JOURNAL OF CATALYSIS 73, 361–365 (1982)

Tellurium NaX Zeolites

I. Deuterium Tracer Studies of Cyclohexane Dehydrogenation to Benzene

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Received July 27, 1981; revised October 5, 1981

Deuterium tracers were used to explore the mechanisms of dehydrogenation of six-membered cyclic compounds to benzene over a Te NaX zeolite catalyst. Dehydrogenation of cyclohexane to cyclohexene (and probably to cyclohexadiene) precedes the formation of benzene. A large primary kinetic isotope effect ($k_{C_6H_{12}}/k_{C_6D_{12}} \sim 2.5$ at 400°C) indicates that cleavage of the C–H bonds in cyclohexane is the rate-determining reaction step. Although the presence of gaseous hydrogen is required to maintain catalyst activity, the dehydrogenation rates are the same in H_2 as they are in D_2. Only a limited amount of exchange occurs between D_2 and H atoms in the hydrocarbons. The exchange which is observed probably arises from double bond shift that occurs in the olefins by an addition/abstraction mechanism on a single Te atom containing one adsorbed D atom. Cyclohexane can be formed from cyclohexene by hydrogen transfer from another cyclohexene molecule much more readily than it can be formed by direct saturation with gaseous H_2. Both the dehydrogenation and isomerization sites are probably Te^0 surface atoms.

INTRODUCTION

Early in the 1970s, researchers at the Mobil Research Labs published several papers dealing with a dehydrocyclization (DHC) catalyst which has the unique feature of promoting aromatics formation from *n*-paraffins without any skeletal isomerization in the nonaromatic hydrocarbons (*1–5*). Their work centered mainly on the structural aspects of this catalyst which was prepared from a physical mixture of elemental tellurium and NaX zeolite. However, they published very little information about the mechanisms of these interesting reactions.

In a previous paper (*6*) we described some studies with ^{14}C-labeled tracers that were designed to elucidate the pathways by which the DHC reactions occur. We presented evidence that the reaction proceeds via successive catalytic dehydrogenation steps to olefins, diolefins, and eventually triolefins which cyclize homogeneously in the gas phase. A final catalytic dehydrogenation step produces the aromatics. Even though cyclohexane readily forms benzene over this catalyst, the tracer results clearly demonstrated that neither cyclohexane nor cyclohexene are intermediates in the DHC of *n*-paraffins. In other words, cyclization occurs *after* extensive dehydrogenation.

The purpose of this work was to investigate in more detail some of the mechanistic steps of the dehydrogenation of cyclohexane to benzene. Deuterium tracers served as a focal point of these studies. Unlike acidic oxide catalysts that promote deuterium exchange with hydrocarbons below 100°C (*7, 8*), Te/NaX does not rapidly scramble deuterium with hydrocarbons even at temperatures exceeding 500°C. Experiments with deuterium tracers have allowed us to draw conclusions about the

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0021-9517/82/020361-05$02.00/0

sequence of reaction steps and the rate-limiting process in the overall reaction.

EXPERIMENTAL

The catalyst used for the deuterium exchange reactions was prepared by researchers at Mobil Research and Development Company (*9*). It contained 11% by weight elemental tellurium, the remainder being NaX zeolite (13X) prepared by Linde. These two constituents were physically mixed for 4 hr in a ball-mill. Another catalyst prepared in exactly the same manner in our laboratory was used for the isotope effect experiments. Comparative tests demonstrated that, within an experimental error of ±10%, the two preparations had the same activity for DHC.

All reactions were carried out in a Pyrex high-vacuum recirculation batch reactor described previously (*10, 11*). Catalysts were activated by treatment in recirculating hydrogen or deuterium at 500°C for at least 3 hr. Water was continuously removed from the recirculating gas with a liquid nitrogen trap during activation. Regeneration of the catalyst was not necessary between successive experiments.

Reaction products were analyzed by gas chromatography and/or mass spectrometry. Separation of the components was achieved by injecting a mixture into a 3-m Carbowax 20M/Chromasorb W column thermostated at 120°C; the helium carrier gas flowed through a thermal conductivity detector. The isolated compounds were transferred to a CEC 21-104 mass spectrometer for deuterium analysis. All spectra were taken at low ionization voltages to minimize fragmentation, and all the data were corrected for naturally occurring ^{13}C.

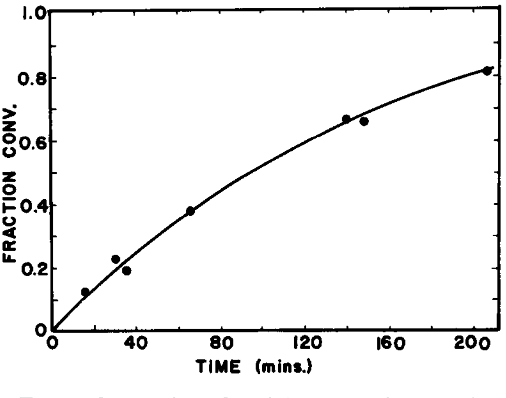


FIG. 1. Conversion of cyclohexane to benzene in a batch recirculation reactor over 100 mg of Te NaX zeolite at 500°C.

