JOURNAL OF CATALYSIS **151**, 315–322 (1995)

Ring-Opening Hydrogenation Reactions of Monoalkyl-Substituted Cyclobutanes over Ni/SiO$_2$ Catalyst

Béla Török and Mihály Bartók[1]

Department of Organic Chemistry, and Center for Catalysis, Surface and Material Science, József Attila University, Dóm tér 8, H-6720 Szeged, Hungary

Received March 25, 1994; revised August 22, 1994

The hydrogenative ring-opening reactions of methyl- and propylcyclobutane were studied over Ni/SiO$_2$ catalyst in wide temperature and hydrogen pressure ranges. Firstly, the temperature dependence of ring opening was determined and maximum curves were observed for both reactants. On the basis of the temperature dependence curves, various temperatures were selected for hydrogen pressure studies. At both 523 and 573 K, only hydrogenative ring opening occurred, and the ring opened mostly in the sterically less hindered direction in the case of methylcyclobutane over clean as well as working catalysts. However, for propylcyclobutane the selectivity was close to statistical or opposite to that for methylcyclobutane, especially at lower hydrogen pressures over the initial catalyst. At the lowest temperature at which ring opening occurred at all, exclusive heptane formation (ring opening in the more hindered direction) was observed. The hydrogen pressure dependence curves over the initial and working catalysts were used to draw mechanistic inferences concerning the ring-opening reactions.

INTRODUCTION

The transformations of cyclopropanes and cyclopentanes (especially methylcyclopentane) over supported and support-free transition metals are model reactions that are widely used to explore the characteristic behaviour of various types of catalysts (1–3). In contrast, only a few publications deal with alkyl-substituted cyclobutanes, including study of the H–D exchange and ring-opening reactions in hydrogen atmosphere. These data have been reviewed (1, 3). We earlier gave an extensive summary concerning the transformations of alkylcyclobutanes over metal catalysts (4, 5). In the present communication, only basic conclusions concerning methyl- and propylcyclobutane and results relating to cyclobutanes and Ni catalysts are summarized briefly as follows:

(i) Gault and co-workers investigated the regioselectivity and kinetics of ring-opening and H–D exchange reactions (6, 7) of methylcyclobutane over Pt, Pd, and Ni catalysts. Zimmermann and Hayek studied the hydrogenative ring opening of methylcyclobutane over supported platinum model catalysts (8).

All authors agree that the sterically less hindered ring scission predominates and that the cyclobutane ring adsorbs reversibly at low temperatures and partly irreversibly at elevated temperatures.

(ii) New results were published recently on the transformations of propylcyclobutane over Pt/SiO$_2$ catalyst. Hydrogenative ring opening (4, 5), ring enlargement and aromatization (9), and the role of surface carbonaceous deposits as selectivity-influencing species were investigated (10). Propylcyclobutane was found to exhibit opposite regioselectivity in ring opening to those for all substituted cyclobutanes studied, yielding mainly heptane via cleavage of the sterically more hindered C–C bond.

(iii) Only sporadic results are to be found concerning the hydrogenolysis of methyl- and 1,2-dimethylcyclobutanes (6, 7b, 11) and H–D exchange reactions of methyl- and ethylcyclobutane (6, 12) over Ni catalysts. It seems that nickel is not frequently used in catalytic transformations of alkylcyclobutanes in contrast with cyclopropanes and methylcyclopentanes. Data related to cyclopropanes (13) and methylcyclopentanes (14) were collected earlier. It was concluded that nickel induced extensive cracking and preferred a sterically less hindered ring opening.

The lack of relevant data to cyclobutanes prompted the present work with the aim of a better understanding of the characteristics of Ni-catalyzed cyclobutane reactions. We report the effects of temperature and hydrogen pressure on the hydrogenative ring opening of methyl- and propylcyclobutane over Ni/SiO$_2$ catalyst. The construction and comparison of hydrogen pressure dependence curves, a method proven to help determine the type of adsorption mechanisms of ring opening of cycloalkanes, are applied in the present study.

---

[1] To whom correspondence should be addressed.

