JOURNAL OF CATALYSIS **162,** 134–137 (1996)
ARTICLE NO. 0267

NOTE

Reaction Pathway for Alkane Dehydrocyclization

Naphtha reforming to produce high octane gasoline is an important process (1). Many reaction mechanisms are involved in this process. For example, the study of the fundamentals of this process led to the concept of bi- or poly-functional catalysis (2). This permits an alkane to be dehydrogenated to an alkene on one function, the metal, and for the alkene to then migrate to a second function, the acid site, where it is isomerized to a branched alkene, and then to be converted to a branched alkane of higher octane number by migration to and hydrogenation on the metallic function. Alkane dehydrocyclization is another reaction that is involved in the process and has been widely studied since its discovery in the 1930s (3–7). Initially it was believed that the alkane underwent cyclization to form an adsorbed cycloalkane (e.g., see Refs. (8–11)); however, more recently the view of a series of dehydrogenation steps to produce a triene that cyclizes either in the adsorbed or in the gaseous phase has become widely accepted (12–23).

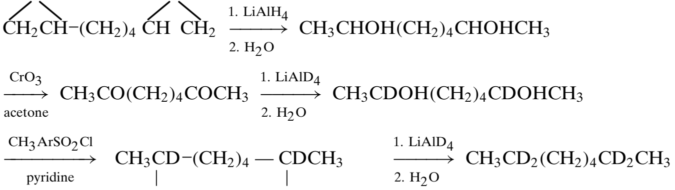
The dehydrocyclization of *n*-octane can produce two aromatics, ethylbenzene and *ortho*-xylene, by a mechanism that includes the direct formation of a six-carbon ring (8, 9). Since there are two modes of forming ethylbenzene (EB) and only one mode for *ortho*-xylene (OX) (Scheme I), the products that result from a mechanism with equal probability for the three ring forming pathways would contain 33% OX and 67% EB. Values approaching this anticipated distribution of aromatics have been reported (24) but Pt supported on a nonacidic alumina or silica usually produces a ratio of EB : OX = 1 : 1 (25–27). With both silica and alumina supports, the inclusion of tin in the catalyst formulation results in a shift in the selectivity for the aromatics that are produced to favor OX. Thus, for an alumina supported catalyst with Sn : Pt = 4 : 1, the EB : OX ratio approaches 1 : 2. This change in EB : OX ratio to favor OX can be explained if it is assumed that the presence of tin alters the cyclization properties of the Pt catalyst to favor rupture of the weaker secondary C–H bond (of the CH_2 groups) over that of the stronger primary C–H bond (of the CH_3 group) that must be broken to form EB (28).

More recently it has been concluded, based on the nearly equal relative conversions of the two reactants of an alkane/cycloalkane mixture, that irreversible adsorption or desorption was the rate limiting step for the cyclization process (29). Furthermore, the lack of exchange in the reactants and significant exchange of H/D in the products during conversion of deuterium labeled reactants show that adsorption is the irreversible step (30).

The conversion of an equimolar mixture of C_8H_{18} and C_8D_{18} produced a large kinetic isotope effect, k_H/k_D, of 3.5 when the mixture was converted with the Pt–SiO_2 catalyst at 482°C and 1 atm pressure (31). There was essentially no H/D exchange between the two reactants or of the reactants with the gaseous hydrogen isotopic mixture; however, there was extensive H/D exchange in the aromatic products to produce the distribution of isotopomers expected for isotopic equilibration. The ratio of ethylbenzene (EB) to *ortho*-xylene (OX) in the product was about EB : OX = 1 : 1.

If adsorption of the reactant occurs by rupture of the C–H bond involved in directly forming the six-carbon ring, the large kinetic isotope effect observed for conversion of *n*-octane (31) should require a change from EB : OX = 1 : 1 for the aromatic product distribution that results from the conversion of a suitably labeled octane. 2,2,7,7-*tetra*-Deutero-octane is a suitable reactant for this purpose. If the aromatic distribution is determined by (i) the location of initial adsorption and (ii) a kinetic isotope effect of $k_H/k_D = 3.5$ as observed earlier (31), the EB : OX ratio should change from 1 : 1 for unlabeled *n*-octane to 3.5 : 1 for the labeled *n*-octane. This change is anticipated because of the large kinetic isotope effect for the rupture of a C–D bond that is required for pathway III in Scheme I to produce OX from 2,2,7,7-*tetra*-deutero-octane.

