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Hydrogen pressure dependence in the ring-opening reactions of propylcyclobutane over Pd / SiO_2 catalyst

Béla Török, István Pálinkó and Mihály Bartók [1]

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

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Temperature dependence and the effects of hydrogen pressure on the rate and regioselectivity were studied in the ring opening of propylcyclobutane over a low-dispersion Pd/SiO_2 catalyst. At a certain composition (1.33 kPa of propylcyclobutane and 20 kPa of H_2) the reaction rate versus temperature curve was found to pass through a maximum. At each temperature the ring opened selectively (or exclusively at 423 K) in the sterically more hindered direction over the clean surface as well as over the steady-state catalyst, yielding *n*-heptane as the major product. The hydrogen pressure versus turnover frequency curves were of saturation type for both products over the initial surface at 523 K. Over the steady-state surface, however, the reaction mechanism changed: ring-opening rate versus hydrogen pressure curve passed through a maximum for *n*-heptane, while it remained of saturation type for 3-methylhexane. For rationalizing the high regioselectivity toward *n*-heptane formation, the anchoring effect of the propyl side-chain was suggested.

Keywords: propylcyclobutane; Pd/SiO_2; hydrogenative ring opening; hydrogen pressure dependence; anchoring effect

1. Introduction

The transition metal catalyzed transformations (isomerization and hydrogenative ring opening) of small hydrocarbon rings, e.g., cyclopropanes or cyclopentanes are frequently studied (for reviews, see refs. [1–3]). The main reason is probably the well-established role of adsorbed cyclopropane and cyclopentane species in bond shift and C_5-cyclic isomerization of saturated hydrocarbons, respectively.

The transformations of cyclobutane derivatives over metal catalysts and a relatively neglected area of research, most probably, because of their complicated preparation. In spite of synthetic difficulties, some aspects of the hydrogenative ring-opening reactions of monoalkylated [4], geminally methylated [5], and in one case

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[1] To whom correspondence should be addressed.

stereoisomeric dimethylated [6] cyclobutane derivatives were studied over supported or monolithic Pd catalysts earlier. The following observations were made:

- Pd generally was found to have lower ring-opening activity but similar ring-opening selectivity (toward the scission of the sterically less hindered C–C bond) than other transition metals (e.g., Pt, Rh, Ru or Ir),
- the proportion of products from the rupture of the more hindered C–C bond was higher than over the metals mentioned before,
- side-reactions (aromatization, cracking) required high temperature to occur.

After these early results, detailed studies concerning the effects of hydrogen pressure, temperature and the length of the substituent were not published. Moreover, to our knowledge, propylcyclobutane has never been studied over Pd catalysts before.

Previously, we studied the hydrogenative transformations of propylcyclobutane over Pt/SiO_2 [7,8]. The molecule was proved to be a good candidate for studying side-chain effect, which caused unusual regioselectivity: the predominant rupture of the sterically more hindered C–C bond. The near to statistical product distribution in the hydrogenative ring opening of methylcyclobutane revealed that a methyl group was too small to influence regioselectivity in a manner as the propyl group could [9].

In this work we report on the hydrogenative ring opening of propylcyclobutane over Pd/SiO_2. The activity and regioselectivity of the ring opening were studied as a function of temperature at a certain composition and of hydrogen pressure at a selected temperature. Particular attention was paid to the possible regioselectivity influencing effect of the propyl substituent.

2. Experimental

Propylcyclobutane and propylcyclopropane were gas chromatographically pure and were used without further purification. Propylcyclopentane was prepared via the Grignard reaction of propyl bromide and cyclopentanone followed by the dehydration and subsequent hydrogenation of the resulting olefin mixture in hexane over Pd/C at room temperature. After removing the catalyst, the liquid was distilled through a Vigreaux column. The resulting propylcyclopentane was gas chromatographically pure.

All the hydrocarbons were degassed by a couple of freeze–evacuate–thaw cycles right before preparing the reaction mixture.

The Pd/SiO_2 catalyst was made by impregnating a Cab-O-Sil M5 support (BDH product) with an acidic solution of $PdCl_2$, followed by reduction in flowing hydrogen at 773 K for 16 h. The high-temperature hydrogen treatment diminished the chlorine content of the catalyst, as revealed by X-ray fluorescence spectroscopy (the quantity of chlorine was less than 10 ppm relative to the Pd loading).