0021-9517/95 $6.00

EXPERIMENTAL

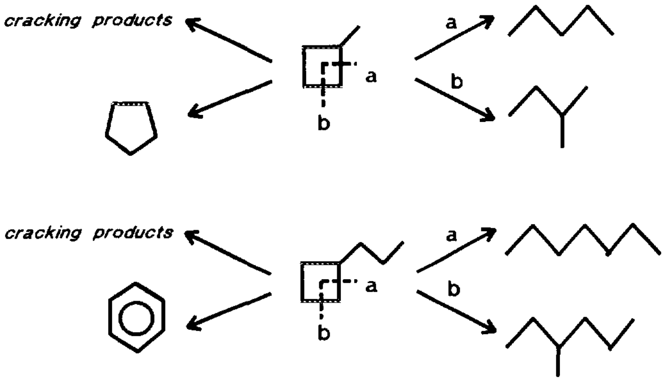
Methylcyclobutane was prepared by a recently published method (15), while propylcyclobutane was kindly donated by the Bragin Laboratory of the Zelinskii Institute (Moscow). They were gas chromatographically pure and were used without further purification except for a couple of freeze–evacuate–thaw cycles immediately before preparation of the reaction mixture.

A 3.0% Ni/SiO_2 catalyst was made by impregnating a Cab-O-Sil M5 support (BDH product) with an aqueous solution of $Ni(NO_3)_2$ in the presence of aqueous NH_4OH. A high-temperature reduction (flowing hydrogen, 773 K, 16 h) ensured the complete elimination of Ni ions (16). After the initial reduction the catalyst was kept in a closed vial in a vacuum desiccator, separately from the place where the reactions were run. The dispersion value of the catalyst (exposed Ni atoms) was determined (6.8%) by hydrogen chemisorption at room temperature in a pulse system (17).

Before kinetic measurements, the catalyst was activated in 26.6 kPa H_2 at 673 K for 1 h. The system was then cooled to the reaction temperature.

Reactions were performed in a conventional closed circulation apparatus (for more details, see (18)). A Carlo Erba Fractovap 2150 gas chromatograph with a flame ionization detector was attached to the system. A 4-m-long 20% squalane/Chromosorb PAW was used for analysis. A mixture of 1.33 kPa hydrocarbon and various amounts of hydrogen (except for the temperature dependence, where 19.9 kPa H_2 was always used) were premixed in the circulation part of the system before reaction.

At a certain hydrogen pressure, the product yield vs time (t) functions were always determined over a fresh sample of catalyst (10 mg). Measurements were reproducible within 10%. Both initial and steady-state rates were determined. These rates were converted to turnover frequency (TOF, molecule exp. $atom^{-1}$ s^{-1}) data on the basis of exposed Ni atoms.



SCHEME 1. Reaction pathways in the transformations of methyl- and propylcyclobutane over a Ni/SiO_2 catalyst.

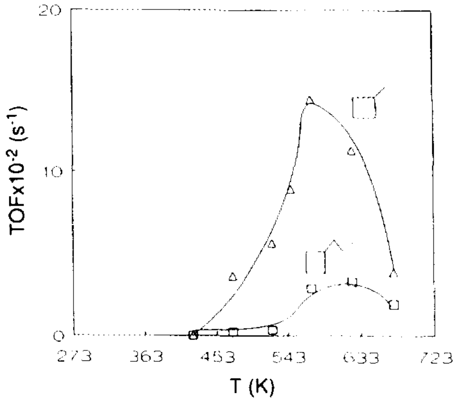


FIG. 1. Turnover frequency of product formation vs temperature curves over the initial surface at 19.9 kPa hydrogen pressure.

RESULTS AND DISCUSSION

Temperature Dependence of Transformations, Especially the Ring-Opening Reactions

It is known that different types of transformations may occur in transition metal-catalyzed reactions of cyclic hydrocarbons, such as hydrogenative ring opening, hydrogenolysis (cracking), isomerization, and aromatization. These transformations were observed in the present study, although the selectivity depended strongly on the reactants and temperature. The reactions which occurred with both reactants were the hydrogenative ring opening and cracking. Ring enlargement also proceeded, leading to different products. Cyclopentane was formed from methylcyclobutane, while propylcyclobutane ring enlargement was followed by aromatization and subsequent cracking, producing benzene exclusively (Scheme 1).

We concentrated on hydrogenative ring opening, the main reaction at most temperatures for both reactants, which gave exclusively saturated hydrocarbons at each temperature, in accordance with the results when supported Ni catalyst prereduced at high temperature was used (13). Experimental results show that the total ring-opening rate vs temperature curves pass through a maximum (Fig. 1).

Besides the activity, the distribution of various reaction pathways and the regioselectivity of the ring opening are important factors in investigation of the temperature dependence. These results are given in Table 1.