2,2,7,7-*Tetradeutero*octane was synthesized using the following reaction sequence:



NMR (^1H and ^2H) analyses indicate that the synthesized octane was 98^+% 2,2,7,7-tetradeuterooctane. The catalyst was prepared by impregnating silica (W. R. Grace; 340 m^2/g) with chloroplatinic acid followed by calcining in air and then reducing in hydrogen at 500°C for 4 h. The reduction was effected *in situ* in the reactor immediately prior to its use

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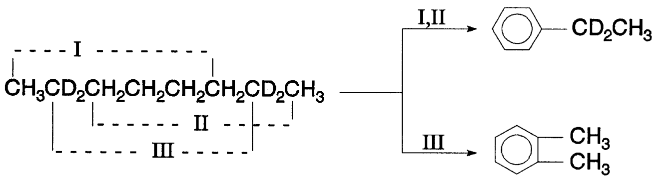


SCHEME I

for the catalytic conversions. Previous studies showed that a nonacidic alumina, even without added Pt, catalyzed significant H/D exchange with hydrocarbons at 482°C, whereas the silica chosen for this study did not (30). The conversion was effected at 482°C and 1 atm pressure without an added gas. Conversions were measured using a GC with a DB-5 column. The deuterium contents of the liquid products were determined by GC/MS using 70 eV ionization voltage. The relative intensities of the parent peaks, corrected for ^{13}C natural abundance, were used to calculate the average number and the number distribution of deuterium in the isotopomers.

Using the EB : OX = 1 : 1 product distribution obtained for the conversion of unlabeled *n*-octane and a value of $k_H/k_D = 3.5$, the aromatic product distribution should be EB : OX = 3.5 : 1 for the aromatization of 2,2,7,7-*tetra*deutero-octane. However, the average of the aromatic distribution in the products collected at the end of each hour during the 6-h run was found to be EB : OX = 1 : 1.2. This is about the same EB : OX ratio as was obtained with unlabeled *n*-octane with this catalyst. Thus, the anticipated isotope effect for the cyclization pathways was not observed. In addition, the number distribution of deuterium of the isotopomers of EB and OX was essentially the same whereas, based upon reaction pathways in Scheme I, it is expected that EB would contain more deuterium than OX.

The results of this study provide additional mechanistic information about the dehydrocyclization of an *n*-alkane to produce aromatics. The reaction coordinate diagram advanced to account for the observation of irreversible adsorption (30) should be modified to account for the present results. Thus, a region labeled H/D exchange in Fig. 1 has been added to the reaction coordinate of Ref. (30), which in turn is a modification of a recently published reaction coordinate in (32). In Ref. (30) it was speculated that the first chemisorbed species (I) was an adsorbed alkyl group, formed in a step that exhibits a kinetic isotope effect, and structure II was an alkylidene group. It is emphasized that direct evidence to confirm these structures is not available; however, for the convenience of discussion we shall refer to these structures. Thus, an overall pathway that accounts for the kinetic isotope effect, the extensive H/D exchange in the aromatic products, and the absence of a kinetic isotope effect in determining the selectivity for aromatic products from the conversion of 2,2,7-*tetra*-deutero-octane is presented in Scheme II, where g is the gas phase, a is the adsorbed phase, and p and c are physical and chemical, respectively.

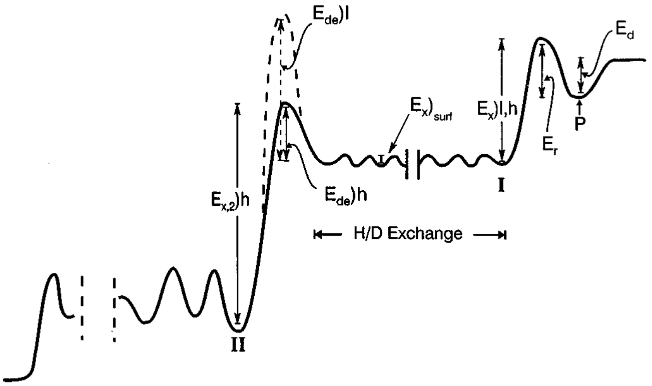
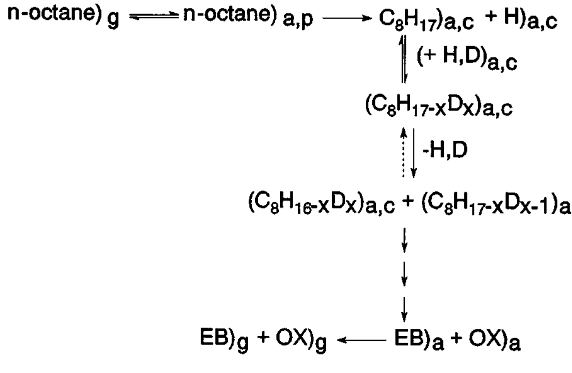


FIG. 1. Schematic reaction coordinate for the conversion of an alkane and H/D exchange at low (l) and high (h) temperature [I, R·; II, Ri; E_d, desorption activation energy; P, precursor physically adsorbed state; E_r, activation energy for rate determining step; $E_x)$l,h activation energy for low, high temperature desorption of H/D exchanged products; $E_x)_{surf}$, activation energy for H/D exchange in adsorbed species; $E_{de})$l and $E_{de})$h, activation energy for second dehydrogenation at low and high temperature, respectively; and $E_{x,2})$h, activation energy for exchange in second step].

