanes on Ni, Pd, and Pt catalysts.

On Pt and Pd catalysts, 2-methyloxacycloalkanes (three- to six-membered cyclic ethers) undergo transformation with high selectivity to products formed by rupture of the bond from oxygen to the least substituted carbon atom (*b*-type cleavage) leading to ketones and secondary alcohols.

This regioselectivity is reversed only by the three-membered cyclic ether (**1**) on the Ni catalyst. Apparently the ketones and secondary alcohols are formed simultaneously.

Although the relative reactivity of the small ringed ethers (**1** and **2**) is uncertain (see Table 4 and footnotes to Table 2) the

TABLE 4

Comparison of Initial rates of Disappearance of 2-Methyloxacycloalkanes (mole m^{-2} min^{-1} × 10^5) Measured at 250°C

Catalyst	1	2	3	4
Ni/CS	723	401	99	24
Pd/CS	331	480	22	10
Pt/CS	258	492	9.6	1.1

reactivity appears to decrease with increasing ring size.

At the lower temperatures, hydrocarbons result mainly from the hydrogenolysis of both C–O bonds, whereas at higher temperatures hydrocarbons which would be formed by the loss of CO or CO plus methane, assume greater importance.

Figure 3 shows the ring size-dependent mechanism of one of the characteristic, main transformations of 2-methyloxacycloalkanes: the formation of ketones and secondary alcohols via *b*-type ring opening.

Our experimental data suggest that processes with a similar mechanism are involved in the cases of the four- to six-membered ring compounds (**2**, **3**, and **4**), whereas alcohols (**6** and **8**) were the main products of the three-membered cycle (**1**), at low temperature; ketones were formed predominantly from the other compounds. This conclusion is also indicated by the difference observed in the case of Ni. The opposite regioselectivity found for the oxacyclopropane (oxirane **1**) on Ni has been attributed to the occurrence of electronic factors (*31*). This phenomenon did not take place with the larger rings, and it may therefore be justifiably assumed that the opposite regioselectivity is connected with the π character of the strained epoxide ring.

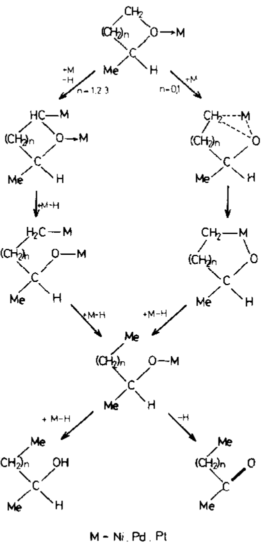

FIG. 3. Mechanism of *b*-type rupture of 2-methyloxacycloalkanes.

The more extensive ketone formation from 2-methyloxacyclobutane (**2**) can be explained by stereochemical reasons (see **II** and **III** in Fig. 1). The above mechanism also supports the assumption that the precursor is the same in the formation of both ketone (**7**) and alcohol (**8**). Rupture of the rings occurs on the action of chemisorbed hydrogen, after dissociative chemisorption of the C–H bond adjacent to the oxygen. The strong effect of steric factors is indicated by the selective splitting of the less sterically hindered bond (*b* rupture). (Nevertheless, in the case of **2** at low temperature it is not possible to exclude the insertion mechanism.)

The presence of the heteroatom in the ring does not lead to an essential change in the geometry of the molecule as compared to the cycloalkanes. At the same time, since the binding begins on the oxygen, the latter atom may be regarded as labeling the molecule, as it were. Thus, it may be expected that future studies on the stereochemistry of the ring opening of oxacycloalkanes will permit the drawing of important conclusions on the behavior of the cycloalkanes too.

This paper summarizes experimental data relating to the rates, regioselectivities, and patterns of the reactions (isomerization, hydrogenolysis) of three-, four-, five-, and six-membered models of 2-methyloxacycloalkanes on some metal catalysts. Studies of these compound types on metal catalysts have not previously been performed under the same experimental conditions, and measurements of their reaction rates have not been reported either.

The experimental work revealed that the selectivity (characterized by b/a) and the reaction rate of the ring-opening reaction due to attack by hydrogen vary as functions of the ring size, the catalyst, and the temperature. Isomerization to ketones and hydrogenolysis to alcohols proceed via the same species. At lower temperatures this common species is desorbed in the form of alcohol and at higher temperatures in the form of ketone.

In subsequent experimental work we wish to obtain further evidence of the new mechanism outlined here. For this purpose, we are now studying the stereochemistry of hydrogenolysis and isomerization of oxacycloalkanes, and are carrying out reaction-kinetic measurements in a circulation system at various H_2/compound and D_2/compound ratios. Important data are expected from adsorption measurements and from ir investigations of the surface complexes.

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