These experimental findings can be interpreted as follows. It is well known that the temperature affects both activity and selectivity in metal-catalyzed hydrocarbon reactions. It can regulate the hydrogen coverage of the

TABLE 1

Distribution of Reaction Pathways and the Selectivity of the Ring-Opening Reaction of Cyclobutane Derivatives at Different Temperatures (1.33 kPa Hydrocarbon, 19.9 kPa Hydrogen, 5 min Sampling Time)

		Selectivity (%)				
Compound	T (K)	Cracking	Ring opening[a]	Aromatization[b]	Ring enlargement[c]	S[d]
Methylcyclobutane	473	—	100	—	—	0.64
	523	—	100	—	—	0.59
	548	—	100	—	—	0.62
	573	1	99	—	—	0.56
	623	16	83	—	1	0.61
	673	50	46	—	4	0.51
Propylcyclobutane	473	—	100	—	—	0
	523	—	100	—	—	0.32
	573	38	62	—	—	0.30
	623	57	40	3	—	0.39
	673	68	21	11	—	0.31

[a] Both ring-opened products.

[b] Benzene.

[c] Cyclopentane.

[d] Selectivity of the ring-opening reaction. $S = r_b(r_b + r_a)$, see Scheme 1.

surface, the extent of coking, and the hydrogen content of the carbonaceous deposits. It is also known that a clean metal surface is necessary for ring-opening reactions of cyclic hydrocarbons such as cyclopropanes (19) and methylcyclopentane (20) to occur, and elevation of the temperature makes the catalyst surface quite complex, generating carbonaceous material on metal crystallites. Thus, the maximum curve observed for the temperature dependence of the ring-opening reaction is to be expected, since coking decreases the clean metal surface at higher temperatures. This type of temperature dependence is usually observed in the ring opening of alkylcyclobutanes (4, 21).

Side reactions such as ring enlargement and aromatization have minor importance. These reactions have been extensively studied for propylcyclobutane over a Pt/SiO_2 catalyst (9). However, the formation of toluene as aromatic product (with the same carbon number as propylcyclobutane) is not observed at all over a Ni/SiO_2 catalyst. Instead, benzene is formed, probably via loss of the methyl group from the adsorbed precursor of toluene. The other possibility, which is toluene readsorption and loss of the methyl group in this adsorbed state, can be excluded on the basis of the complete absence of toluene among the products.

The formation of cyclopentane, as the sole ring enlargement product of methylcyclobutane, can be interpreted on the basis of the general ring enlargement mechanism for cyclic hydrocarbons (2), which assumes an adsorbed C_5 cyclic intermediate in ring enlargement reactions. Under these relatively mild conditions, products of homologization reactions cannot be observed.

Hydrogen Pressure Dependence of Hydrogenative Ring-Opening Reactions

On the basis of the experimental findings various temperatures were selected for hydrogen pressure studies: 523 and 573 K for methylcyclobutane and 523 K for propylcyclobutane. The main reasons for this selection were that 523 K was convenient for kinetic measurements of ring opening for both reactants, while for methylcyclobutane the highest ring opening rate with negligible side reactions occurred at 573 K. The ring opening of propylcyclobutane could not be studied at 573 K due to side reactions.

The hydrogen pressure dependence studies were performed in the hydrogen pressure range 0–60 kPa. Typical product yield vs time curves can be seen in Fig. 2.

From these curves both initial and steady-state rates were determined when possible. One is from the initial rates (first linear part), while the other is from the second linear part, which were thought to be characteristic for the clean and the working catalyst, respectively (for more details, see Refs. (4, 21)).

