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HYDROGEN PRESSURE-DEPENDENCE IN THE RING-OPENING REACTIONS OF SUBSTITUTED CYCLOPROPANES OVER Rh/SiO_2 CATALYST

Ferenc NOTHEISZ, István PÁLINKÓ and Mihály BARTÓK

Department of Organic Chemistry, József Attila University, Szeged, Dómtér 8, H-6720, Hungary

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The hydrogen coverage and the structures of the reactants influence the selectivity and mechanism of the ring-opening reactions of ethyl-(ECP), *cis*-1,2-dimethyl- (*c*DMCP), *trans*-1,2-dimethyl- (*t*DMCP), 1,1-dimethyl- (1, 1DMCP) and 1, 1, 2, 2-tetramethylcyclopropane (TMCP) over Rh/SiO_2 catalyst; a new phenomenon was observed for the transformations of ECP, *t*DMCP and 1, 1DMCP, viz. the turnover frequency vs. H_2 pressure functions pass through a minimum.

1. Introduction

The ring-opening reactions of cyclopropanes over supported and unsupported transition metals are model transformations that are widely used to explore the characteristic features of different catalyst preparations [1–3]. In this way, much has been learnt about the laws governing these reactions [1–7]. We know, for example, that saturated hydrocarbons form in a hydrogen atmosphere; the sterically less hindered C-C bond breaks with fairly high selectivity, and with the elevation of the temperature the probability of multiple ring rupture rises. These observations hold for Rh catalysts too, though papers concerning the transformations of substituted cyclopropanes on this metal are rare [3,6].

The earlier literature claims that the cyclopropane is weakly held over the surface of the catalyst or even reacts from the gas phase with the strongly adsorbed hydrogen. These assumptions were used to explain the experimentally obtained maximum curves [8,9] and close to saturation-type curves [10], respectively, when the reaction rate was measured as a function of hydrogen pressure. More recently, however, the adsorption strengths of the reactants have been studied and it has been established that cyclopropane adsorbs more strongly than hydrogen [11]. As the rate-limiting step is the reaction between the adsorbed moieties [10,12], analysis of the shapes of the function under discussion may

reveal important mechanistic details not yet fully exploited by earlier studies [8–10].

2. Experimental

The substituted cyclopropanes (ethylcyclopropane, *cis*- and *trans*-1,2-dimethylcyclopropane, 1, 1-dimethylcyclopropane and 1, 1, 2, 2-tetramethylcyclopropane) were prepared by methods given in the literature [13].

The Rh/SiO_2 catalyst was made by impregnating a Cab-O-Sil M5 support (BDH product) with an aqueous solution of $RhCl_3$, followed by reduction in flowing hydrogen 773 K for 16 hours. The high-temperature hydrogen pretreatment diminishes the chlorine content of the catalyst as revealed by X-ray fluorescence measurements (the quantity of the residual chlorine is less than 10 ppm). 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 13.3 kPa H_2 at 373 K for an hour; then the system was evacuated again and cooled back to the reaction temperature.

The resulting low-dispersion catalyst (3.2% loading and 27.0% dispersion, determined by hydrogen chemisorption) was placed in a closed circulation reactor, where the reactions were performed [14]. The reactants (1.33 kPa of the cyclopropane and different amounts of hydrogen) were premixed in the circulation part of the system before the reaction. The product accumulation was monitored with a Carlo Erba Fractovap 2150 GC coupled to a Perkin-Elmer Data Station. A Matheson 8236 generator with a Pd membrane provided oxygen-free hydrogen.

At a certain hydrogen pressure, product yield vs. time (t) functions were determined always over a fresh sample of catalyst (usually 5 mg). Initial rates were obtained through differentiation of these functions at $t = 0$. These rates were converted to TOF (molecule exp. $atom^{-1}$ s^{-1}) data based upon the number of surface Rh atoms.