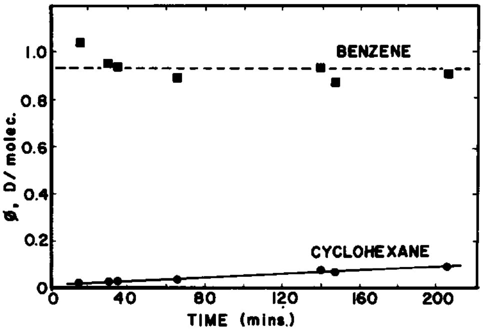


FIG. 2. Deuterium incorporation into cyclohexane and benzene during reaction described in Fig. 1.

RESULTS

1. Cyclohexane Reaction in Presence of D_2

Figure 1 shows the conversion of cyclohexane as a function of time in the recirculation reactor. The initial mixture consisted of 50 Torr (1 Torr = 133.3 N m^{-2}) cyclohexane and 200 Torr D_2. Figure 2 shows the simultaneous incorporation of D atoms into the cyclohexane reactant and the benzene

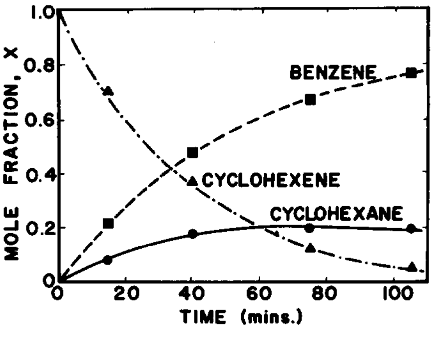


FIG. 3. Hydrocarbon distribution from reaction of cyclohexene and D_2 over 25 mg Te NaX zeolite in a batch recirculation reactor at 440°C.

product as a function of time. ϕ represents the average number of deuterium atoms contained in each molecule (*12*). In every case the deuterium incorporation could be statistically accounted for by the binomial distribution equation (*13, 17*) indicating stepwise exchange.

Figure 2 shows that cyclohexane has very little propensity for deuterium exchange. This result is quite peculiar considering that the reaction takes place at 500°C. The benzene product, however, contains an almost constant amount of deuterium indicating that most deuterium incorporation occurs during the dehydrogenation reactions and not after the benzene product is formed. Another experiment demonstrated that a benzene/D_2 mixture similar to the cyclohexane/D_2 mixture showed very little exchange under the same conditions. Furthermore, a $C_6D_6 : C_6H_6 = 1:1$ mixture reacting in D_2 showed almost no H/D mixing among the benzene molecules (*10*).

2. *Cyclohexene Reaction in Presence of D_2*

Figure 3 shows the hydrocarbon distribution for the cyclohexene reaction in the recirculation reactor as a function of time at 440°C. The initial mixture consisted of 50 Torr cyclohexene and 300 Torr D_2. The dehydrogenation of cyclohexene to benzene as well as the hydrogenation of cyclohexene to cyclohexane occurred simultaneously.

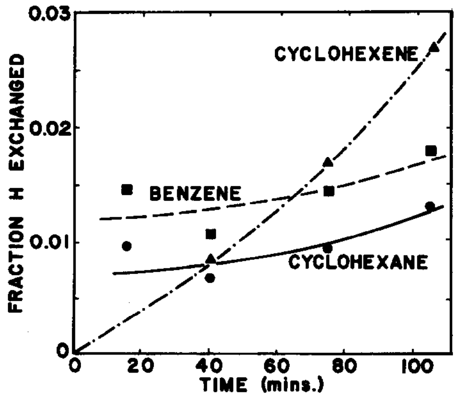


FIG. 4. Deuterium incorporation into hydrocarbons during reaction of cyclohexene and D_2 described in Fig. 3.

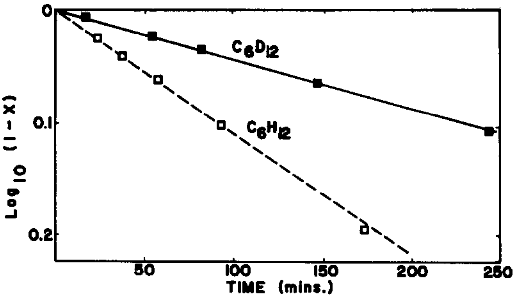


FIG. 5. First-order rate plot for the reaction of perdeuterated cyclohexane (C_6D_{12}) and nondeuterated cyclohexane (C_6H_{12}) over 2.0 g Te NaX zeolite in a recirculation reactor at 400°C. X is the fractional conversion of cyclohexane.

Figure 4 shows the deuterium incorporation into the various species. In this case the *fraction* of the molecules' H atoms that have been replaced by D atoms is plotted as a function of time. Fraction exchange is defined as ϕ/n, where n is the number of (H + D) atoms in the molecule. The very low level of D incorporation (compared with that in Fig. 2) is due to the lower temperature in the cyclohexene experiment, 440 vs 500°C. The temperature had to be reduced considerably to decrease the rate of cyclohexene reaction below the point where mixing in the recirculation reactor could have influenced the results.

