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NOTE

Hydrogen Pressure Dependence in the Ring-Opening Reactions of Substituted Cyclobutanes over Rh/SiO$_2$ Catalyst at Various Temperatures

Studying the hydrogenative transformations of alkyl-substituted cyclic hydrocarbons is a significant area of catalytic research. They are important models in at least two respects. On one hand, adsorbed cyclopropanes are thought to be intermediates in bond shift isomerization of alkanes and adsorbed five-membered rings play crucial role in catalytic reforming as well as in C_5-cyclic isomerization. Therefore, numerous papers and reviews are devoted to the catalytic properties of variously substituted cyclopropanes and cyclopentanes (e.g., (1–6)). On the other hand, substituted ring systems offer the possibility of studying the regioselectivity as well as the stereoselectivity of the ring opening (for a review, see (7)). In this respect, four-membered carbocycles must also be taken into account, although papers concerning their transformations appear to be relatively rare. Papers dealing with such reactions over Rh catalysts (bulk or supported) are even scarcer (8–16). Furthermore, to our knowledge, the reactions of propylcyclobutane were not investigated over Rh/SiO$_2$ previously except our work (17), which concerned the ring enlargement and aromatization reactions of propylcyclobutane (as side-reactions of the hydrogenative ring opening) over silica-supported Pt, Pd, and Rh. Consequently, detailed investigations may fill considerable gap in the literature contributing to the better understanding of surface events in hydrogenative ring opening in general and those of alkyl-substituted cyclobutanes in particular.

In this work we report on the hydrogenative ring-opening reactions of alkyl-substituted cyclobutanes over a Rh/SiO$_2$ catalyst. The crucial role of hydrogen pressure on activity and selectivity of these reactant–catalyst systems is shown. It is manifested in hydrogen pressure curves of highly irregular shape, which seems to be general in the hydrogenative interactions of small hydrocarbon rings and Rh.

Methylcyclobutane was synthesized following a published method (18), while the propylcyclobutane sample originated from the laboratory of the late O. V. Bragin (Zelinskii Institute, Moscow, Russia). Their purity was checked by ^{1}H NMR spectroscopy (Bruker AM 400) and GC-MS (Hewlett-Packard 5970 MS) method. The compounds were used without further purification except a couple of freeze–evacuate–thaw cycles right before preparing the reaction mixture. Oxygen-free hydrogen was prepared in a Matheson 8326 generator, operating with a palladium membrane.

A 3.2% Rh/SiO$_2$ catalyst was made by impregnating a Cab-O-Sil M5 support (BDH product with 241.6 m^2 g^{-1} BET surface area) with RhCl$_3$ solution, followed by reduction in flowing hydrogen at 773 K for 16 h (19). The high-temperature hydrogen treatment diminished 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 Rh loading), for details see (20). The dispersion of the catalyst (number of exposed Rh atoms/total number of Rh atoms) was determined by H$_2$ titration in a pulse system at room temperature. The dispersion value, assuming 1 : 1 adsorption stoichiometry, was 0.27.

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 each experiment, the catalyst samples were activated with 26.6 kPa of H$_2$ at 473 K for 1 h.

The reactions were carried out in a conventional closed circulation reactor (for more details, see (21)). The analysis of samples withdrawn from the reaction mixture was performed with a Carlo Erba Fractovap 2150 gas chromatograph equipped with a flame ionization detector. Either a 4-m or a 3.6-m-long glass column filled with 5% bis(methoxy-ethyl)adipate/Chromosorb PAW or 20% squalane/Chromosorb PAW, respectively, were used for analysis.

Reactants (1.33 kPa of hydrocarbon and various amounts of hydrogen) were premixed in the circulation part of the system before the reaction. In temperature dependence measurements, 19.9 kPa hydrogen was always used. At a certain hydrogen pressure, product yield vs time (t) functions were always determined over a fresh sample of catalyst (10 mg) and initial rates were measured. The rates were converted to turnover frequency (TOF, molecule exp atom^{-1} s^{-1}). Measurements at certain hydrogen pressures were repeated with fresh samples of catalysts and were found to be reproducible within 15%. Also, in the vicinity of maxima and minima of the hydrogen pressure dependence

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curves sufficient number of measurements were performed to check the validity of the irregular shape and to allow determination of positions of the extremes.