3. Results and discussion

As mentioned before, the hydrogen-dependence can usually be described by a saturation-type curve or a curve passing through a maximum [15]. On the Rh/SiO_2 catalyst, however, the shapes of some of the curves are quite strange: after the maximum there is a minimum as well, and after it the reaction rate increases monotonically in the reactions of ECP and *t*DMCP (fig. 1). In the latter case, the monotonic part even surpasses the local maximum. The behavior of

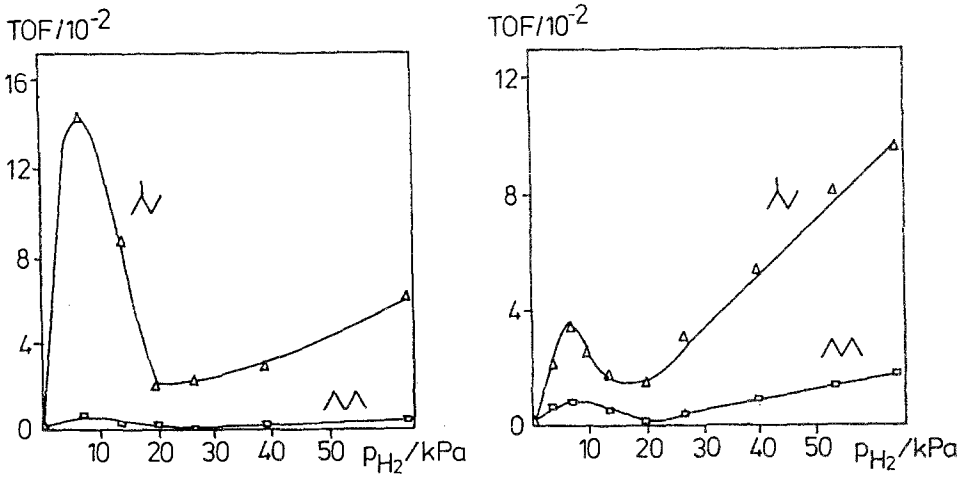

Fig. 1. Formation rate of ring-opening products vs. H_2 pressure functions over Rh/SiO_2 catalyst at 318 K: a: ECP, b:P *t*DMCP.

1, 1DMCP is similar, but only a slight increase can be seen after the minimum, while there is no increase in the case of TMCP (fig. 2). The reaction rate of *c*DMCP is slightly lowered by increasing hydrogen pressure (fig. 3).

In every case the ring-opening occurs predominantly via rupture of the sterically less hindered C–C bond and there is no fragmentation whatsoever.

The ring-opening selectivities (ratio of ring-opening rate in the sterically less hindered to that of the sterically more hindered direction) do not change much with the hydrogen pressure for ECP, *c*DMCP and *t*DMCP, but they fall dramatically for 1, 1DMCP and TMCP as the hydrogen pressure increases (fig.

