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Dehydrocyclization of *n*-Octane: Role of Alkene Intermediates in the Reaction Mechanism

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The objective of the present study is to define whether alkenes, formed during alkane dehydrocyclization, are reconverted to the alkane and to elucidate the role of alkanes in the dehydrocyclization mechanism. In a competitive conversion, an alkene is converted much more rapidly than *n*-octane (C_8D_{18}). The lack of H/D exchange indicates that the adsorption of the *n*-octane is essentially irreversible, whereas some H/D exchange in the added alkene suggests that alkene desorption does occur; however, the added alkene does not desorb as the alkane, in conformity with irreversible adsorption of the alkane. The results demonstrate that the addition of a labeled alkene cannot provide data to establish the validity of the sequential dehydrogenation reaction pathway. © 1997 Academic Press

INTRODUCTION

One of the widely accepted mechanisms for the dehydrocyclization of alkanes features the formation of aromatics in a pathway that involves sequential dehydrogenation reactions—the alkene, diene, and triene [e.g., (1)]. The triene then undergoes cyclization, either on the catalyst surface or in the gas phase, and subsequent dehydrogenation to form an aromatic product. The major support for this mechanism comes from the addition of a ^{14}C-labeled compound that is a possible intermediate in the reaction pathway and to then infer the role of the added compound in the reaction mechanism from the isotope distribution in the products following the reaction (1–22). Some contend that only adsorbed trienes undergo cyclization and that this may be limited to the *cis–cis* isomer [e.g., (23)]. Other support for the sequential dehydrogenation mechanism comes from the dependence of the conversion of an alkane on the partial pressure of hydrogen; these data are consistent with, but do not require, a sequential dehydrogenation mechanism [e.g., (18–22, 24)]. On the other hand, results from the conversion of mixtures of an alkane and cycloalkane led to the conclusion that the slow step of the reaction was either the irreversible adsorption of the reactant(s) or the desorption of the aromatic product(s) (25). Later studies using a mixture of deuterium-labeled and unlabeled compounds produced results that were consistent with the adsorption step being irreversible at the temperature (482°C) used for dehydrocyclization (26). Thus, the aromatic products had H/D ratios that were consistent with significant exchange on the surface to a near or actual equilibration of H/D atoms prior to the desorption as the aromatics. On the other hand, the unconverted alkane and cycloalkane molecules did not undergo H/D exchange. These are the results expected if irreversible adsorption of the reactant(s) was the rate-limiting step for dehydrocyclization. When the Pt–SiO_2 catalyst contained tin, there was some exchange of the reactants as well as the aromatic products; this was considered to be due to the tin altering the adsorption character of the platinum so that the adsorption–desorption equilibrium of the alkane reactant was at least partially established (27). Additional evidence to support the view that adsorption was the slow step of the dehydrocyclization mechanism was the observation of a large kinetic isotope effect for the conversion of *n*-octane using a Pt–SiO_2 catalyst at 482°C (28, 29).

In view of the recent results obtained with the deuterium tracer studies, it is of interest to learn more about the competitive conversion of a mixture containing an alkene and an alkane. If adsorption of the alkane and the alkene requires C–H bond rupture, the relative conversion of each reactant should be similar to their relative molar ratio in the feed (25, 26). On the other hand, as seems likely, the alkene adsorption may be favored because it involves the C=C double bond. It is also of interest to learn whether the adsorbed olefin will desorb as an alkane or will only be converted to aromatic products. We have therefore converted mixtures of perdeuteriooctane and either undeuterated 1-octene or 1-heptene with a Pt–SiO_2 catalyst at 482°C.

EXPERIMENTAL

The reaction was carried out in a conventional flow apparatus described previously (29). Runs were effected at atmospheric pressure and a liquid hourly space velocity (LHSV) of 1.0. Liquid samples were collected at intervals and analyzed by gas chromatography using a DB-5 or SPB-5 column. The deuterium content was obtained using

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a GC/MS operated at 70 eV. Because of an inverse isotope effect, it is possible to separate highly deuterated and undeuterated alkane hydrocarbons (30, 31).

The unlabeled organic compounds and the C_8D_{18} were purchased from Aldrich Chemical Company, Inc. All of the reagents used in this study were 99% pure or higher and were used without further purification.

$Pt–SiO_2$ (1 wt% Pt) was prepared by the incipient wetness technique using an aqueous solution of H_2PtCl_6 and SiO_2 (200 mesh, 300 m^2/g) obtained from W. R. Grace. The dried catalyst was calcined overnight in air at 400°C and then reduced in flowing hydrogen at 482°C for at least 4 h.