Exclusive ring opening occurred at 523 K, whereas

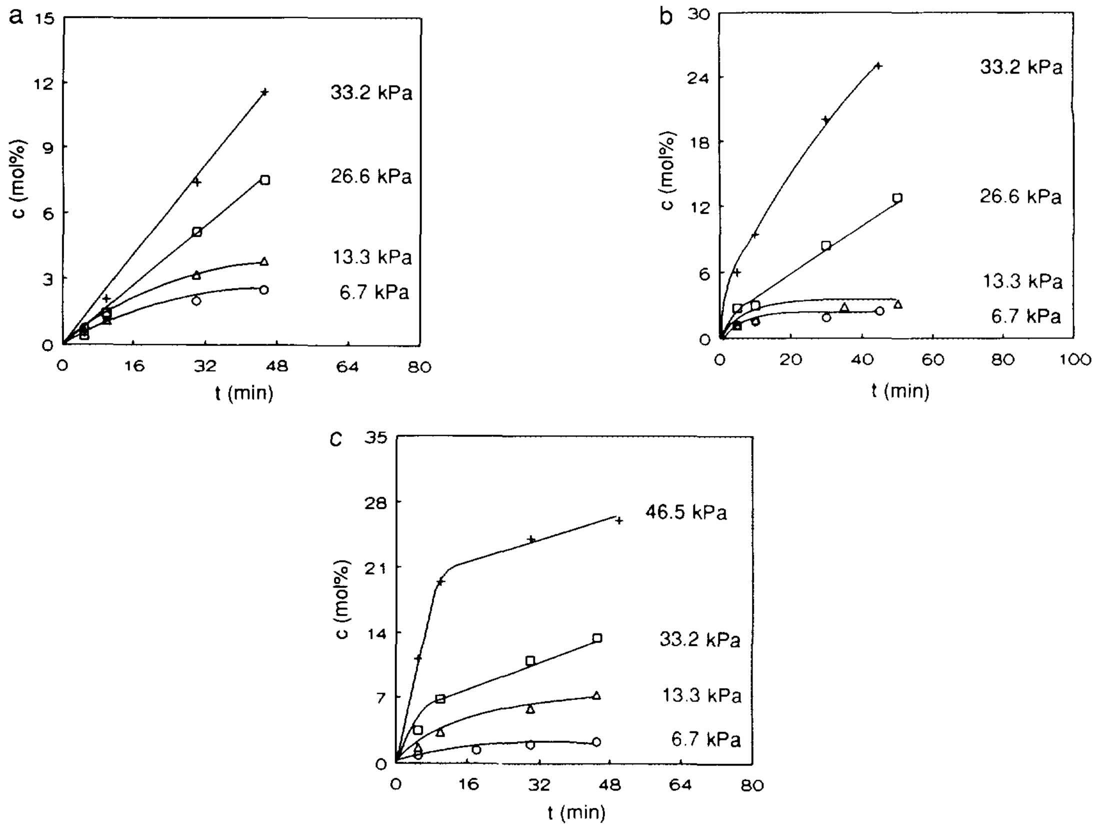


FIG. 2. Product yield vs time curves in the ring-opening reactions of methyl- and propylcyclobutane over Ni/SiO_2 catalyst at (a) isopentane (from methylcyclobutane), 523 K; (b) heptane (from propylcyclobutane), 523 K; (c) isopentane (from methylcyclobutane), 573 K.

cracking products were observed to some extent at 573 K (Table 1). In general, two types of H_2 pressure dependence curves were observed over the initial catalyst (Fig. 3).

At 523 K, the curve exhibited a maximum for both compounds, while at 573 K the curve increased monotonically in the lower hydrogen pressure range and displayed saturation character at higher hydrogen pressures in the pressure range studied.

The unsaturated character of the adsorbed species can be deduced from the shapes of these curves. This topic has been discussed extensively in previous papers (4, 22, 23) and a recent book (24); here, those results are used only to interpret hydrogen pressure dependence curves.

The initial ring-opening rate (expressed as TOF) vs H_2 pressure functions at 523 K describe a curve with a maximum for both reactants (Figs. 3a, 3b). These maximum curves may reflect the inhibition of C–H rupture in surface species; thus dissociative adsorption is also suggested for both compounds. However, this shape does not exclude the hydrogen excess simply being large enough to remove any reacting intermediates from the surface (Langmuir–Hinshelwood mechanism).

It may also be clear that nondissociative adsorption takes place at 573 K, since there is a monotonic increase in the hydrogen pressure functions in the hydrogen pressure range studied (Fig. 3c). Gault and co-workers reported that the adsorption becomes largely irreversible as the temperature is elevated, and the competitive adsorption changes to noncompetitive. Thus, since the hydrocarbon adsorbs more strongly, excess hydrogen cannot remove it from the surface. Therefore, the only role of hydrogen remains to be reactant for hydrogenation.

After the initial catalysts, we can analyze the TOF vs H_2 pressure functions determined over the working catalysts (Fig. 4).

As described earlier (4, 21), these curves were constructed from the steady-state part of the product yield vs time functions.

The formation of surface carbonaceous deposits in catalytic hydrocarbon reactions is a well-known fact. Many results are to be found on the formation and effects of the carbonaceous overlayer (25). The continuous formation of different types of surface carbonaceous deposits in the transformation of propylcyclobutane has also been observed (10). However, our previous results show that at

