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Hydrogen Pressure Dependence of the Ring-Opening Reactions of Propylcyclobutane over Pt/SiO$_2$ Catalyst at Different Temperatures

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The hydrogen pressure dependence of the ring-opening reactions of propylcyclobutane was studied at three different temperatures over Pt/SiO$_2$ catalyst. At 373 and 573 K, only hydrogenative ring opening occurs, while appreciable amounts of aromatics, ring enlargement, and cracking products are formed at 673 K. At 373 K, the ring opens selectively in the sterically more hindered direction over both the clean and the working catalyst, yielding heptane as the major product. The selectivity is lost at 573 K and 673 K: 2,3 C–C bond scission, i.e., formation of 3-methylhexane occurs with initial rates comparable to that of 1,2 C–C bond scission. Over the working catalyst, the selectivity is close to statistical, with a slight excess of 3-methylhexane. An increase of hydrogen pressure has different effects on the ring-opening reactions, depending on the reaction temperature. The initial rate of product formation vs hydrogen pressure curves exhibit three extremes at 373 K, but they increase monotonously at 573 and 673 K. Over the working catalyst, the hydrogen pressure dependence curves display three extremes at 373 K, pass through a maximum at 573 K, and increase monotonously at 673 K. Mechanisms over both the initial and working catalysts are discussed on the basis of regioselectivity data and hydrogen pressure dependence curves.

INTRODUCTION

The transition-metal-catalyzed reactions of cyclic hydrocarbons in hydrogen atmosphere provide the possibility of studying reactions occurring simultaneously. Several different types of transformations may take place, such as cracking (hydrogenolysis), hydrogenative ring opening, isomerization, aromatization, and ring enlargement (*1–3*). The actually occurring transformations depend on numerous factors, perhaps most importantly on the transition metal and temperature. For instance, over platinum, cracking reactions and isomerization leading to olefins do not occur up to high temperatures. Over nickel, however, these two types of reactions can be very significant.

The transformations of alkyl-substituted cyclobutanes over metal catalysts do not belong among the frequently studied reactions. Merely a few communications concern their H–D exchange (*4–7*) and ring-opening reactions in hydrogen atmosphere (*8–14*). The main observations are mentioned only briefly in one older (*2*) and a more recent review (*3*). Two groups have mainly been involved in the investigations. The Russian group mostly used a pulse microreactor with injection techniques (*7, 11–13*) and obtained only qualitative information about the products. Gault and his co-workers were able to study the regioselectivity and the kinetics of the ring opening (*9*) as well as those of the H–D exchange reactions (*4*). Both groups concluded that the ring opens mostly, if not exclusively in the sterically less hindered direction over a highly dispersed catalyst (selective mechanism). Furthermore, Gault *et al.* determined through H–D exchange reactions that over the catalysts the ring adsorbs reversibly at

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low, and partly irreversibly at elevated temperatures.

A third group, that of Paál *et al.*, studied the hydrogenative ring-opening reactions of five-membered hydrocarbon rings, and incidentally those of ethylcyclobutane as well (*10*).

In the present study, we report the effects of hydrogen pressure and temperature on the rate and selectivity of ring opening of propylcyclobutane over Pt/SiO_2 catalyst. The emphasis is placed on hydrogenative ring opening, which leads to saturated hydrocarbons. Side-reactions occurring at high temperature (673 K) will be discussed elsewhere. At low temperatures (lower than 623 K), only hydrogenative ring opening occurs, and thus the picture is simplified to a large extent. Nevertheless, in principle two ring-opening routes remain, which allow the study of ring-opening selectivities as well.

EXPERIMENTAL

Propylcyclobutane was kindly donated by Dr. J. Apjok. It was gas chromatographically pure and was used without further purification, except for a couple of freeze–evacuate–thaw cycles immediately before preparation of the reaction mixture.

A 3% Pt/SiO_2 catalyst was made by impregnating a Cab-O-Sil M5 support (BDH) with H_2PtCl_6 solution, followed by reduction in flowing hydrogen at 773 K for 16 hours (*15*). The high-temperature hydrogen treatment diminishes the chlorine content of the catalyst, as revealed by X-ray fluorescence spectroscopy (the quantity of residual chlorine is negligible; it is less than 10 ppm relative to Pt loading); for details, see (*16, 17*).

The dispersion of the catalyst (no. of exposed Pt atoms/total no. of Pt atoms) was determined by H_2 chemisorption in a pulse system at room temperature, assuming 1 : 1 adsorption stoichiometry. The dispersion value obtained (11.8%) was checked by O_2–H_2 titration at the same temperature and by electron microscopy with a Hitachi H500H transmission electron microscope (the particle size is 8.8 nm which corresponds to a dispersion of 11.5%).