RESULTS AND DISCUSSION

The conversions were effected using essentially an equal molar mixture of perdeuteriooctane (C_8D_{18}) and either 1-heptene or 1-octene. The results for the runs with a mixture of C_8D_{18} (43 mol%) and 1-heptene (53 mol%) (Table 1) indicate that the conversion of 1-heptene is much (at least 50 times) greater than that of *n*-octane-d_{18}. This is in contrast to the results obtained when an equal molar mixture of *n*-octane and methylcyclohexane was converted since, in this instance, the methylcyclohexane conversion was retarded by the presence of *n*-octane. In addition, the added 1-heptene undergoes extensive isomerization to other *n*-heptene isomers. More importantly, about 15% of unidentified cracked products as well as aromatics with greater than the C_8-carbon numbers were formed during the conversion of the mixture that contained a 1-alkene. In contrast, during the run with the *n*-octane and methylcyclohexane mixture, only traces of the cracked products and C_8^+ aromatics were formed. Thus, the cracked products and the C_8^+ aromatics were formed by reactions that involved the added 1-heptene.

If competitive, irreversible adsorption of both the alkane and the alkene by C–H bond breaking was the rate-limiting step, the *n*-octane and 1-alkene should have undergone essentially the same extent of conversion. If the kinetic isotope effect was involved in the rate-limiting step the conversion of the 1-alkene should have been about three times that of the *n*-octane-d_{18}. Since these expectations were not found, it is concluded that the activated adsorption of the alkene that leads to the production of aromatics occurs primarily through interaction of the C=C double bond with the Pt metal surface. In addition, the adsorption of the alkene by this mode is more rapid than the adsorption of *n*-octane by rupture of a C–H bond.

TABLE 1

Distribution of Products from the Dehydrocyclization of a Mixture of Octane-d_{18} and 1-Heptene Using a Pt/SiO_2 at 482°C and 1 atm

Compound	wt%
Benzene	0.96
Heptene isomers	17.92
Toluene	10.30
Octane-d_{18}	53.98
Ethylbenzene	0.84
o-Xylene	0.83
Others	15.17

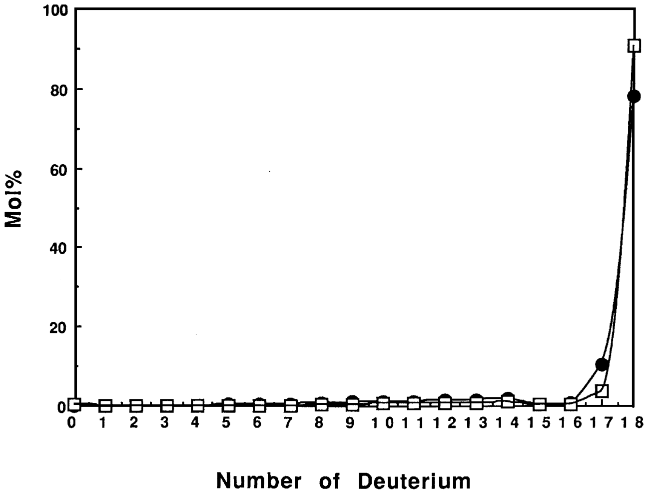

FIG. 1. Deuterium distribution in the unconverted *n*-octane (C_8D_{18}) from the conversion of a mixture of *n*-octane-d_{18} and 1-heptene (●) and of *n*-octane-d_{18} and 1-octene (□).

If the alkene is formed as an intermediate during the dehydrocyclization of the alkane, then the behavior of the intermediate alkene must be different from the behavior of that formed when an alkene is adsorbed from the gas-phase feed. The large amounts (15%) of cracked products formed during the run that contained 1-heptene and the minor amounts in the case of the conversion of the alkane alone indicate that the alkene could not be formed as a gas-phase intermediate leading subsequently to the formation of the aromatic products. In other words, it appears alkene formation is in competition with aromatization and that alkenes are not a gas-phase intermediate in the formation of the dominant fraction of the aromatics.

The unconverted C_8D_{18} undergoes essentially no H/D exchange in this study (Fig. 1). This is consistent with our previous studies (25–27) and with the view that adsorption is essentially irreversible at this reaction temperature (482°C). Extensive H/D exchange occurred in the isomerized heptenes as is evident from the data shown in Table 2. This exchange could have occurred during the double-bond isomerization process or it could be the result of reversible adsorption modes in the case of the alkene. This result

TABLE 2

Deuterium Distribution of Deuterium in the Heptene Isomers Produced during the Conversion of a Mixture of C_8D_{18} and 1-Heptene with a Pt–SiO_2 Catalyst at 482°C and 1 atm

Isotopomer	mol%
d_0	47
d_1	26
d_2	14
d_3	7
d_4	3
d_5	2
d_6	1
d_8	0.8

makes it apparent that at least a part of the adsorption of the alkene occurs by a mode that differs from that of the alkane.