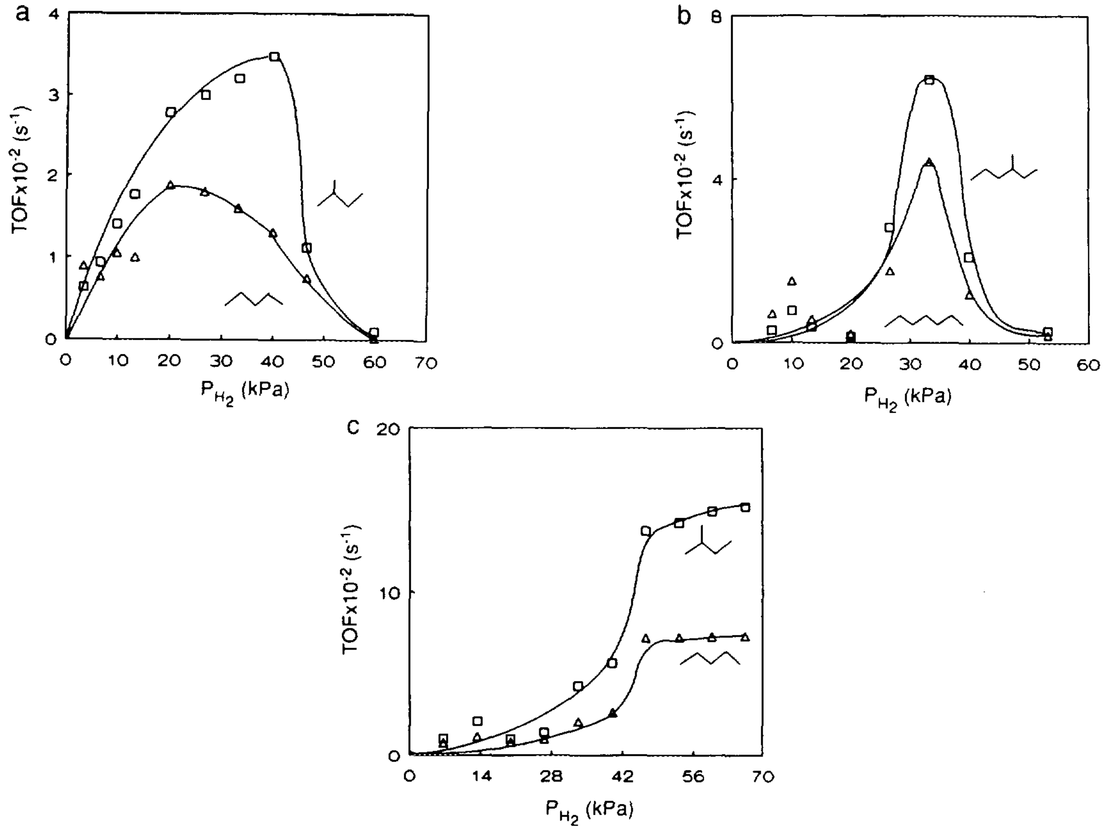


FIG. 3. Turnover frequency of product formation vs hydrogen pressure curves over the initial catalyst at (a) methylcyclobutane, 523 K (□, isopentane; △, pentane); (b) propylcyclobutane, 523 K (□, 3-methylhexane; △, heptane); (c) methylcyclobutane, 573 K (□, isopentane; △, pentane).

lower temperatures, or especially at lower reaction rates, the building up of a carbonaceous overlayer is very slow, and thus the formation of a working catalyst is not necessarily observed. This is precisely what was found here at 523 K. The working surface did not exhibit significant differences from the initial one at low reaction rates. The shape of the H_2 pressure dependence curves of the working catalyst was very similar to that of the curves obtained over the initial catalysts for both reactants (Figs. 4a, 4b), in agreement with product accumulation curves where the two parts can hardly be distinguished. Thus, it can be deduced that the adsorption over the working catalyst did not change significantly, i.e., dissociative adsorption was the main type. A simple Langmuir–Hinshelwood mechanism, however, cannot be excluded. In contrast, at higher temperature (or activity) for methylcyclobutane the working catalyst differed appreciably, as is clearly shown by the shape of the product yield vs time curves (Fig. 2c); the two parts of these curves can easily be separated. Hydrogen pressure dependence curves (Fig. 4c) also show this difference. A large maximum is now observed, indicating that the adsorbed species are very different from those initially formed. This means that the nondissociative adsorption has become dissociative or that the large excess of hydrogen simply sweeps the reacting species from the metal surface.

Selectivities of Ring-Opening Reactions

The hydrogen pressure dependence curves permit a quick conclusion; nevertheless ring-opening selectivities yield additional information concerning the mechanisms of the ring-opening reactions. Selectivity data are shown in Table 2.