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. Before kinetic measurements, the catalyst samples were activated in the following manner: the reactor (with the catalyst) was evacuated and the catalyst sample was treated with 26.6 kPa of H_2 at 473 K for 0.5 h. The system was then cooled or heated to the reaction temperature.

The reactions were carried out in a conventional closed circulation reactor (for more details, see (*18, 19*). A Carlo Erba Fractovap 2150 gas chromatograph with a flame ionization detector was attached to the system. Either a 4-m- or a 3.6-m-long glass column filled with 5% bis(methoxyethyl)-adipate/Chromosorb PAW or 20% squalane/Chromosorb PAW, respectively, was used for analysis.

The reactants (1.33 kPa of propylcyclobutane and different amounts of hydrogen) were premixed in the circulation part of the system before the 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 the number of exposed Pt atoms, determined by H_2 titration.

RESULTS AND DISCUSSION

As already mentioned, propylcyclobutane may, in principle undergo several types of reactions simultaneously and/or sequentially, such as hydrogenative ring opening, isomerization, cracking, ring enlargement, and aromatization.

Our experimental results show that only hydrogenative ring opening takes place at 373 and 573 K. At 673 K, however, cracking (hydrogenolysis) products appear and ring enlargement and aromatization also occur, producing methylcyclohexane and aromatics (benzene and toluene), respectively. These reactions can be identified from 623 K. More details concerning temperature dependence, self-poisoning effects, cracking, ring enlargement, and aromatization will be published elsewhere (*20*).

Effects of Hydrogen Pressure on the Hydrogenative Ring-Opening Reactions

The hydrogen pressure dependence was studied at three different temperatures: 373, 573, and 673 K. Typical product yield vs time curves are seen in Fig. 1. A comparison of these curves clearly shows that there are significant differences in their shapes. At 373 K, for instance, the curve is almost linear, i.e., the initial and steady-state parts can hardly be distinguished. At 673 K, however, the two parts can easily be separated. The curves at 573 K resemble those at 673 K.

From these products accumulation vs. time curves, two types of product formation rate vs hydrogen pressure functions were constructed. One is from the initial rates (first linear part) thought to be characteristic of the reaction of the compound over the clean surface, while the other is from the second linear part thought to be characteristic of the working catalyst.

Let us consider first the initial rate of product formation vs hydrogen pressure dependence curves (Fig. 2). As a function of temperature, two types of hydrogen pressure dependence curves can be distinguished. At 373 K, the curve has three extremes (two maxima and a minimum), while at 573 and 673 K, the curves change monotonously in the hydrogen pressure range applied.

The question arises as to whether any information concerning the structure of the initially formed adsorbed intermediates can be deduced from the shapes of these curves. In our previous papers (*17, 21*) and also in a recent book (edited by Paál and Menon) (*22*), this topic is treated extensively; here, only the basic points are repeated. When the compound to be transformed in hydrogen atmosphere is adsorbed over the surface equally as or less strongly than hydrogen, the excess hydrogen will sweep the adsorbed intermediates off the surface: the product formation rate passes through a maximum as the hydrogen pressure rises (Langmuir–Hinshelwood mechanism). When the compound adsorbs entirely or largely irreversibly, then the competition is lost for hydrogen and the adsorbed hydrogen may now regulate the hydrogen content of the adsorbed species. If the surface intermediates are formed through C–H bond rupture, then there may be an optimal hydrogen concentration for maximizing the turnover of dissociatively adsorbed species. As the hydrogen pressure is further increased, C–H bond fission is inhibited, i.e., curves with one or more extremes are expected. When no C–H bond scission occurs and the ring opens only through the rupture of C–C bond(s), the hydrogen pressure does not affect the relative abundance of these associatively adsorbed species, i.e., monotonously increasing or saturation-type curves are obtained.

One would expect a maximum curve (reflecting a Langmuir–Hinshelwood mechanism) for the product accumulation rate vs hydrogen pressure function from the ring opening of propylcyclobutane over Pt/SiO_2, since H–D exchange studies revealed that 1,2-dimethylcyclobutanes adsorb reversibly over, e.g., platinum (*6*). However, it is also known that the adsorption becomes increasingly irreversible as the temperature is raised. For our model compound, the two maxima in the hydrogen pressure curve reveal that a simple Langmuir–Hinshelwood mechanism does not operate; the adsorption is certainly irreversible to some extent and hydrogen regulates the hydrogen content of the surface species. This is undoubtedly true for the first maximum, since the formation of these, possibly dissociatively adsorbed surface species is only suppressed and, as the hydrogen pressure is increased further, new types of reaction intermediates appear.