The palladium content of the catalyst (3.0%) was determined by atomic absorption spectroscopy. The dispersion of the 3.0% Pd/SiO_2 catalyst (number of exposed Pd atoms/total number of Pd atoms) was determined by CO chemisorption in a pulse system at room temperature, assuming 1 : 1 adsorption stoichiometry. The dispersion value obtained (15.4%) was checked by O_2–H_2 titration at 373 K, and by electron microscopy with a Hitachi H500H transmission electron microscope. The results verified the assumed adsorption stoichiometry.

The reactions were carried out in a conventional closed circulation apparatus [10]. A Carlo Erba Fractovap 2150 gas chromatograph with a flame ionization detector was attached to the system. At certain time intervals, samples were withdrawn for gas chromatographic analysis. A 4 m long glass column filled with 15% squalane on Chromosorb PAW/100 mesh was used for analysis.

The reactants (1.33 kPa of the hydrocarbons and various amounts of hydrogen) were premixed in the circulation part of the system before the reaction. Before each run, a fresh sample of catalyst was pretreated in hydrogen (26.7 kPa) for 1 h at 523 K. After evacuation, the hydrocarbon–hydrogen mixture was introduced to the reactor.

The reaction were studied in the temperature range of 423–673 K for propylcyclobutane, up to 673 K for propylcyclopentane, and at 373 K for propylcyclopropane [11].

At a certain hydrogen pressure, product yield versus time (t) functions were always determined over a fresh sample of catalyst (10 mg). For propylcyclobutane, both initial and steady-state rates (rates over the working catalyst) 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 Pd atoms determined by CO chemisorption.

3. Results and discussion

3.1. RATES AND SELECTIVITIES AT CONSTANT HYDROGEN PRESSURE AND AT VARIOUS TEMPERATURES

For preliminary screening, the transformations of propylcyclobutane were investigated at constant composition (1.33 kPa of propylcyclobutane and 20 kPa of hydrogen), but varying temperature in the 423–673 K range (fig. 1). This temperature range was studied, since there was no detectable reaction below 423 K. Between 423 and 523 K hydrogenative ring opening only occurred. Above 523 K side-reactions, such as cracking, ring enlargement and aromatization appeared and they soon became the major routes of transformations [12] (for major reaction pathways, see scheme 1). Although ring opening was the fastest at 548 K, 523 K seemed to be a better choice for a more detailed study. At this temperature, the ring opened with an appreciable rate and no side-reaction could be detected. It is to be mentioned that at each temperature the ring opened predominantly in the sterically

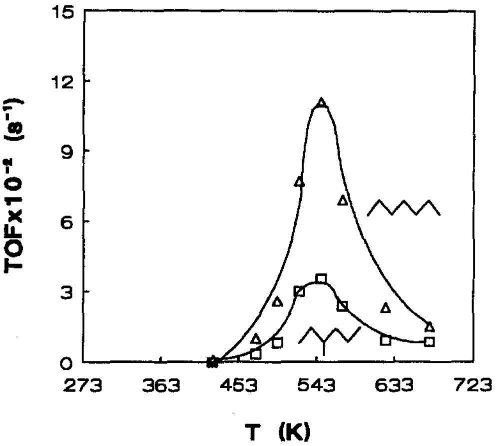


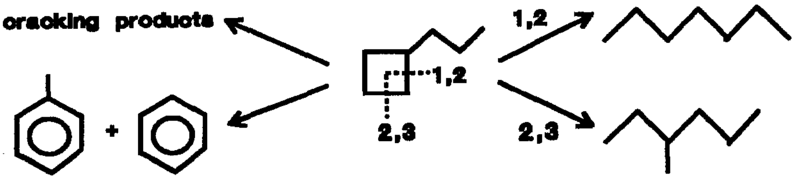
Fig. 1. Turnover frequency of product formation versus temperature curves for 1.33 kPa of propylcyclobutane and 20 kPa of hydrogen mixture over Pd/SiO$_2$ ((□) 3-methylhexane, (△) *n*-heptane).

more hindered direction (1,2 C–C bond scission). At the lowest reaction temperature (423 K), *n*-heptane was only formed. This is an indication of the anchoring effect of the propyl side-chain, which was also found over Pt/SiO$_2$ [7], but not over Rh/SiO$_2$ [13].

For mechanistic considerations, however, measurements at a certain composition are not enough. It is well known that hydrogen, beside being a reactant, is active in forming and transforming the catalytic surface, thus, it has a crucial role in determining the mechanism of surface reactions [14]. Consequently, it seemed appropriate to study the effect of hydrogen on the activity and regioselectivity of ring opening at the optimal temperature (i.e. at 523 K).