In order to establish the basic characteristics of the reactions, the cyclobutane derivatives were studied at constant hydrogen pressure (19.9 kPa) as the function of temperature. No reaction could be detected under 323 K for methylcyclobutane and under 373 K for propylcyclobutane. Above these temperatures only hydrogenative ring opening took place up to 423 K producing saturated hydrocarbons (1,2 C–C bond scission, *n*-pentane and *n*-heptane for methylcyclobutane and propylcyclobutane, respectively; 2,3 C–C bond scission, isopentane and 3-methylhexane for methylcyclobutane and propylcyclobutane, respectively). Raising the reaction temperature further promoted multiple C–C bond rupture. Above 548 K aromatization was observed for propylcyclobutane (17). First, toluene appeared, however, at 673 K only benzene was found. Experimental results revealed that the total conversion of hydrocarbons vs temperature curves pass through a maximum (Fig. 1). Hydrogenative ring opening was the fastest at 423 K for both compounds. As far as ring-opening selectivity is concerned, the ring cleavage pattern of propylcyclobutane was near statistical, while isopentane formation was predominant in the ring opening of methylcyclobutane.

The effect of hydrogen is crucial in the reaction because beside being a reactant it actively takes part in forming and transforming the catalytic surface. It regulates coke formation and influences the rearrangement of the surface region of the catalyst. Its surface concentration can alter the mechanism of transformations. When the temperature is varied, its surface concentration changes, thus, the environment of the reactions can be widely different. All these factors (and also others not mentioned here, but summarized in a voluminous monograph (22)) justify expanding the study including hydrogen pressure dependence studies at various temperatures.

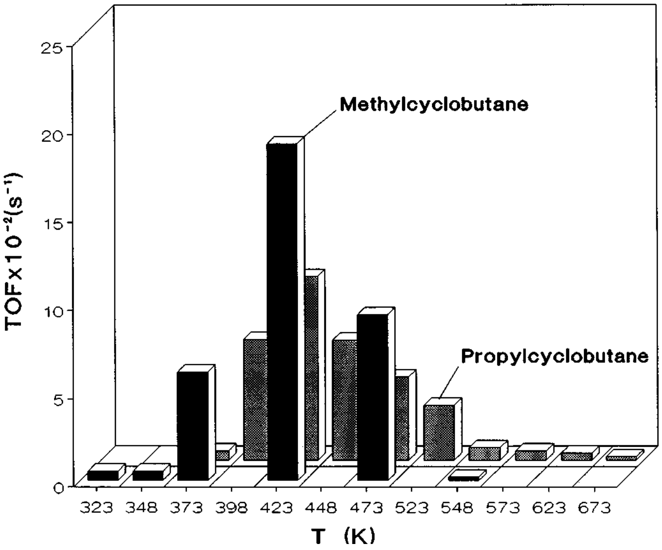

FIG. 1. Gross ring-opening rate vs temperature in the hydrogenative transformation of methyl- and propylcyclobutane over Rh/SiO$_2$ (H$_2$ pressure, 19.9 kPa).

Temperatures chosen for hydrogen pressure measurements were 348 and 423 K for methylcyclobutane, 373, 423, and 548 K for propylcyclobutane. The lowest temperatures allowed the investigation of hydrogenative ring opening without side-reactions. There were not any side-reactions at 423 K either and ring opening for propylcyclobutane was the fastest here. The highest temperatures where side-reactions did not overwhelm hydrogenative ring opening were 423 K for methylcyclobutane and 548 K for propylcyclobutane.

As far as the shape of the hydrogen pressure curves is concerned, they fall in two categories. The hydrogenative ring opening of methylcyclobutane at 348 K could be described by simple maximum curves, which are generally observed in hydrocarbon reactions (22). The maximum reflects an optimal hydrogen coverage for the reaction and may also reflect a transformation of dissociative type. As the temperature was raised to 423 K, the shape of the product curves changed: the maxima moved towards higher hydrogen pressures and monotonous increase could be observed after minima at 40 kPa.

Product formation vs hydrogen pressure curves for propylcyclobutane at any of the temperatures studied revealed that the above-described, highly irregular curve shape was not incidental. Very sharp drops in product formation rates were observed after the large maxima at 373 K (Fig. 2a). Gradual flattening of the maxima was observed as the temperature was raised (Figs. 2b and 2c). At higher hydrogen pressures, after the minima, ring opening accelerated considerably. Rates became higher than they were at the local maxima.

To our knowledge, a hydrogen pressure curve of this shape was only found in the hydrogenative ring opening of alkyl-substituted cyclopropanes (for ethylcyclopropane, *trans*-1,2-dimethylcyclopropane, and, to a significantly smaller but still detectable extent, for 1,1-dimethylcyclopropane), interestingly, over Rh/SiO$_2$ catalyst (19).

A simple maximum curve may not but a hydrogen pressure curve with a maximum and a minimum surely does reflect basic features of the ring-opening mechanism. These drastic variations evidence substantial changes in the mechanism of ring opening. The first part should correspond to predominantly dissociatively adsorbed species. (C–H bond rupture occurs upon adsorption preceding the ring C–C bond rupture or concomitantly with it), while the monotonously increasing part is an indication of associative mechanism (in which C–C bond scission in the ring occurs upon adsorption).

