JOURNAL OF CATALYSIS 42, 282–287 (1976)

Mechanisms of Methylcyclopentane Ring Opening over Platinum–Alumina Catalysts

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Received September 16, 1975

Ring opening of methylcyclopentane has been investigated over mono-functional platinum/silica and acidic alumina catalysts as well as a dual-functional platinum/alumina reforming catalyst. Both platinum and the acidic alumina catalyze ring opening. The acid-catalyzed ring-opening reaction occurs by direct opening of the methylcyclopentane ring and is inhibited by methylcyclopentenes. The acid-catalyzed reaction leading to an acyclic olefin is proposed to proceed via a protonated ring structure and an acyclic carbonium ion.

INTRODUCTION

The reactions of alkylcyclopentanes over platinum/alumina (Pt/Al_2O_3) catalysts comprise an important part of the chemistry of catalytic reforming. Consequently these reactions have been investigated extensively. Aromatics formation has been shown to occur by a dual-functional mechanism involving dehydrogenation of the cyclopentane to the cyclic olefin, acid-catalyzed isomerization of the cyclopentene to a cyclohexene, and dehydrogenation of the cyclohexene to an aromatic over the platinum function (*1*, *2*). Recently the ring closure of paraffins has been investigated and shown to occur by two parallel mechanisms, one platinum catalyzed and the other catalyzed by the acidic function (*3*). Under typical reforming conditions ring closure is predominantly to the five-membered ring. Thus cyclopentanes are not only a reactant in catalytic reforming but also constitute an intermediate in the conversion of paraffins to aromatics.

In addition to the above reactions, cyclopentanes also can undergo a ring-opening reaction, and although the metal-catalyzed reaction has been investigated extensively, the reaction mechanisms of ring opening over reforming catalysts have received relatively little attention. However, it has been shown that, in addition to platinum-catalyzed ring opening, a second ring-opening reaction does occur over the alumina (*4*, *5*). This result and the observed duality of ring-closure mechanisms are consistent (*3*). Two mechanisms have been proposed for the acid-catalyzed ring-opening reaction. One mechanism occurs by dual-functional catalysis via the cyclic olefin intermediate; the second mechanism proposed involves direct ring opening of methylcyclopentane. Kinetic evidence has been presented which is consistent with a combination of the two acid-catalyzed mechanisms (*5*).

The present investigation was undertaken to elucidate the mechanisms of ring opening, especially that of the acid-catalyzed reaction, in greater detail and to gain additional insight regarding the reverse reaction, paraffin ring closure.

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METHODS

Materials. For all experiments, Phillips pure grade methylcyclopentane, further purified by percolation over activated alumina and drying over Linde 4A molecular sieves, was the feed. Methylcyclopentane prepared in this manner contained less than 10 ppm(w) water. The only detectable hydrocarbon impurity was 0.1% *n*-hexane.

The electrolytic hydrogen used in this investigation was purified further by catalytic removal of any traces of oxygen, carbon monoxide, carbon dioxide, and chloride. A portion of the hydrogen stream was saturated with water and recombined with the dry hydrogen to provide a known and constant water level in the reaction system. In all experiments, water partial pressure was 1.2×10^{-3} atm.

Catalysts. The platinum/silica (Pt/SiO_2) catalyst was prepared by impregnation of Davison silica with a solution of $Pt(NH_3)_4(OH)_2$. Platinum content was 0.71 wt% and surface area was 390 m^2/g. Hydrogen chemisorption, measured by a flow technique, was 16.7 μmol of H_2/g of catalyst (*6*).

The Pt/Al_2O_3 catalyst contained 0.65% platinum on η-alumina. Catalyst chloride content was 0.75 wt% and surface area was 345 m^2/g. To minimize platinum surface area and thereby the catalytic activity of the supported platinum, the catalyst was heat treated in flowing hydrogen at 482°C for 68 hr. By the flow technique, hydrogen chemisorption was 2.5 μmol of H_2/g of catalyst.

The acidic alumina catalyst was prepared by impregnation of η-alumina with 0.5 *N* hydrochloric acid. After drying in a hydrogen flow for 4 hr at 482°C, chloride content was 0.98 wt% and surface area 474 m^2/g.

Procedures. The catalytic conversions reported in this investigation were carried out in a microflow reactor with catalyst loadings of 0.1 g. Hydrocarbon flow rates were from 10 to 100 g/hr (weight-hourly space velocities from 100 to 1000 hr^{-1}). These conditions provided differential or near-differential conversions, thus permitting direct calculation of reaction rates from the observed conversion. The low conversion also permitted a close approach to isothermal conditions and minimized back reactions and product inhibition.