These data are in agreement with the results mentioned in the introduction, but there are significant differences between the two reactants. Although methylcyclobutane opens in both positions, good selectivity is exhibited in the sterically less hindered position. In contrast, the selectivity is close to statistical for propylcyclobutane, or even selectivity to the more hindered position is observed, especially over the initial catalyst. This is in accordance with our previous findings on this topic (4, 5). A comparison of the ring-opening selectivities of methyl-

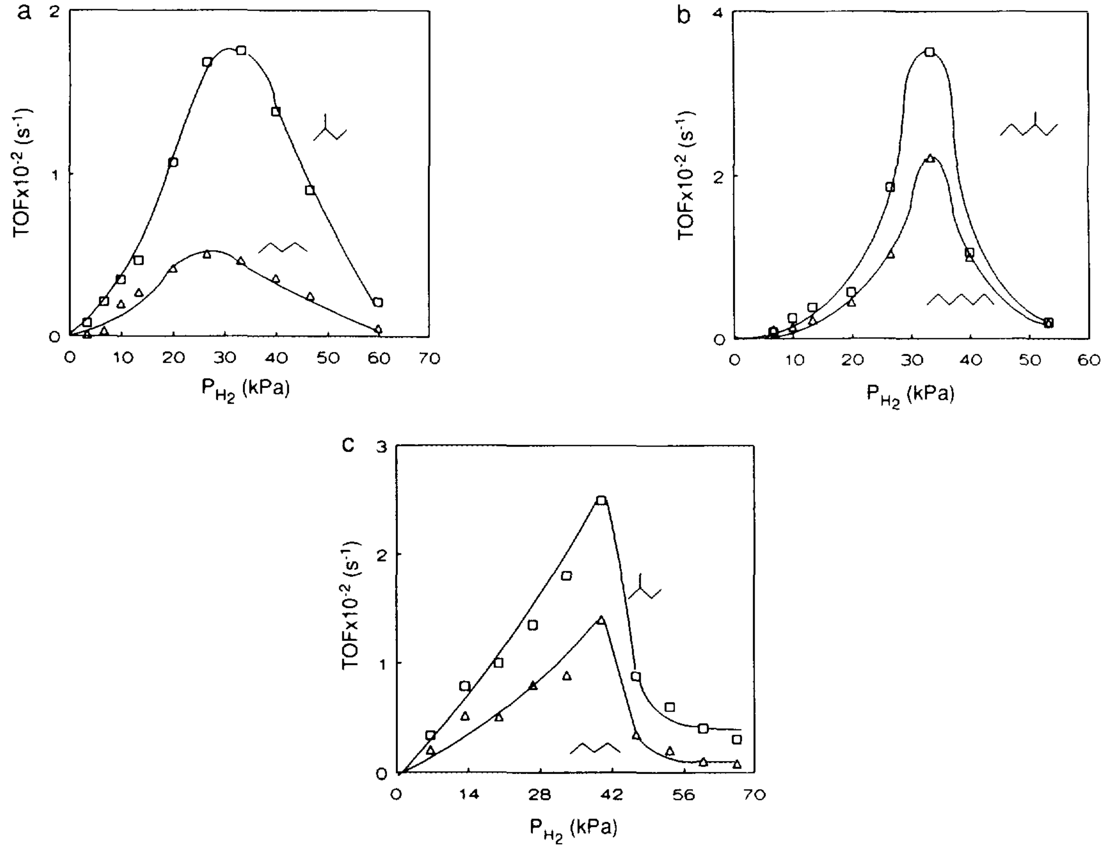


FIG. 4. Turnover frequency of product formation vs hydrogen pressure curves over the working catalyst at (a) methylcyclobutane, 523 K (□, isopentane; △, pentane); (b) propylcyclobutane, 523 K (□, 3-methylhexane; △, heptane); (c) methylcyclobutane, 573 K (□, isopentane; △, pentane).

TABLE 2

Selectivity of the Ring-Opening Reaction

p_{H_2} (kPa)	Methylcyclobutane 523 K *a*	Methylcyclobutane 523 K *b*	Methylcyclobutane 573 K *a*	Methylcyclobutane 573 K *b*	Propylcyclobutane 523 K *c*	Propylcyclobutane 523 K *d*
3.3	0.43	0.95	—	—	—	—
6.6	0.55	0.87	0.57	0.55	0.31	0.41
9.9	0.57	0.57	—	—	0.32	0.74
13.3	0.62	0.63	0.65	0.60	0.36	0.63
19.9	0.59	0.66	0.53	0.62	0.32	0.54
26.6	0.60	0.72	0.55	0.57	0.54	0.59
33.2	0.72	0.76	0.68	0.64	0.56	0.61
39.9	0.76	0.76	0.69	0.65	0.54	0.51
46.6	0.68	0.77	0.66	0.71	—	—
53.2	—	—	0.65	0.72	0.52	0.50
59.8	0.72	0.78	0.67	0.66	—	—
66.5	—	—	0.66	0.71	—	—