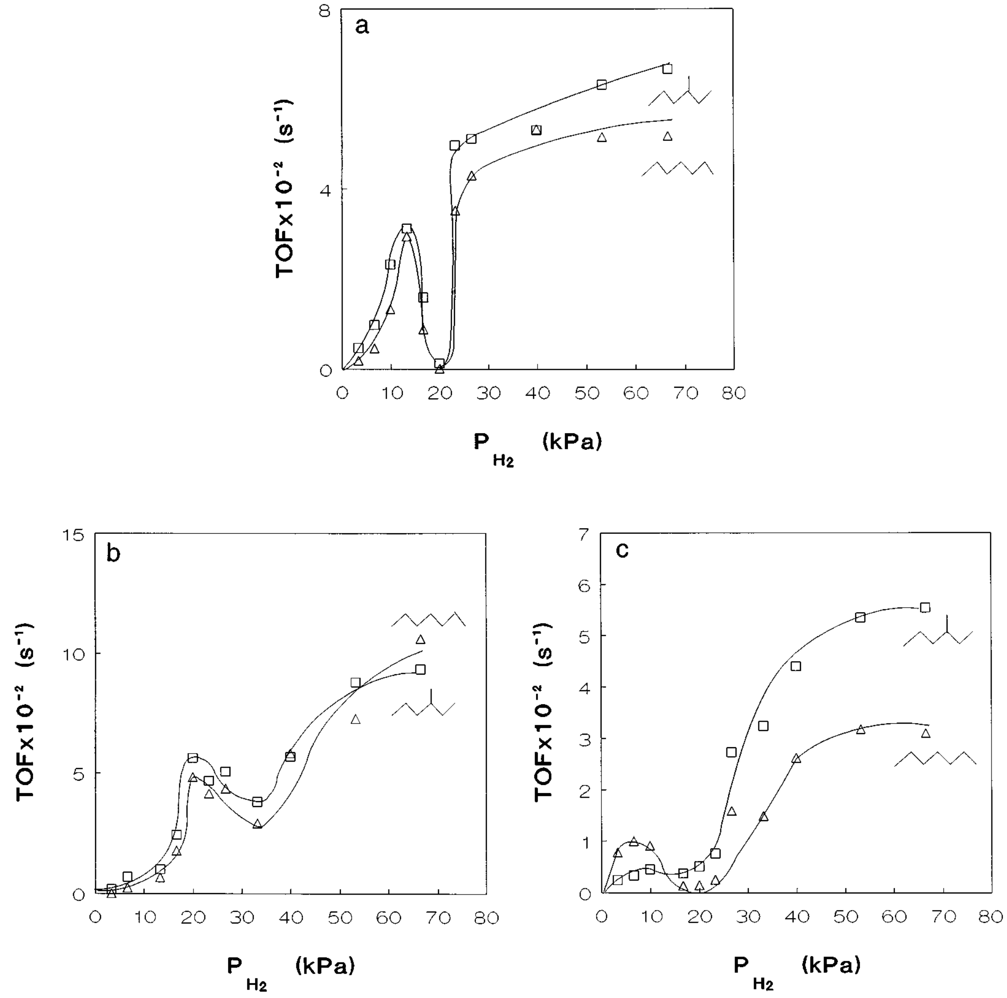

FIG. 2. Turnover frequency of product formation vs hydrogen pressure curves of the ring-opening reactions of propylcyclobutane over Rh/SiO$_2$ catalyst at (a) 373, (b) 423, and (c) 548 K.

Some thoughts should be devoted to ring-opening selectivities as well. The picture emerged from temperature dependence measurements is not altered significantly when hydrogen pressure dependence measurements are considered. The predominance of 2,3 C–C bond scission is typical of methylcyclobutane, especially at 348 K (Table 1, columns 2 and 3). The ring-opening selectivity is closer to statistical selectivity for propylcyclobutane with some excess of 2,3 C–C bond scission (Table 1, columns 4 and 5 and column 6 above 13.3 kPa hydrogen pressure). The anchoring effect of the propyl side-chain, observed over Pt/SiO$_2$ (23) or Pd/SiO$_2$ (24), was not substantial here. It may have a role though, in increasing the relative rate of 1,2 C–C bond rupture leading to near statistical cleavage pattern.