Catalyst decline during a series was corrected for by carrying out the initial and final run periods at identical conditions. The observed reaction rates for intervening run periods were corrected to initial activity level by assuming a linear rate of catalyst decline.

Analyses. The liquid product was collected in a dry-ice trap and analyzed by gas–liquid chromatography at 100°C with a 20-ft column of Dow–Corning silicone oil on firebrick. This column provided a complete analysis of the liquid products, including the methylcyclopentene-1 and -3.

Noncondensable gas was analyzed by mass spectrometry.

RESULTS AND DISCUSSION

The platinum-catalyzed ring opening of methylcyclopentane was investigated first over the mono-functional Pt/SiO_2 catalyst. The results of these experiments define the role of platinum catalysis in ring opening and also provide the necessary data for the separation of platinum catalysis and acid catalysis of ring opening over the dual-functional catalyst.

Platinum-Catalyzed Ring Opening

Results of methylcyclopentane (MCP) ring opening at several hydrogen partial pressures are shown in Table 1. The absence of acidic activity with this catalyst is demonstrated by the absence of benzene formation. Other than the hexanes, the only products formed were equilibrium amounts of the methylcyclopentenes and trace amounts of the C_1–C_5 paraffins. Total ring opening thus can be attributed to

TABLE 1

Platinum-Catalyzed Ring Opening[a]

H_2 partial pressure (atm)	6.8	10.2	13.6	17.0
Ring-opening rate (μmol/sec·g)	9.8	14.0	17.6	19.9
Hexane composition (mol%)				
2-Methylpentane	36.8	39.6	41.0	39.6
3-Methylpentane	24.1	20.9	22.0	22.3
n-Hexane	39.1	39.5	37.0	38.1

[a] 0.71 wt% Pt/SiO_2, 485°C, 3.4 atm MCP.

platinum catalysis. In contrast to numerous other studies of hydrogenolysis, especially of ethane, hydrogen-pressure dependence of ring-opening rate is positive rather than negative (*7*). The conditions of the present study, however, are far removed from conditions of the usual kinetic studies of hydrogenolysis. Although the hydrogen dependence observed in the present study can be described by a Langmuir isotherm, it seems likely that a complete, detailed study of ring opening over a sufficiently wide range of conditions will reveal a more complex kinetic form.

Also shown in Table 1 is the hexane composition obtained from platinum-catalyzed ring opening of methylcylopentane. The relative amounts of 2-methylpentane, 3-methylpentane, and *n*-hexane formed are consistent with a nonselective or statistical breaking of ring carbon–carbon bonds. This result has been observed previously for platinum-catalyzed ring opening at reforming temperatures (*5*, *8*). However, other modes of platinum-catalyzed ring opening have been observed. At different conditions, especially at low temperatures, the methylcyclopentane is ring opened selectively to 2-methylpentane and 3-methylpentane (*8*).

As a final comment on the platinum-catalyzed reaction, it should be noted that the rate of ring opening is directly proportional to platinum surface area. This relationship has been demonstrated for platinum-catalyzed ring closure of paraffins and, from consideration of microscopic reversibility, also should hold for the ring-opening reaction (*3*).

Ring Opening over Mono-Functional Acidic Catalysts

Ring opening in the absence of a metal catalyst is demonstrated by the results of Fig. 1. The major product of this reaction catalyzed by the acidic alumina is the acyclic olefin; however, some saturated products also are formed, presumably by a hydride transfer process. In this connection, it is pertinent to note that methylcyclopentenes were formed in quantities closely corresponding to the amount of hexanes produced. The decrease in ring-opening rate at lower space velocities can be attributed to inhibition by olefinic products.

Although hexanes do not appear to be primary products, their isomer distribution is informative. At high space velocities, *n*-hexane is the major product (61% of the C_6H_{14} product at 1070 WHSV). If it is assumed that the hexane product structure reflects the structure of the initial ring-opened product then it would appear that ring opening occurs by breaking of the 1,2-carbon–carbon bond to give a linear product.

These results suggest that ring opening occurs directly from methylcyclopentane rather than through a methylcyclopentene

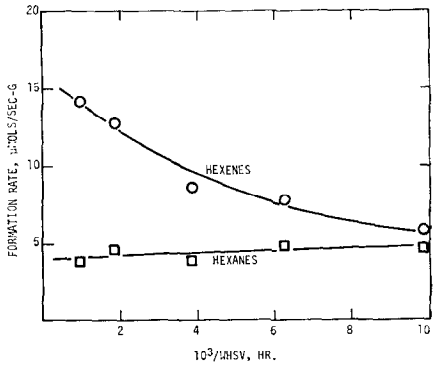


FIG. 1. Ring opening over an acidic alumina at 470°C, 18.0 atm, and 4 hydrogen-to-methylcyclopentane mole ratio.