Note. $a = r_{\text{initial,isopentane}}/(r_{\text{initial,isopentane}} + r_{\text{initial,pentane}})$; $b = r_{\text{working,isopentane}}/(r_{\text{working,isopentane}} + r_{\text{working,pentane}})$; $c = r_{\text{initial,3-methylhexane}}/(r_{\text{initial,3-methylhexane}} + r_{\text{initial,heptane}})$; $d = r_{\text{working,3-methylhexane}}/(r_{\text{working,3-methylhexane}} + r_{\text{working,heptane}})$.

and propylcyclobutane shows that there is a difference between the adsorbed species of the reactants. It is clear that the results observed cannot be explained by a single mechanism for both compounds and all temperatures. At 523 K, dissociatively adsorbed species predominate for both reactants over clean and working catalysts. Since the selectivities are good for methylcyclobutane in the sterically less hindered direction, a 2,3 C–C bonded, edge-on species is suggested as the major adsorbed intermediate. The minor product (pentane) is probably formed through either 1,2 C–C bonded intermediate. In contrast, the selectivity is close to statistical for propylcyclobutane, and the sterically more hindered ring scission is the major ring-opening route at low H_2 pressures (0–20 kPa). Our recent results (4, 5 10) led to the proposal of side-chain bonded adsorbed intermediates for propylcyclobutane. This anchoring effect is probably also the basis of the interpretation of the selectivity differences. A side-chain bonded edge-on species exists probably over the initial catalyst in the low hydrogen pressure range (0–20 kPa) proposed by good selectivities in the sterically more hindered position. The geometry changes as the H_2

pressure increases; propylcyclobutane lies to the surface and anchoring disappears. This flat-lying species provides very similar opportunities for both 1, 2 and 2, 3 C–C bond rupture as selectivities show. The working catalyst does not differ to a large extent from the initial one at this temperature; a dissociatively adsorbed simple flat-lying complex is proposed over working catalyst.

At 573 K the picture is significantly changed. First, the reaction rate vs H_2 pressure function determined over the initial catalyst suggests a noncompetitive adsorption between the hydrocarbon and hydrogen. The adsorption of methylcyclobutane is probably irreversible to a large extent; the hydrogen cannot remove it from the surface and affects the ring-opening reaction practically only as a reactant. The selectivity is similar to that at 523 K, and thus the same edge-on adsorption geometry is suggested for the adsorbed intermediates. In contrast with the situation at 523 K, at 573 K the working catalyst differs from the initial one, in agreement with our earlier findings (4, 21). H_2 pressure functions and selectivity data allow the proposal of a dissociatively adsorbed edge-on species since the selectivities are good in the sterically less hindered position and they are nearly identical in the whole hydrogen pressure range applied.

CONCLUSIONS

The transformations, especially the ring-opening reactions of substituted cyclobutanes over a Ni/SiO_2 catalyst, have been studied in hydrogen atmosphere. Ring opening was found to be the main reaction pathway at most temperatures. At higher temperatures, cracking, ring enlargement, and aromatization occurred as side reactions. Cyclopentane was formed from methylcyclobutane, and benzene from propylcyclobutane.

Analysis of the shapes of turnover frequency vs H_2 pressure functions and geometrical considerations permits conclusions concerning the intermediates of the transformations. Over the initial as well as the working catalysts dissociatively adsorbed species characterize the ring opening of both reactants at 523 K. Edge-on intermediates are formed from methylcyclobutane, while propylcyclobutane reacts via a side-chain anchored edge-on (0–20 kPa H_2), flat-lying complex over the initial catalyst and via flat-lying intermediates over the working catalyst. At 573 K methylcyclobutane adsorbs probably nondissociatively over the initial catalyst, in contrast with the working catalyst, where dissociative adsorption occurs. On the basis of the selectivity data edge-on intermediates are suggested for both types of catalysts.

ACKNOWLEDGMENTS

We acknowledge the financial support provided for this research by the Hungarian National Science Foundation through Grant OTKA 1885/1991. Thanks are due to the Foundation for Hungarian Science for Research Fellowship (B. T.) (Grant 43/94/I). We also thank Professor Árpád Molnár and Dr. István Pálinkó for valuable discussions.