However, at the highest temperature and low hydrogen pressure the cleavage of the sterically more hindered C–C bond predominates. For explanation let us offer the following reasoning. The geometry of the adsorbed intermediate changes as the hydrogen pressure increases. It is a side-chain anchored edge-on intermediate at low hydrogen pressures, which lies down on the surface when the hydrogen pressure increases and side-chain anchoring ceases. In our view, side-chain anchoring is promoted by the increase in the relative quantity of interfaces, let it be either metal–support or metal–carbonaceous deposit interfaces (23). The relative quantity of this latter type of interface is higher at low hydrogen pressures. Thus the cleaning of the metal surface by hydrogen may be considered as the driving force of the change in the binding arrangement.

The above detailed results clearly show that, among other things, hydrogen pressure (and thus hydrogen coverage) significantly influences the mechanism of hydrogenative ring opening. It is also revealed that in certain instances hydrogen pressure curves together with selectivity data help in acquiring information about surface chemical events.

TABLE 1

Selectivity Data (Rate of 2,3 C–C Bond Scission/Total Rate of Ring Opening) in the Ring-Opening Reactions of Methyl- and Propylcyclobutane over Rh/SiO_2 at Varying Hydrogen Pressure

Hydrogen pressure (kPa)	Methylcyclobutane		Propylcyclobutane		
	348 K	423 K	373 K	423 K	548 K
3.3	—	—	0.72	1.00	0.24
6.6	0.92	0.65	0.68	0.73	0.25
9.9	—	—	0.63	—	0.34
13.3	0.81	0.69	0.51	0.60	—
16.6	—	—	0.64	0.58	0.73
19.9	—	0.70	0.55	0.54	0.77
23.2	—	—	0.58	0.53	0.75
26.6	0.91	0.72	0.54	0.54	0.63
33.2	0.83	0.71	—	0.56	0.68
39.9	1.00	0.78	0.50	0.49	0.63
46.6	1.00	0.76	—	—	—
53.2	0.78	0.77	0.55	0.55	0.63
66.5	—	—	0.56	0.47	0.64

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REFERENCES

1. Newham, J., *Chem. Rev.* **63**, 123 (1963).
2. Paál, Z., *Adv. Catal.* **29**, 273 (1980).
3. Gault, F. G., *Adv. Catal.* **30**, 1 (1981).
4. Paál, Z., and Tétényi, P., *in* "Specialist Periodical Reports on Catalysis," Vol. 5, p. 80. Royal Soc. Chemistry, London, 1982.
5. Maire, G., and Garin, F., *in* "Catalysis Science the Technology," Vol. 6, p. 162. Springer-Verlag, Berlin/New York/Tokyo, 1984.
6. Paál, Z., *in* "Catalytic Naphta Reforming" (G. J. Antos, A. M. Aitani, and J. M. Parera, Eds.), p. 19. Dekker, New York/Basel/Hong Kong, 1995.
7. Zsigmond, A. G., and Bartók, M., *in* "Stereochemistry of Heterogeneous Metal Catalysis," p. 17. Wiley, Chichester/New York/Brisbane/Toronto/Singapore, 1985.
8. Kazanskii, B. A., Lukina, M. Yu, and Nakhapetyan, L. A., *Izv. Akad. Nauk SSSR Ser. Khim.,* 1274 (1956).
9. Maire, G., Plouidy, G., Prudhomme, J. C., and Gault, F. G., *J. Catal.* **4**, 556 (1965).
10. Maire, G., and Gault, F. G., *Bull. Soc. Chim. France,* 894 (1967).
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-Sergeeva, 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).
14. Bragin, O. V., Khelkovskaya-Sergeeva, E. G., Preobrazhenskii, A. V., and Liberman, A. L., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 2023 (1975).
15. Clarke, J. K. A., Hegarthy, B. F., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. 1* **84**, 2511 (1988).
16. Török, B., and Bartók, M., *Catal. Lett.* **27**, 281 (1994).
17. Török, B., Pálinkó, I., Molnár, Á., and Bartók, M., *J. Mol. Catal.* **91**, 61 (1994).
18. Török, B., and Molnár, Á., *J. Chem. Soc. Perkin Trans. 1* 801 (1993).
19. Notheisz, F., Pálinkó, I., and Bartók, M., *Catal. Lett.* **5**, 229 (1990).
20. Pálinkó, I., Kiss, J. T., Notheisz, F., and Bartók, M., *J. Mol. Catal.* **77**, 313 (1992).
21. Bartók, M., Notheisz, F., Zsigmond, Á. G., and Smith, G. V., *J. Catal.* **100**, 39 (1986).
22. Paál, Z., and Menon, P. G., Eds., "Hydrogen Effects in Catalysis." Dekker, New York/Basel, 1988.
23. Török, B., Molnár, Á., Pálinkó, I., and Bartók, M., *J. Catal.* **145**, 295 (1994).
24. Török, B., Pálinkó, I., and Bartók, M., *Catal. Lett.* **31**, 421 (1995).

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