(MCP$^=$) intermediate. This point was investigated further by ring-opening feeds containing added methylcyclopentene-1 over the mono-functional alumina; results are shown in Fig. 2. For the three cyclic olefin levels investigated, rate decreases markedly with increasing methylcyclopentene concentration. This result is consistent with a mechanism whereby direct methylcyclopentane ring opening is strongly inhibited by methylcyclopentenes. Although a ring-opening reaction of methylcyclopentenes is not necessarily excluded by these results, the rate of such a reaction, at the concentrations available in catalytic reforming, is clearly much lower than the rate of methylcyclopentane ring opening.

Results from the initial and final weight periods of each run series (at 112 WHSV or 8.92×10^{-3} WHSV^{-1}) show no evidence for coking during these experiments. The rates obtained from the final run period (shaded points, Fig. 2) either equal or exceed the rates obtained from the initial run period. The effect of methylcyclopentene thus appears to be inhibitory rather than irreversibly coke forming. In the latter case all three runs would be expected with time to lead to a common, low rate.

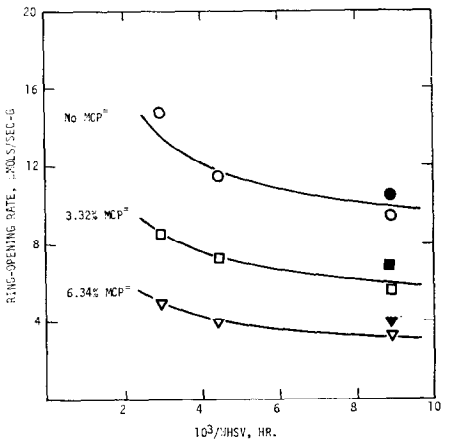


FIG. 2. Methylcyclopentene (MCP$^=$) inhibition of methylcyclopentane ring opening over an acidic alumina at 485°C, 20.4 atm, and 5 hydrogen-to-methylcyclopentane mole ratio.

TABLE 2

Ring Opening over a Platinum/Alumina Reforming Catalyst

P_{H_2} (atm)	Ring-opening rate (μmol/sec·g)[a,b]		
	Total	Pt[c]	Acid[d]
6.8	18.0	1.5	16.5
10.2	25.9	2.1	23.8
13.6	36.5	2.6	33.9
17.0	42.9	3.0	39.9

[a] 3.4 atm methylcyclopentane and 485°C.

[b] Corrected for catalyst decline.

[c] Calculated from the rate over Pt/SiO_2 (Table 1) and the known platinum surface areas of the Pt/SiO_2 and Pt/Al_2O_3 catalysts.

[d] By difference.

Ring Opening over a Dual-Functional Catalyst

Ring opening was investigated over the Pt/Al_2O_3 catalyst which had been heat treated to decrease platinum surface area and thus to minimize platinum-catalyzed ring opening. However, platinum activity was sufficient to maintain methylcyclopentane–methylcyclopentene equilibrium when the hydrogen partial pressure was varied to obtain the results of Table 2. Total ring-opening rate was measured experimentally. From the known ring-opening rate of the Pt/SiO_2 and the known platinum surface areas of the mono-functional catalyst and the dual-functional catalyst, the contribution of platinum catalysis to the total ring-opening rate was calculated. By difference, the acid-catalyzed ring-opening rate was obtained.

Consistent with a direct ring opening of methylcyclopentane inhibited by methylcyclopentenes, ring-opening rate is found to increase as hydrogen partial pressure is increased. Since it is well established that dehydroisomerization of methylcyclopentane to form benzene proceeds through the methylcyclopentene intermediate, it is informative to compare the rates of ring

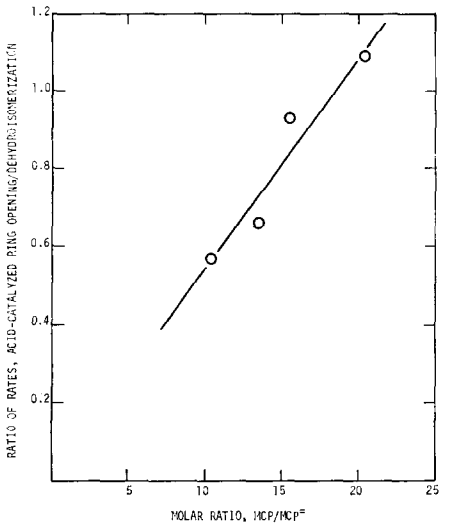


FIG. 3. Comparison of acid-catalyzed ring opening and dehydroisomerization rates at 485°C, 3.4 atm hydrocarbon, and WHSV of 200 hr^{-1}.