3. *Cyclohexane Isotope Effect*

Data presented to this point clearly indicate that rapid scrambling of D_2 with H atoms in the hydrocarbons does not occur. One might then expect that the cleavage of C–H bonds may be the rate-determining step in the dehydrogenation reaction. This thesis was tested by comparing the reactivities of perdeuterated cyclohexane, d_{12} with undeuterated cyclohexane, d_0 in the presence of H_2 and/or D_2.

In one set of experiments, the rate of cyclohexane dehydrogenation was independent of whether the gaseous hydrogen was H_2 or D_2. This demonstrated that there is no isotope effect associated with activation of the hydrogen molecules.

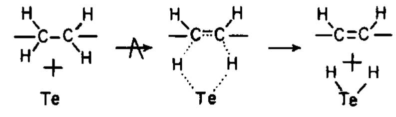
On the other hand, the reaction rate was strongly dependent on the presence of D atoms in the cyclohexane. Figure 5 shows the first-order rate plots obtained for the reactions of C_6H_{12} and C_6D_{12} cyclohexane. In each case the reactant mixture contained 40 Torr of cyclohexane and 300 Torr of D_2. Identical curves were observed when the D_2 was replaced with an equivalent pressure of H_2. Note that the C_6H_{12} reacted almost 2.5 times as fast as did the C_6D_{12} at 400°C. Several experiments were carried out over a limited temperature range near 400°C, and the resulting linear Arrhenius plots indicated apparent activation energies of 40.1 kcal/mole for the C_6H_{12} reaction and 42.9 kcal/mole for C_6D_{12}.

DISCUSSION

To explain all these observations, let us assume the following set of reactions.

$$\begin{array}{rll} CH \rightarrow CH' + H_2, & \text{where } CH = \text{cyclohexane}, & (1)\\ 2CH' \rightleftharpoons CH'' + CH, & CH' = \text{cyclohexene}, & (2)\\ CH' \rightleftharpoons CH'' + H_2, & CH'' = \text{cyclohexadiene}, & (3)\\ CH'' \rightarrow Bz + H_2, & Bz = \text{benzene}. & (4) \end{array}$$

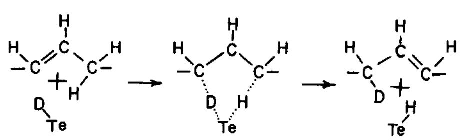
The first reaction must be rate limiting and irreversible to account for the large C_6H_{12}/C_6D_{12} isotope effect (Fig. 5) and the absence of significant D incorporation into the unreacted CH (Fig. 2). This step likely involves the simultaneous removal of *two* H atoms, since the observed isotope effect is larger than one would reasonably expect for a single C–H cleavage at this high temperature of 400°C (*14*). The two atoms may become attached to a single Te^0 atom, viz.,



with the olefin and H_2 being desorbed into the gas phase to regenerate the site. Supported tellurium has been shown to adsorb up to 2 H/Te (*4*, *15*). In a similar way, steps (3) and (4) produce cyclohexadiene and finally benzene. Both steps are relatively facile with the ease of reaction increasing in the order (3) < (4). The last step occurs so rapidly that no cyclohexadiene was observed among the products in any of these experiments. It must also be essentially irreversible since almost no D is scrambled into the benzene when a benzene/D_2 mixture is recirculated over the catalyst at 500°C (*10*).

The hydrogen transfer reaction step (2) must be invoked to account for the formation of *both* cyclohexane and cyclohexadiene (which is manifested among the products as benzene due to the very rapid step (4)) which are formed from cyclohexene (Fig. 4). The tracer results shown in Fig. 4 rule out the possibility that a significant fraction of the cyclohexane is formed by the reversal of step (1). Had this occurred, the excess gaseous D_2 would have led to the formation of cyclohexane $C_6H_{10}D_2$, which would have had a "fractional exchange" value of 0.167; the observed value in Fig. 5 is less than 0.01.

As also seen in Fig. 4, there is considerable D incorporation into unreacted cyclohexene when it is circulated over the catalyst in presence of D_2. This exchange may well occur through an olefin isomerization (double bond shift around the ring) mechanism on a Te site that contains one D atom, viz.,



Only molecules capable of both accepting and donating hydrogen atoms from a different C atom can undergo exchange by such a push–pull mechanism (*16*). Thus, cyclohexane (which has no unsaturated bonds to accept an H atom) and benzene (which cannot donate an atom from the third C removed) will not be expected to undergo exchange. This is consistent with the observations. Compared with the dehydrogenation, this exchange reaction should be relatively fast since only a single C–H bond is broken rather than the two required for dehydrogenation.

Additional information about the nature of the active sites for these reactions is described in the second paper in this series (*15*).

ACKNOWLEDGMENTS

The authors are grateful to Phillips Petroleum Company for the Phillips Fellowship (GLP) and the National Science Foundation (Grants GP-39482 and CHE-77-10541) for support of the US/USSR Scientific Exchange Program (ZRI). We also thank the Mobil Corporation for providing the catalyst samples and the Robert A. Welch Foundation for equipment and supplies.

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