REFERENCES

1. Newham, J., *Chem. Rev.* **63,** 123 (1963).
2. Paál, Z., and Tétényi, P., *in* "Specialist Periodical Reports on Catalysis," Vol. 5, p. 80. The Royal Society of Chemistry, London, 1982; Paál, Z., *Adv. Catal.* **29,** 273 (1980); Gault, F. G., *Adv. Catal.* **30,** 1 (1981).
3. Bartók. M., and Zsigmond, Á. G., *in* "Stereochemistry of Heterogeneous Metal Catalysis," p. 17. Wiley, Chichester, 1985.
4. Török, B., Pálinkó, I., Molnár, Á., and Bartók, M., *J. Catal.* **143,** 111 (1993).
5. Bartók. M., Török, B., Molnár, Á., and Apjok, J., *React. Kinet. Catal. Lett.* **49,** 111 (1993).
6. Maire, G., Plouidy, G., Prudhomme, J. C., and Gault, F. G., *J. Catal.* **4,** 556 (1965).
7. (a) Hilaire, L. H., Maire, G., and Gault, F. G., *Bull. Soc. Chim. Fr.*, 886 (1967); (b) Maire, G., and Gault, F. G., *Bull. Soc. Chim. Fr.*, 894 (1967).
8. Zimmerman, C., and Hayek, K., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), p. 319. Akadémiai Kiadó, Budapest, 1993.
9. Török, B., Pálinkó, I., Molnár, Á., and Bartók, M., *J. Mol. Catal.* **91,** 61 (1994).
10. Török, B., Molnár, Á., Pálinkó, I., and Bartók, M., *J. Catal.* **145,** 295 (1994).
11. Willstatter, R., and Bruce, J., *Ber.* **40,** 3979 (1907).
12. Rosanov, N. A., *J. Russ. Phys-Chem. Soc.* **61,** 2291 (1929); Rowlinson, H. C., Burwell, R. L., Jr., and Tuxworth, R. H., *J. Phys. Chem.* **59,** 255 (1955).
13. Pálinkó, I., Notheisz, F., and Bartók, M., *J. Mol. Catal.* **68,** 237 (1991).
14. Roberti, A., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **28,** 381 (1973); Miki, Y., Yamadaya, S., and Oba, M., *J. Catal.* **49,** 278 (1977); Paál, Z., and Tétényi, P., *Nature* **267,** 234 (1977).
15. Török, B., and Molnár, Á., *J. Chem. Soc., Perkin Trans. 1,* 801 (1993).
16. Boudart, M., and Cheng, W. C., *J. Catal.* **106,** 134 (1987).
17. Notheisz, F., Zsigmond, Á. G., and Bartók, M., *J. Chromatogr.* **241,** 101 (1982).
18. Bartók, M., Notheisz, F., Zsigmond, Á. G., and Smith, G. V., *J. Catal.* **100,** 39 (1986); Pálinkó, I., Molnár, Á., Kiss, J. T., and Bartók. M., *J. Catal.* **121,** 396 (1990).
19. Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **50,** 494 (1977); Hattori, T., and Burwell, R. L., Jr., *J. Chem. Soc., Chem. Commun.*, 127 (1978); Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **53,** 414 (1978); Wong, S. S., Otero-Schipper, P. H., Wachter, W. A., Inoue, Y., Kobayashi, M., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **64,** 84 (1980); Pitchai, R., Wong, S. S., Takahashi, N., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **94,** 478 (1985); Karpinski, Z., Chuang, T.-K., Katsuzawa, H., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **99,** 184 (1986).
20. Zaera, F., Godbey, D., and Somorjai, G. A., *J. Catal.* **101,** 73 (1986); Zaera, F., Gellman, A. J., and Somorjai, G. A., *Acc. Chem. Res.* **19,** 24 (1986).
21. Török, B., Török, M., and Bartók, M., submitted for publication.
22. Pálinkó, I., Kiss, J. T., Notheisz, F., and Bartók, M., *J. Mol. Canal.* **77,** 313 (1992).

23. Pálinkó, I., Notheisz, F., and Bartók, M., *J. Mol. Catal.* **63**, 43 (1990); Notheisz, F., Pálinkó, I., and Bartók, M., *Catal. Lett.* **5**, 229 (1990).
24. Paál, Z., and Menon, P. G. (Eds.), "Hydrogen Effects in Catalysis." Dekker, New York/Basel, 1988.
25. Somorjai, G. A., "Chemistry in Two Dimensions: Surfaces." Cornell Univ. Press, Ithaca, NY, 1981; Somorjai, G. A., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 1, p. 113, and references 22 and 23 therein. Dechema, Frankfurt-am-Main, 1984; Sárkány, A., *J. Chem. Soc., Faraday Trans.* **84,** 2267 (1988); Pálinkó, I., Notheisz, F., and Bartók, M., *Catal. Lett.* **1,** 127 (1988).