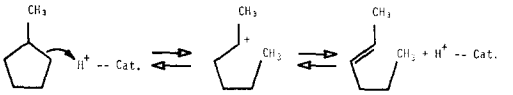
opening and benzene formation at varying hydrogen partial pressures or varying methylcyclopentane/methylcyclopentene ratios (*1*, *2*). Assuming common inhibition terms for the kinetics of the reactions, it is reasonable to expect the following relationship to hold provided methylcyclopentane is ring-opened directly:

$$\frac{\text{rate (ring opening)}}{\text{rate (benzene formation)}} \propto \frac{[\text{MCP}]}{[\text{MCP}^{=}]}.$$

Results shown in Fig. 3 are consistent with the above relationship and support a ring-opening mechanism in which methylcyclopentane is ring opened directly and the cyclic olefin is excluded as an intermediate. Other workers have treated ring-opening data in a similar manner and reached the conclusion that direct methylcyclopentane ring opening is the major reaction pathway but that a second, minor route involves a methylcyclopentene intermediate (*5*). Complete exclusion of methylcyclopentene as an intermediate or assignment of the cyclic olefins as intermediates in a minor, secondary reaction pathway depends on data extrapolation; however, these results, and especially the data showing that methylcyclopentene-1 inhibits ring opening of methylcyclopentane over the acidic alumina (Fig. 2), clearly demonstrate that methylcyclopentene is not an important intermediate in the acid-catalyzed ring opening of methylcyclopentane.

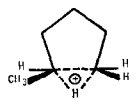
These conclusions also are consistent with the recent results of Selman and Voorhies obtained over a bimetallic reforming catalyst (*9*). They observed that ring-opening selectivity increased relative to benzene selectivity as hydrogen pressure was increased. *n*-Hexane selectivity relative to methylpentanes also increased with hydrogen partial pressure. This is reasonable as the initial ring-opened product from MCP would be expected to be the linear secondary cation; methylpentanes would arise from secondary isomerization reactions whose rate would be dependent on the equilibrium hexene concentration.

The results discussed above lead to the following reaction mechanism for acid-catalyzed methylcyclopentane ring opening:



A ring carbon–carbon bond is cleaved heterolytically by attack of a protonic catalyst site. The secondary acyclic cation thus formed eliminates a proton to give the acyclic olefin with regeneration of the catalyst proton site. This mechanism is simply the reverse of that formulated for ring closure (*3*).

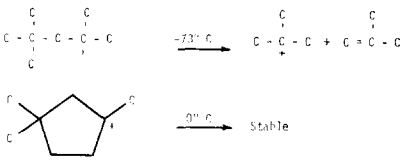
In the ring-opening step leading to the acyclic carbonium ion, a protonated ring structure as formulated below appears to be a plausible representation of the transition state or high-energy intermediate.



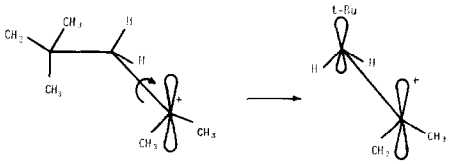
The positive charge is distributed over the

entering proton and the two adjacent carbon atoms. Ring-opening rate should thus be enhanced by alkyl substitution at each of the two carbon atoms. Consistent with this mechanism is the observation that *cis*- and *trans*-1, 2-dimethylcyclopentanes are the major products of heptene-2 ring closure over an acidic alumina (*3*). This formulation of the ring-opening step is analogous to that proposed for acid-catalyzed ring opening of cyclopropane (*10*).

An interesting aspect of this system is that the cyclic olefin is not a significant intermediate in methylcyclopentane ring opening. This conclusion implies that the cyclic carbonium ion formed by protonation of methylcyclopentene does not undergo the β-cleavage reaction characteristic of acyclic carbonium ions. This result appears to be a general phenomenon, however, and is best understood by reference to the work of Brouwer and Hogeveen (*11*). These investigators discuss the following results obtained in a strong-acid (FSO_3H–SbF_5–SO_2ClF) medium:



Even though β-cleavage of the cyclic structure should be strongly favored by formation of a tertiary cation as in the acyclic β-cleavage, the cyclic carbonium ion is remarkably stable. This difference in reactivities is explained by Brouwer and Hogeveen in terms of orbital orientation.



The coplanarity of the vacant p-orbital and the adjacent sp^3 orbital bonding with the leaving group permits overlap of the vacant p-orbital and the incipient electron-pair-containing p-orbital, thus lowering the energy of the transition state of β-cleavage. This orientation of bonds is not possible in the case of the cyclic structure.

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