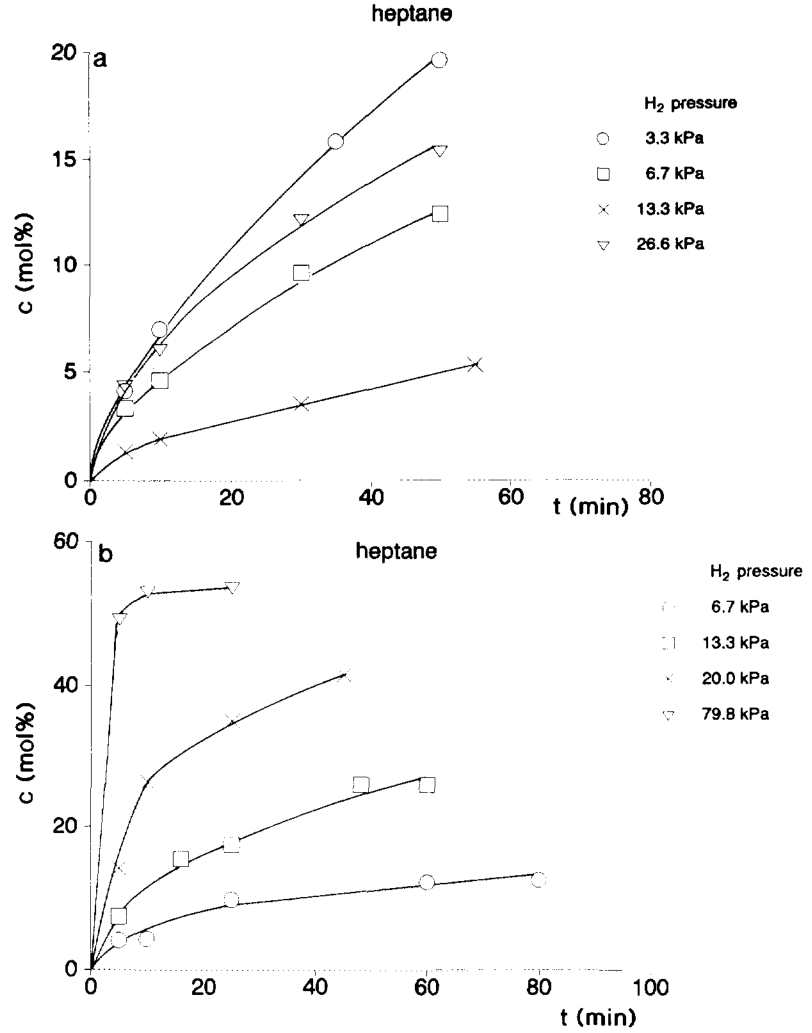


FIG. 1. Product yield vs time curves of 1,2 C–C bond scission at (a) 373 K, (b) 573 K, and (c) 673 K.

Another decrease in rate at elevated hydrogen pressures may reflect the inhibition of C–H bond rupture in another, less unsaturated surface intermediate, or simply the hydrogen excess is now large enough to remove any kind of reacting species from the surface.

As the temperature is raised, the adsorption becomes irreversible to a large extent, since a monotonous increase in the hydrogen pressure functions can be observed. These curves indicate that, at least initially, only C–C bond scission, i.e., associative adsorption, occurs.

Let us now analyze the hydrogen pressure curves constructed from the second part of the product yield vs time functions (Fig. 3). As already mentioned, these rates are thought to be characteristic of the working catalyst. It is well known that during reaction the initially clean metal surface becomes contaminated by carbonaceous residues. Thus, the real catalyst becomes quite complex, containing metal islands decor-