3.2. EFFECT OF HYDROGEN PRESSURE ON THE HYDROGENATIVE RING-OPENING REACTION

As it was reasoned above, hydrogen pressure dependence was studied at 523 K. Typical product yield versus time curves are to be seen in fig. 2. These curves may be modeled by two straight lines of different slopes. The slope of the first straight



Scheme 1. C–C bond scission directions in the hydrogenative ring opening of propylcyclobutane over Pd/SiO$_2$.

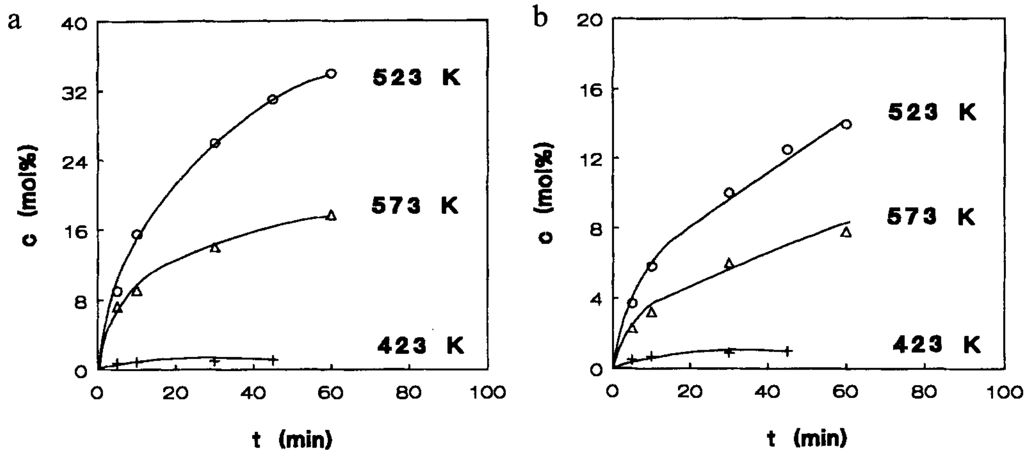


Fig. 2. Product yield versus time curves of (a) 1,2 and (b) 2,3 C–C bond scissions at 423 K (+), 523 K (○) and 573 K (△) (composition: 1.33 kPa of propylcyclobutane and 20 kPa of hydrogen) over Pd/SiO_2.

line was taken as the initial rate, while that of the second as the rate on the steady-state catalytic surface (for more details, see ref. [7]). From these data, two types of product formation rates versus hydrogen pressure functions were constructed. One is from the initial (fig. 3) and the other is from the steady-state rates (fig. 4).

First, the initial rates versus hydrogen pressure functions are examined (fig. 3). It is clearly seen that product formation versus hydrogen pressure curves are of saturation type for both products. These saturation type curves mean non-competitive adsorption: propylcyclobutane adsorbs more strongly over the surface of the catalyst than hydrogen and C–H bond rupture occurs without cleaving the C–H

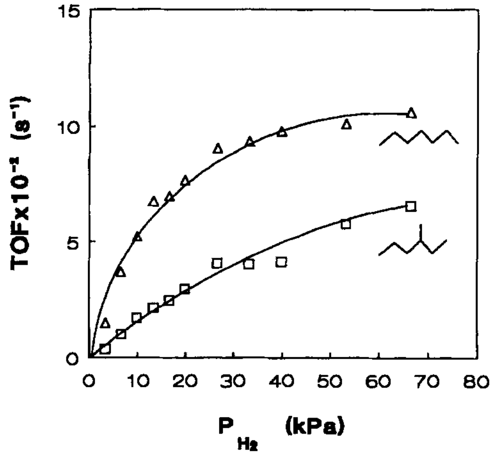


Fig. 3. Turnover frequency of product formation versus hydrogen pressure curves over the initial surface of Pd/SiO_2 at 523 K ((□) 3-methylhexane, (△) *n*-heptane).

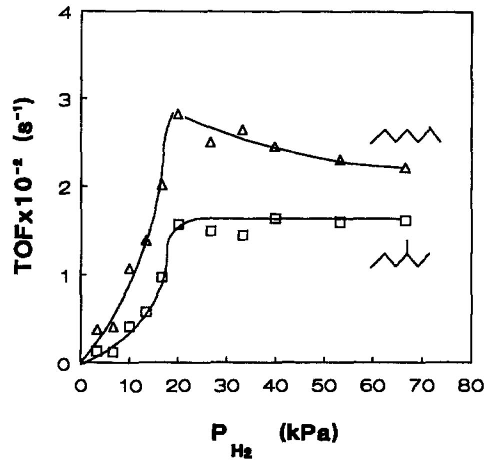


Fig. 4. Turnover frequency of product formation versus hydrogen pressure curves over the steady-state surface of Pd/SiO_2 at 523 K ((□) 3-methylhexane, (△) *n*-heptane).

bonds. Thus, the role of hydrogen is negligible in the formation of adsorbed species, however, it is absolutely necessary in further steps, i.e. in product formation and desorption.