The distribution of H in the unconverted *n*-octane is similar in the runs when the added alkene was 1-heptene or 1-octene (Fig. 1). This result demonstrates that the adsorbed 1-octene is not hydrogenated to *n*-octane that subsequently desorbs.

It has been shown that the rate-determining step of dehydrocyclization of an alkane is the adsorption of the reactant. To define the details of this step and the ones that follow is of great interest but presents a demanding experimental situation. Without question, the formation of the aromatic product requires the formation of carbon–carbon unsaturation (C=C double-bond formation) at some stage of the pathway. Furthermore, it is reasonable to assume that the aromatic could result by consecutive dehydrogenation steps that produce the ene, diene, triene, and then a six-carbon ring structure; however, since the formation of any carbon–carbon double bond follows the rate-limiting step which exhibits a large kinetic isotope effect, the addition of labeled unsaturated suspected reaction intermediates cannot validate the proposed "triene mechanism." While the results of studies in which a ^{13}C- or ^{14}C-labeled ene, diene, or triene compound was added to an alkane reactant may be of interest, it appears that these results cannot be used to define the mechanism for dehydrocyclization of alkanes.

The deuterium isotopomers of the ethylbenzene produced during the conversion of C_8D_{18} and 1-heptene exhibit a near-Gaussian distribution (Fig. 2). In this case, the ethylbenzene was formed from the C_8D_{18} and the H was incorporated by H/D exchange on the surface from H derived from the conversion of 1-heptene. In the case of the competitive conversion of C_8D_{18} and 1-octene, the ethylbenzene was formed from both reactants, and the larger portion of the ethylbenzene was derived from 1-octene.

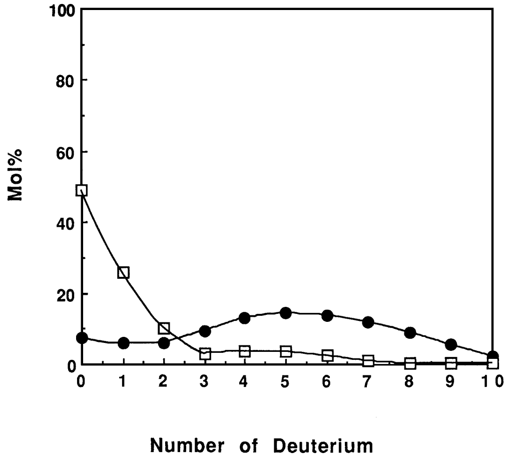

FIG. 2. Deuterium distribution in the ethylbenzene product from the conversion of a mixture of *n*-octane-d_{18} and 1-heptene (●) and of *n*-octane-d_{18} and 1-octene (□).

The deuterium distribution in the *ortho*-xylene product is essentially the same as was obtained for ethylbenzene (Fig. 3). Thus, any H/D exchange of the adsorbed species prior to, during, or following the cyclization step is the same for the species that leads to these two aromatic products.

In summary, the data for the conversion of an alkene/alkane mixture are consistent with a mechanism that involves irreversible adsorption of the alkane reactant. Based on this study, it appears that the alkene is initially adsorbed due to the interaction between the C=C double bond and the Pt surface. The results of this study, and previous studies that used added isotopically labeled suspected intermediates, do not provide data that can distinguish between mechanisms that involve cyclization followed by dehydrogenation and those that involve dehydrogenation to a diene or triene followed by cyclization.

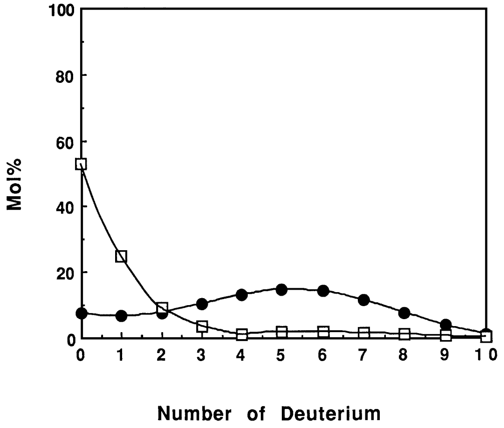

FIG. 3. Deuterium distribution in the *o*-xylene from the conversion of a mixture of *n*-octane-d_{18} and 1-heptene (●) and of *n*-octane-d_{18} and 1-octene (□).

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