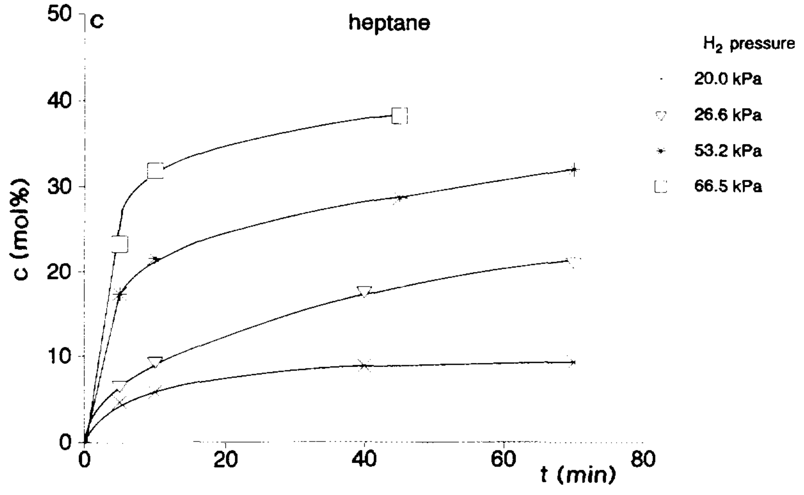


FIG. 1—*Continued*

ated by carbonaceous material. Hydrogen plays several roles in this system. It controls the hydrogen content of the carbonaceous material and regulates that of the reacting intermediates. It keeps part of the surface clean by helping product desorption, and in hydrogenation reactions it is also a reactant. Temperature is an additional factor. This has a significant effect on both the hydrogen content of the carbonaceous material and the extent of coking. An elevation of temperature does not necessarily result in an acceleration of the reaction as is usual for transformations in the homogeneous phase. High temperature may transform the catalyst surface to such an extent that the actual reaction slows down, new reaction paths may open up, and even new reactions may appear.

This is precisely what is observed. After an initial period, a steady-state ("working") surface is formed, following which the rate of the hydrogenation reaction no longer changes. The working surface is not very different from the initial clean catalyst at 373 K: the two parts of the product yield vs time curves can hardly be distinguished. At 573 K, however, the initial and steady-state rates differ appreciably, thus the initial and the working surfaces can be easily distinguished. At 673 K, the rate of hydrogenative ring opening falls dramatically and new reactions appear, such as cracking, ring enlargement, and aromatization. At this temperature, extensive coking occurs, which cannot be counterbalanced even by high hydrogen pressure.

As far as the hydrogen pressure dependence curves are concerned, they also show that the initial surface is not very different from the working one at 373 K, as the shapes of the curves are very similar. At 573 K, this picture changes significantly. A large maximum is now observed, indicating that the actually reacting species differ from those initially formed: the associative adsorption has turned to dissociative.

At 673 K, the initial and the steady-state shapes of the hydrogen dependence functions are not much changed, showing that essentially the initially formed intermediates react further. However, the rate is lower by an order of magnitude, which is due to extensive coking, i.e., the formation of hydrogen-poor carbonaceous residues.

One of our basic points is that the initial and the working catalysts can be quite different. The gap between the two states of the catalyst becomes wider as the temperature is raised. This is shown by comparisons of (i) the rates of product formation, (ii) the shapes of the hydrogen pressure depen-

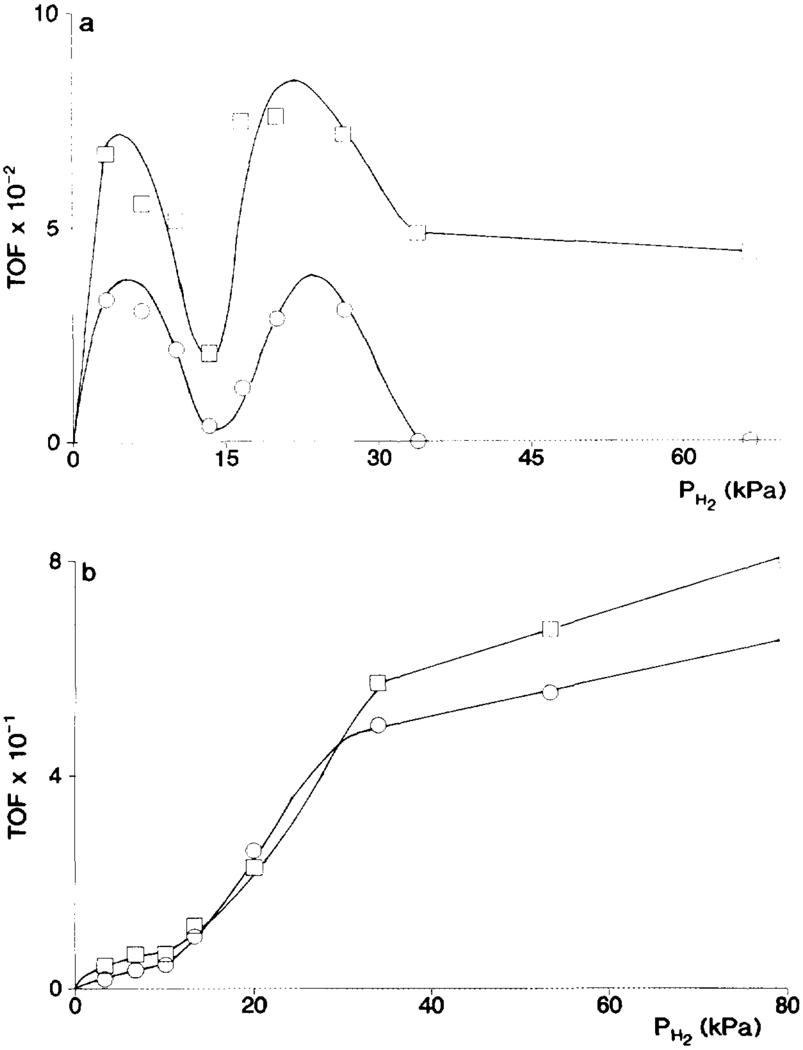


FIG. 2. Turnover frequency of product formation vs hydrogen pressure curves over the initial surface at (a) 373 K, (b) 573 K, and (c) 673 K (○, 3-methylhexane; □, heptane).