Second, we analyze the hydrogen pressure curves constructed from the second part of the product yield versus time functions (fig. 4). As it has been mentioned, these rates are thought to be characteristic of the steady-state catalyst. It is well known that during reaction, the initially clean metal surface becomes contaminated by carbonaceous residues. Thus, the working catalyst is quite complex, containing metal islands decorated with carbonaceous overlayer, adsorbed intermediates, and hydrogen [15]. Since a smaller part of the metal surface is available for the reactant, the reaction rate decreases considerably. This phenomenon was expected, however, the shape for *n*-heptane formation versus hydrogen pressure function was also changed. At higher hydrogen pressure 1,2 C–C bond scission decreased. The shape of the 3-methylhexane formation versus hydrogen pressure function remained of saturation type. This means that the adsorption leading to *n*-heptane turned dissociative over the steady-state catalyst, while the mechanism of 2,3 C–C bond scission remained associative.

3.3. RING-OPENING SELECTIVITIES OVER THE CLEAN AND THE STEADY-STATE CATALYSTS

Data concerning regioselectivities of ring opening (ratio of *n*-heptane/(*n*-heptane + 3-methylhexane)) at different hydrogen pressures, are displayed in table 1. It contains data typical of both the initial and the steady-state catalysts.

In contrast with the results concerning the regioselectivities of hydrocarbon ring systems [1–3], we found that the ring of propylcyclobutane predominantly

Table 1
Regioselectivity data on the ring-opening reaction over the initial (a) and the steady-state (b) surfaces of Pd/SiO_2 at 523 K[a]

Hydrogen pressure (kPa)	S(a)	S(b)
3.3	0.8	0.7
6.7	0.8	0.7
9.9	0.8	0.7
13.3	0.8	0.7
16.6	0.7	0.7
20.0	0.7	0.7
26.6	0.7	0.6
33.9	0.7	0.6
53.2	0.7	0.6
73.2	0.7	0.6

[a] $S = r_{n\text{-heptane}} / (r_{n\text{-heptane+3-methylhexane}})$.

opened through the rupture of the sterically more hindered C–C bond over the initial and also over the steady-state surfaces. This type of selectivity was observed over Pt/SiO_2 [7] as well, but it was less pronounced at comparable temperature (573 K [7]) than over Pd/SiO_2. This unusual selectivity may be due to two quite different reasons: (i) the catalyst (or support) was acidic, (ii) a special type of adsorption occurred over the metal crystallites or at the metal–support [16] or metal–carbonaceous residue interfaces [17]. Explanation (ii) should be valid since explanation (i) can be discarded on the following grounds:

– Cab-O-Sil fumed silica support is usually used when inertness is a requirement,

– the support itself was not active at all,

– Cab-O-Sil supported Pt, Pd, Ni and Rh catalysts displayed a normal ring-opening pattern with alkyl-substituted cyclopropanes [18]: the ring opened through the predominant scission of the sterically less hindered C–C bond.

Consequently, the above mentioned special type of adsorption, anchoring by the side-chain, is suggested.

3.4. COMPARISON TO PROPYLCYCLOBUTANE OVER Pt/SiO_2 AND PROPYLCYCLOPROPANE OR PROPYLCYCLOPENTANE OVER Pd/SiO_2

Propylcyclobutane transformed over Pt/SiO_2 [7,12] in a similar way as over Pd/SiO_2. The main reaction was also hydrogenative ring opening below a certain temperature (673 K: Pt/SiO_2, 623 K: Pd/SiO_2). At low temperature (373 K: Pt/SiO_2, 523 K: Pd/SiO_2) side-chain anchoring determined the ring-opening selectivity as well [7,17]. Hydrogenative ring opening, however, was measurable at lower temperature over Pt/SiO_2 (373 K) than over Pd/SiO_2 (423 K). The activity of Pt/SiO_2 remained higher too.

When propylcyclopropane was compared to propylcyclobutane each over Pd/SiO_2 [11], the disappearance of the side-chain effect was observed. At 373 K (no β-hydride formation is expected at this temperature and above), the rate of hydrogenative ring opening was fast with ring-opening selectivity toward the scission of the sterically less hindered C–C bond. At temperatures above 373 K, only cracking reactions were found.

Propylcyclopentane proved to be completely inactive in hydrogenative ring opening up to 673 K.

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