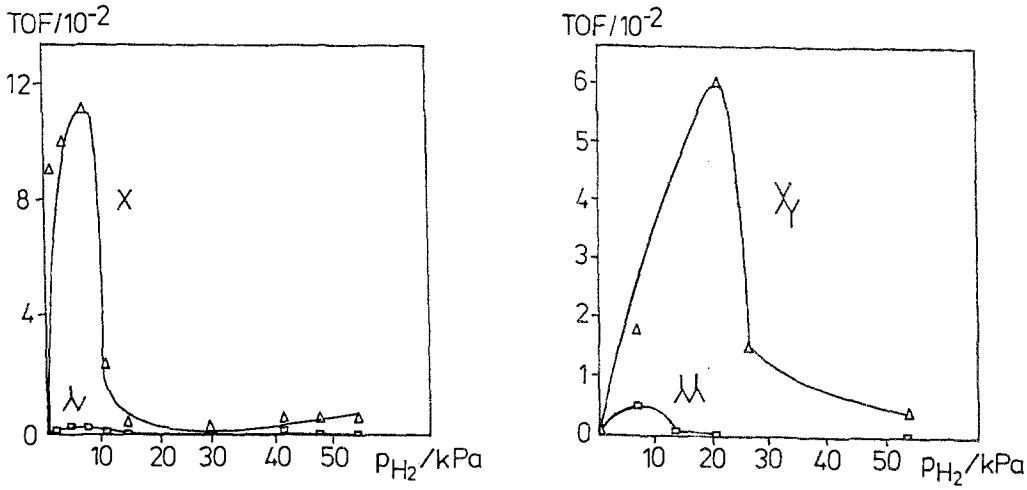

Fig. 2. Formation rate of ring-opening products vs. H_2 pressure functions over Rh/SiO_2 catalyst at 318 K: a: 1, 1DMCP b: TMCP.

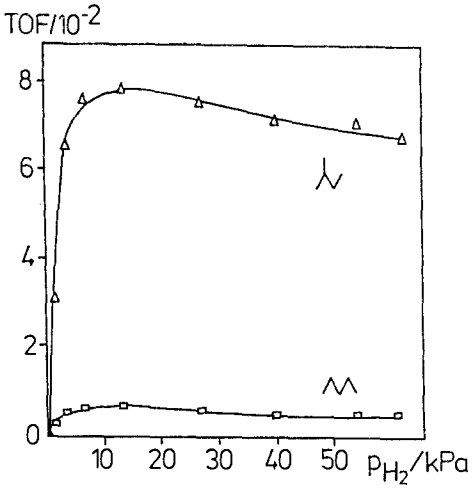

Fig. 3. Formation rate of ring-opening products vs. H_2 pressure functions over Rh/SiO_2 catalyst at 318 K for *c*DMCP.

4). This effect may be connected with the quaternary-secondary C–C bonds to be found in these latter two molecules.

As far as the geometry of adsorption is concerned, the steric hindrance caused by the substituents must be taken into account. It seems unlikely that for *t*DMCP, 1, 1DMCP and TMCP the surface intermediates leading to ring-opening reactions lie "flat" (i.e. the plane of the ring is parallel to the metal surface) over the surface, but rather stand "edge-on" [16]. The differences in the turnover frequency vs. H_2 pressure functions for *c*DMCP and *t*DMCP indicate that the former adsorbs differently from the latter (i.e. the *c*DMCP is "flat" adsorbed). However, these functions for ECP and *t*DMCP are very similar, therefore they adsorb similarly (i.e. "edge-on"). The difference in regioselectivity in the ring-openings of *c*DMCP and *t*DMCP may be accounted for by the difference in their adsorption. The accessibility of the C–C bond between the substituents of the seemingly sterically more hindered *t*DMCP increases when it adsorbs "edge-on", while the "flat" adsorption of *c*DMCP provides (at least) twice the probability of rupture of the sterically less hindered C–C bonds.

The shapes of the turnover frequency vs. H_2 pressure functions most certainly do not always give information about the extent of unsaturation in the reaction intermediates. It was mentioned earlier that competitive adsorption results in a maximum curve, while a saturation-type curve may describe the noncompetitive adsorption of the two reactants. The strong, irreversible adsorption of the cyclopropane is probably weakened by the crowding of the ring, and it is therefore conceivable that the relative abundance surface intermediates leading to 1, 2 C–C bond scission for TMCP is decreasing with increasing hydrogen pressure. If a saturation-type curve indicates noncompetitive adsorption, this should mean the strong adsorption of the *cis* compound, which is in accordance