dence curves, and (iii) the regioselectivities for the clean and the working catalysts. The first two points have already been treated and the third one is considered here.

Ring-Opening Selectivities over the Clean and the Working Catalysts

Data concerning ring-opening selectivities at different temperatures and hydrogen pressures are summarized in Table 1. The table contains data typical for the initial and the working surfaces of the catalyst (first and second columns, respectively, at each temperature) and also the ratio of the quantities of products at 50 min, referred to as the overall selectivity (third column at each temperature).

In contrast with the results of the articles mentioned in the introduction, we found that for propylcyclobutane the ring initially opens selectively (but not exclusively) in the sterically more hindered direction, espe-

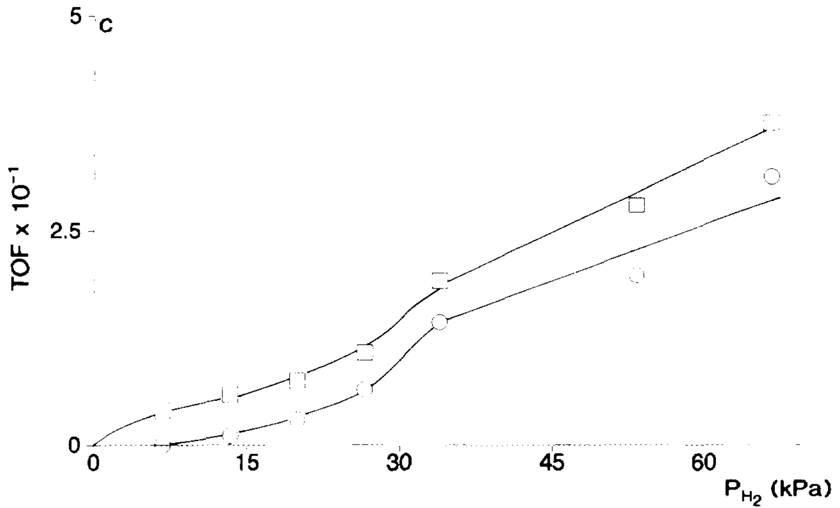


FIG. 2—*Continued*

cially at 373 K. This selectivity is decreased considerably when the temperature is 573 or 673 K, but even then mostly 1,2 C–C bond scission predominates initially. This regioselectivity is unusual, since over the most often used transition metal catalysts (Pt, Pd, Rh, and Ni) ring opening predominantly (if not exclusively) occurs in the sterically less hindered direction (*1–3, 17, 21*). The unusual selectivity may be due to two quite different reasons: (a) the support is acidic or (b) a special type of adsorption occurs over the metal crystallites or at the metal–support or metal–carbonaceous residue interfaces. Explanation (b) probably holds, while explanation (a) can be discarded on the following grounds: (i) Cab-O-Sil fumed silica is known to be inert (we found that the support itself was not active at all); (ii) the concentration of residual chlorine is negligible, moreover, it was shown that neither the rate nor the regioselectivity for the hydrogenative ring opening of methylcyclopropane was changed even over an excessively chlorinated Pt/SiO_2 (*23*); (iii) selectivity for 1,2 C–C bond scission is the greatest at low temperature; (iv) the regioselectivity for alkyl-substituted cyclopropanes is normal, i.e., the sterically less hindered C–C bond cleaves over the same Cab-O-Sil supported Pt (*17*), as well as over Pd, Rh, or Ni (*21*); and (v) our preliminary results with propylcyclobutane over Rh/Cab-O-Sil (prepared through impregnation with $RhCl_3$ and reduced in the same way as Pt/Cab-O-Sil) show that over this catalyst, the predominant mode of ring opening is 2,3 C–C bond rupture, even initially.

As far as selectivities over the working catalyst are concerned, it is clear that at 373 K the values are lower, but 1,2 C–C bond scission still remains the main ring-opening route. This is in accordance with our earlier statement that the initial and the working catalyst differ only slightly. At higher temperatures, however, the ring-opening pattern tends to be close to the statistical. This is mainly reflected in the selectivity values at 50 min at 573 and 673 K.