There should be a kinetic isotope for the conversion of 2,2,7,7-*tetra*deutero-octane relative to *n*-octane; however, the limited amount of the deuterium isotopomer that was available prevented us from making this measurement. Nevertheless, the kinetic isotope effect is established for alkane dehydrocyclization so that the only question that could be answered in this study is whether the kinetic isotope effect, k_H/k_D, is determined by rupture of the C–H/C–D bonds indicated in Scheme I for the three cyclization pathways (i.e., 4/10) or by the total C–H bonds in *n*-octane (i.e., 4/18). The presence of an overall kinetic isotope effect for dehydrocyclization (30, 31) and the absence of any isotope effect in determining the selectivity for the formation of aromatics are consistent with a series of exchange steps following the formation of I (the C_7H_{17}



SCHEME II

radical) to approach a statistical H/D distribution with respect to each carbon position in the hydrocarbon chain prior to the step that produces the alkylidene intermediate (II) or the rapid exchange in the intermediate (II) prior to cyclization. The H/D exchange thus eliminates any isotope effect in defining the aromatic product. The H/D exchange must precede the step that determines whether EB or OX is formed; otherwise, there would be a measurable difference in the EB : OX ratios for C_8H_{18} and $C_8H_{14}D_4$.

The present results cannot define whether aromatization proceeds by: (1) cyclization to a six-carbon ring followed by dehydrogenation or (2) dehydrogenation to a diene and/or triene prior to cyclization and subsequent dehydrogenation to produce aromatics. However, the data presented in Refs. (30) and (31) together with those in this study show that irreversible adsorption occurs at *n*-alkane pressures of 1 atm or lower. This means that those tracer studies (12–23) where a potential intermediate compound, labeled with ^{13}C or ^{14}C, was added with the alkane or the cycloalkane cannot produce data which can be utilized to make a reliable determination of mechanistic pathways for dehydrocyclization.

The dehydrocyclization studies using deuterium as a label are consistent with the initial adsorption to a precursor state (30). In a competitive conversion of an alkane/naphthane or C_nH_{2n+2}/C_nD_{2n+2} mixture, the relative concentrations in the precursor state, P, are related almost directly to the relative concentrations in the gas phase; this has been shown to be true for a variety of alkane and alkane/naphthene mixtures (29). The chemisorption to form the intermediate I, assumed to be R·, is a reversible reaction at low ($< \sim 400°C$) temperature where H/D exchange readily occurs (31). However, at higher temperatures ($> \sim 460°C$), the H/D exchange is essentially negligible in comparison to the dehydrocyclization reaction. To explain this, it is assumed that the activation energy to form the chemisorbed state II (assumed to be R**:**) is lower at high temperatures ((E_{de})h) than at low temperatures ((E_{de})l); furthermore, the order of the activation energies is: $E_{\mathrm{de}})\mathrm{l} > E_{\mathrm{x}})\mathrm{l,h} > E_{\mathrm{de}})\mathrm{h}$ in order to account for the differences in H/D exchange rates at low and high temperatures. One could obtain a similar experimental result if E_r became much larger at the higher temperature than it is for the lower temperature; however, this is considered to be less likely. The curve in Fig. 1 shows a common intermediate (I) and different heights for the activation barrier to intermediate (II); a similar change in events could occur if the stability of intermediate I was temperature dependent and the activation barrier was temperature dependent. The present data are not applicable in defining which of these two possibilities, if either, are correct. In the initial version of our Fig. 1 (30, 31) the region labeled H/D exchange in the present figure was not included. However, if H/D exchange does not occur prior to the conversion from state I to state II, there must be an isotope effect for determining the formation of the aromatics and this was not found to be the case. Thus, the H/D exchange to produce a distribution of H and D in the chemisorbed isotopomers is rapid compared to chemisorption to state II.

In summary, the results of the present tracer study are consistent with a dehydrocyclization pathway that includes a rate determining step that involves irreversible adsorption of the hydrocarbon and this introduces a large kinetic isotope effect. Following chemisorption, the chemical specificity of the hydrogens in the chemisorbed alkane species is lost due to hydrogen migration and/or exchange steps that cause H/D exchange to produce a, or nearly a, statistical distribution of hydrogen isotopes within the intermediate adsorbed on the catalyst surface. The rapid H/D exchange of the irreversibly adsorbed species eliminates the possibility of defining the timing of the cyclization step. Furthermore, the irreversible nature of chemisorption at temperatures of about 480°C and higher preclude the use of the results of the competitive conversion of isotopically labeled and unlabeled compounds for defining the identity of the species that undergoes the cyclization step. The present data do, however, clearly demonstrate that the initial dissociative adsorption does not determine the aromatic product distribution.

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Received March 2, 1995; revised April 29, 1996; accepted May 1, 1996