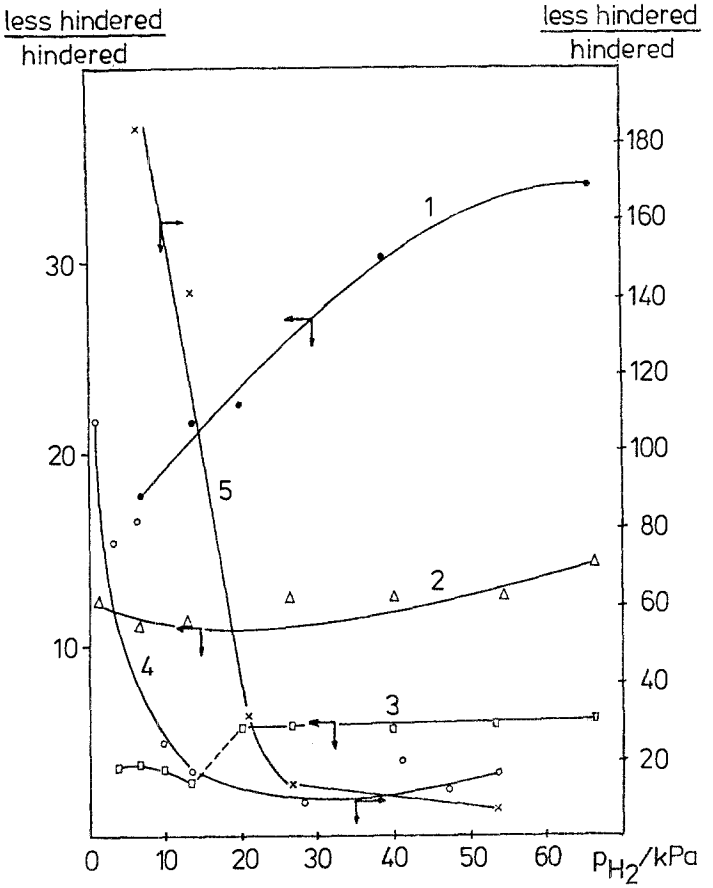

Fig. 4. The effect of hydrogen pressure on the ring-opening selectivity: 1: ECP, 2: *c*DMCP, 3: *t*DMCP, 4: 1, 1DMCP 5: TMCP.

with the assumption of its planar adsorption. The curves with two extremes (ECP, *t*DMCP and to a lesser extent 1, 1DMCP), however, cannot be rationalized on the basis that competitive adsorption becomes noncompetitive as the hydrogen pressure rises (even if it could be explained in this way, this would be an interesting phenomenon). If we stick to the competitive-noncompetitive explanation, it must be said that originally (at low hydrogen pressures) the cyclopropane adsorbs over the metal surface; as the hydrogen pressure increases, its coverage decreases and at the minimum only a small fraction remains covered by the hydrocarbon or the hydrogen reacts with the molecules arriving from the gas phase (Eley-Rideal mechanism) and further increase of hydrogen pressure should have no impact on the rate of the ring-opening. It can be seen in the graphs in fig. 1, however, that this is not the case. The increase of hydrogen pressure does have a marked effect on the rate of the reaction; for e.g. *t*DMCP, the transformation becomes even faster than it was at the local maximum. Thus the curves should

reflect a change in the mechanism of the transformation, which change should be related to the extent of unsaturation of the reacting moieties. The facts that the maximum is at low hydrogen pressure and the monotonicly rising part of the function is at higher hydrogen pressures make it reasonable to claim that hydrogen-rich conditions favor associatively adsorbed species (no C–H bond cleavage as the ring opens), while hydrogen-poor conditions allow the formation of more dissociated species (C–H bond scission also occurs upon ring-opening). This effect is well documented for molecules capable of "choosing" pathways leading to differently saturated products [15,17], but has not yet been described for molecule(s) not having such opportunities.

4. Conclusions

The kinetics of the ring-opening reactions of substituted cyclopropanes over silica-supported Rh catalyst has been studied in a hydrogen atmosphere. Geometric considerations and analysis of the shapes of the turnover frequency vs. hydrogen pressure (coverage) functions permit conclusions concerning the mechanisms of the transformations. "Edge-on"adsorption characterizes the ring-openings of ECP, 1, 1DMCP, TMCP and *t*DMCP, while *c*DMCP reacts via a "flat" adsorbed transition complex. The originally dissociative mechanism for ECP, *t*DMCP and 1, 1DMCP becomes associative as the hydrogen pressure rises. This latter fact is supported by deuterolysis results for 1, 1DMCP [5].

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