Mechanisms of the Hydrogenative Ring-Opening Reactions

On the basis of the above findings, conclusions can be drawn and reaction mechanisms can be proposed, as detailed below.

At 373 K, dissociatively adsorbed species predominate at low hydrogen pressures, both initially and over the working catalyst. At higher hydrogen pressures, the type of adsorbed intermediates changes. However,

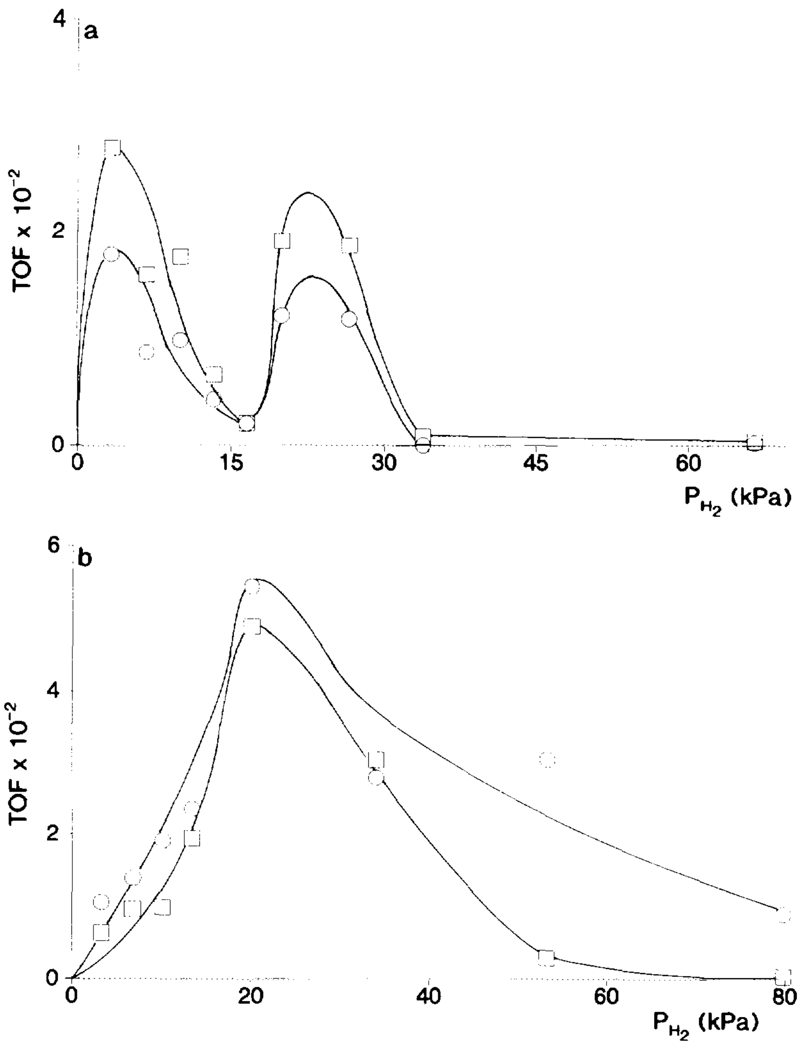


FIG. 3. Turnover frequency of product formation vs hydrogen pressure curves over the working catalyst at (a) 373 K, (b) 573 K, and (c) 673 K (○, 3-methylhexane; □, heptane).

because of the possibly partly reversible adsorption, the unsaturated character of these adsorbed species cannot be determined. As far as the adsorption geometry is concerned, the high regioselectivity towards 1,2 C–C bond scission suggests that the cyclobutane ring is anchored to the support–metal interface, resembling the mechanism proposed by Kramer and co-workers (*24*). This adsorption allows a tilted geometry with the loss of two hydrogen atoms in the suggested mechanism, and results in the predominance of 1,2 C–C bond scission over the initial surface. Over the working surface the overall reaction rate and the selectivity towards 1,2 C–C bond scission decrease (but 1,2 C–C bond rupture remains faster than that of 2,3 C–C bond), therefore a more dissociated but less anchored surface intermediate may be assumed (Scheme 1a). 2,3 C–C bond scission may occur through a dissociatively adsorbed edge-on or a flat-lying surface intermediate of less abundance.

At 573 K, the initial adsorption largely

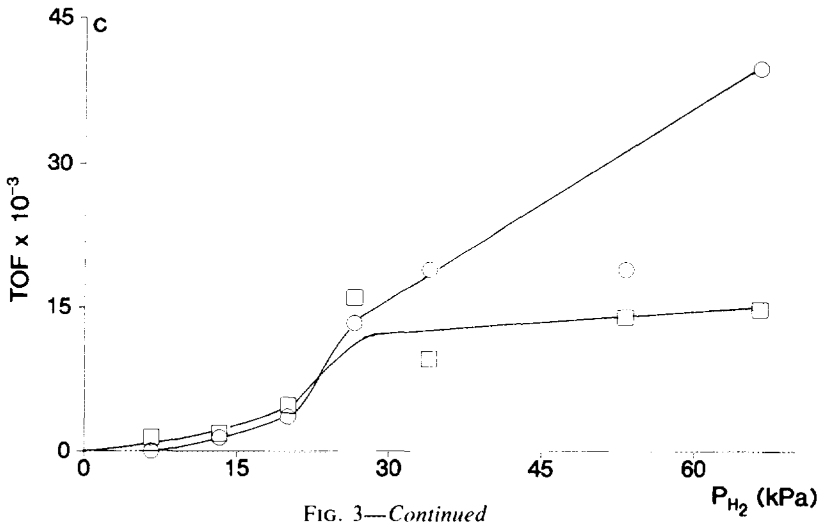


FIG. 3—*Continued*

differs from that typical for the working catalyst. Initially, associative adsorption takes place in both directions, but on the working catalyst dissociative adsorption predominates. The regioselectivity towards heptane formation is lowered to some extent on the working catalyst, and it becomes nonselective at moderate hydrogen pressures. At this temperature, anchoring does not occur: flat-lying associatively or dissociatively adsorbed intermediates may account for the close to statistical bond rupture over either the clean or the working surfaces, respectively (Scheme 1b).

At 673 K, the working surface differs considerably from the initial one: the hydrogenation activity over the working catalyst drops by an order of magnitude. Initially, 1,2 C–C bond scission occurs with a higher rate than that of 2,3 at every hydrogen pres-

TABLE 1

Selectivity of the Ring-Opening Reaction

p_{H_2} (kPa)	373 K			573 K			673 K		
	a[a]	*b*[b]	*c*[c]	*a*	*b*	*c*	*a*	*b*	*c*
3.3	2.0	1.6	1.7	—	—	—	*	*	*
6.7	1.8	1.8	2.1	1.9	0.7	1.0	*	*	*
13.3	5.4	1.6	1.9	1.2	0.8	1.0	5.3	1.3	1.6
20.0	2.7	1.6	1.9[d]	0.9	0.9	1.0	2.5	1.3	1.6
26.6	2.4	1.6	1.9	—	—	—	1.7	1.2	1.3
33.9	*	*	*	1.2	1.1	1.1	1.3	0.5	1.0
53.2	*	*	*	1.2	0.1	1.0	1.4	0.7	1.0
66.5	*	*	*	—	—	—	1.2	0.4	1.2

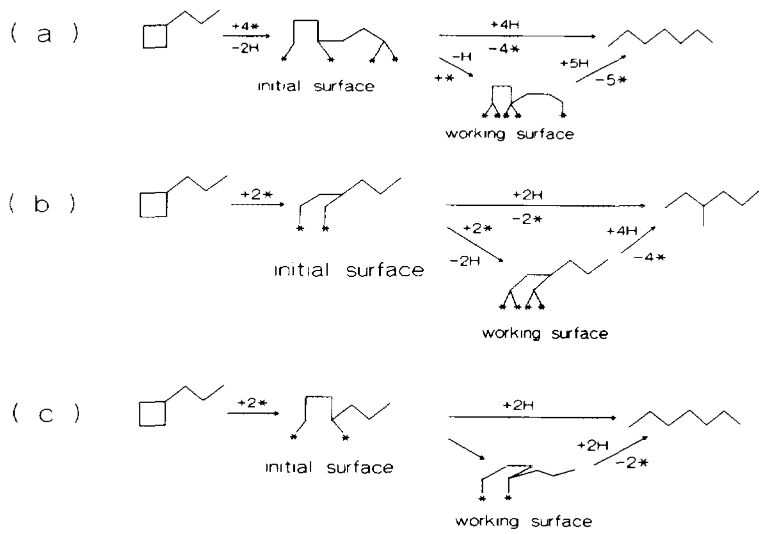
Note. * indicates there is no 3-methylhexane.

[a] $a = r_{\mathrm{initial,heptane}}/r_{\mathrm{initial,3\text{-}Me\text{-}hexane}}$.

[b] $b = r_{\mathrm{steady,heptane}}/r_{\mathrm{steady,3\text{-}Me\text{-}hexane}}$.

[c] *c* is the ratio of concentrations of heptane and that of 3-methylhexane at 50 min.

[d] Ratio of concentrations of heptane and that of 3-methylhexane at 30 min.



SCHEME 1. Mechanisms of the ring-opening reaction: (a) 1,2 C–C bond scission through an anchored tilted complex at 373 K over the initial surface and a more dissociated, less anchored intermediate over the working catalyst; (b) 2,3 C–C bond scission route over the initial and the working catalysts at 573 K through flat-lying surface intermediates; and (c) 1,2 C–C bond scission over the initial and the working catalysts at 673 K, a change from an edge-on tilted complex to a flat-lying intermediate.

sure. The reaction takes place through associatively adsorbed species, possibly via an intermediate standing on C(1) and C(2) and an edge-on complex standing on C(2) and C(3) of less abundance. Over the working catalyst, the ring-opening pattern is nearly statistical, which suggests a flat-lying intermediate (Scheme 1c).

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REFERENCES

1. 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).
2. Newham, J., *Chem. Rev.* **63,** 123 (1963).
3. Zsigmond, Á. G., and Bartók, M. *in* "Stereochemistry of Heterogeneous Metal Catalysis," p. 17. Wiley, Chichester/New York/Brisbane/Toronto/Singapore, 1985.
4. Hilaire, L. H., Maire, G., and Gault, F. G., *Bull. Soc. Chim. Fr.*, 886 (1967); Maire, G., and Gault, F. G., *Bull. Soc. Chim. Fr.* 894 (1967).
5. Rooney, J. J., *J. Catal.* **2,** 53 (1963).
6. Rowlinson, H. C., Burwell, R. L., Jr., and Tuxworth, R. H., *J. Phys. Chem.* **59,** 255 (1955).
7. Gudkov, B. S., Balandin, A. A., and Savin, E. P., *Dokl. Akad. Nauk SSSR* **162,** 843 (1965).
8. Raik, S. E., *Zh. Obshch. Khim.* **11,** 324 (1941).
9. Maire, G., Plouidy, G., Prudhomme, J. C., and Gault, F. G., *J. Catal.* **4,** 556 (1965).
10. Paál, Z., and Dobrovolszky, M., *React. Kinet. Cat. Lett.* **1,** 435 (1974); Paál, Z., Dobrovolszky, M., and Tétényi, P., *React. Kinet. Cat. Lett.* **2,** 97 (1975).
11. Lukina, M. Yu., Olfereva, T. V., Bragin, O. V., Liberman, A. L., and Kazanskii, B. A., *Dokl. Akad. Nauk SSSR* **193,** 106 (1970).
12. Kazanskii, B. A., Bragin, O. V., Khelkovskaya-Segeeva, E. G., and Liberman, A. L., *Dokl. Akad. Nauk SSSR* **214,** 103 (1974).
13. Bragin, O. V., Khelkovskaya-Sergeeva, E. G., Zotova, S. V., Vostokova, E. I., and Liberman, A. L., *Izv. Akad. Nauk SSSR Ser. Khim.*, 363 (1974); Bragin, O. V., Khelkovskaya-Sergeeva, E. G., Preobrazhenskii, A. V., and Liberman, A. L., *Izv. Akad. Nauk SSSR*, 2023 (1974).
14. Clarke, J. K. A., Hegarthy, B. F., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. 1* **84,** 2511 (1988).
15. Notheisz, F., and Bartók, M., *J. Catal.* **71,** 331 (1981).
16. Smith, G. V., Bartók, M., Ostgard, D., and Notheisz, F., *J. Catal.* **101,** 212 (1986).

17. Pálinkó, I., Kiss, J. T., Notheisz, F., and Bartók, M., *J. Mol. Catal.* **77**, 313 (1992).
18. Bartók, M., Notheisz, F., Zsigmond, Á. G., and Smith, G. V., *J. Catal.* **100**, 39 (1986).
19. Pálinkó, I., Molnár, Á., Kiss, J. T., and Bartók, M., *J. Catal.* **121**, 396 (1990).
20. Török, B., Molnár, Á, Pálinkó, I., and Bartók, M., submitted for publication; Török, B., Pálinkó, I., Molnár, Á, and Bartók, M., submitted for publication.
21. 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); Pálinkó, I., Notheisz, F., and Bartók, M., *J. Mol. Catal.* **68**, 237 (1991).
22. Paál, Z., and Menon, P. G. (Eds.), "Hydrogen Effects in Catalysis." Dekker, New York and Basel, 1988.
23. Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **53**, 414 (1978).
24. Kramer, R., and Zuegg, H., *J. Catal.* **85**, 530 (1984); Kramer, R., and Fischbacher, M., *J. Mol. Catal.* **51**, 247 (1989).