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Tracer Studies of Acid-Catalyzed Reactions

IX. Exchange of D_2 with Noncyclic Olefins over Alumina

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The mechanism of deuterium exchange with hydrogen atoms in small noncyclic olefins has been investigated over a pure alumina catalyst. In reactions of 1-butene, *cis*-2-butene, isobutene, and *tert*-butylethylene with D_2, only the vinyl C–H bonds underwent exchange below 100°C. The exchange occurred most readily with terminal vinyl hydrogen atoms of α-olefins and probably involved a dissociative mechanism on acid–base or ion-pair sites on the dehydroxylated surface. Isomerization and exchange were independent processes. NMR studies of the products obtained at two different temperatures showed that the activation energy for the exchange reaction in isobutene was considerably lower than that for double-bond migration.

INTRODUCTION

In earlier work, Larson, Hightower, and Hall (*1*) demonstrated that hydrogen atoms in noncyclic olefins and cyclopropane could be replaced with deuterium atoms by exchange with D_2 over a pure alumina catalyst at room temperature. This process was used successfully to prepare perdeuteroolefins from C_2 to C_5 having isotopic purities of greater than 98%. Neither saturation nor skeletal rearrangements occurred to an appreciable extent below 200°, although both double-bond migration and cis–trans rotation did accompany the exchange.

Kemball (*2*) has clearly demonstrated the usefulness of D_2 exchange reactions to investigate interactions of hydrocarbons with metal surfaces, and Burwell (*3*) and co-workers have applied similar techniques to study exchange reactions over several oxides, including chromia-alumina. The present authors have previously shown that whereas the isomerization reactions of the *n*-butenes over silica-alumina could be described satisfactorily by a single carbonium ion common intermediate, the same reactions over alumina could not (*4*). Moreover, over silica-alumina carbonaceous residues appeared to provide sites for reaction; over alumina, residue did not form extensively and the relatively small amount which did, did not appear to function as a catalytic site. A large primary isotope effect was found over alumina for the isomerization reactions, suggesting that a C–H or C–D bond was ruptured in the rate-determining step. The present work was undertaken to learn more about the intermediates which form when olefins are adsorbed on alumina.

EXPERIMENTAL

Catalyst. The alumina was the same GA-48 preparation used earlier (*1*). It was prepared by the MK Research and Development Co. of Pittsburgh, Pennsylvania from the neutral hydrolysis of very pure aluminum isopropoxide. Metallic impurities were less than 50 ppm, and its surface area was 158 m^2/g. Pretreatment included slowly heating under vacuum to 530°, treatment with O_2 for 2 hr, and overnight evacuation to a "sticking" vacuum at the same temperature. No polymerization or catalyst deactivation, such as that which occurs on

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silica-alumina, was observed, and for this reason the same catalyst sample could be reused without reactivation. Alumina catalysts are, however, very sensitive to small amounts of poisons (particularly H_2O). Therefore, it was always given the standard pretreatment with oxygen and vacuum before each experiment to assure attainment of the same initial surface condition, and its activity was consistently reproducible.

Reactants. All the butenes were Phillips Research grade shown by GLC to be better than 99.2% pure. Each was twice distilled from −78° to −195° and thoroughly outgassed before use. The *tert*-butylethylene (Columbia Organic Chemicals Co., Inc.) was also distilled from −30° to −195° and outgassed. Deuterium (Liquid Carbonics Div., General Dynamics Corp.) had an isotopic purity of 99.5% and was dried by passage through a trap filled with glass beads which was thermostated at −195°.

Equipment. Two types of reactors were used. A static reactor, which had a total volume of about 300 cc, was made from a 250-cc spherical flask connected through a stopcock and standard taper joint to a BET-type vacuum system. Catalyst samples were placed at the bottom of a 20-mm od well which extended 4 inches below the spherical bulb and which could be surrounded by a furnace or bath during pretreatment or reaction.

The recirculation reactor which consisted of a closed loop of total volume of about 1 liter contained a vertical catalyst tube, a mixing chamber which made up about 80% of the entire volume of the system, a small trap filled with glass beads, an all-glass circulation pump, and provisions for removing samples by expansion into evacuated tubes.

Butene isomers were separated by GLC using a $\frac{1}{4}''$ × 30 ft propylene carbonate-on-Chromosorb W column thermostated at 0°. The separated compounds were trapped at −195° and distilled before analysis.

Mass spectral analyses for deuterium content were made using a 6-inch radius magnetic sector Nuclide instrument. Ionizing voltages were kept sufficiently low (below 12 eV) to prevent hydrogen fragmentation exceeding 10%, and analyses were based on parent peak heights after corrections had been made for ^{13}C isotopic impurities and for fragmentation.

A high-resolution Varian A-60 NMR spectrometer was used for quantitative determination of the amounts and location of deuterium in various parts of the butene molecules. Integrated intensities of peaks in the NMR spectra of partially exchanged hydrocarbons were compared with intensities of the same peaks in identical samples of undeuterated material. From 24 to 45 cc NTP of the gases were dissolved in 0.5 cc of carbon tetrachloride and sealed into standard NMR sample tubes. Tetramethylsilane was used as an internal reference, and the spectra were run at 37°.

Procedures. A known pressure of olefin was frozen into the reactor system, and then a measured pressure of D_2 was admitted. The static reactor was rapidly warmed to reaction temperature; samples were periodically withdrawn by expansion for analysis. Convection currents within the reactor provided mixing. In the circulation system, each hydrocarbon-D_2 mixture was first thoroughly mixed before being exposed to the catalyst at reaction temperature. Again samples were removed by expansion. The reaction could be stopped at any time simply by bypassing the catalyst by stopcock manipulation; the hydrocarbon could be separated from the H_2–HD–D_2 mixture by collection in the trap at −195° followed by evacuation.

RESULTS

n-Butenes and D_2

Results of two experiments in which 500 torr mixtures of 1-butene and D_2 or *cis*-2-butene and D_2 in ratios of 100:400 were reacted over alumina in a static reactor at room temperature are shown in Figs. 1 and 2. The ordinates represent the average amount of deuterium incorporated into each butene isomer as calculated by the equation

$$\text{D atoms/molecule} = \Sigma i d_i \qquad (1)$$

where d_i represents the fraction of the molecules containing i deuterium atoms.

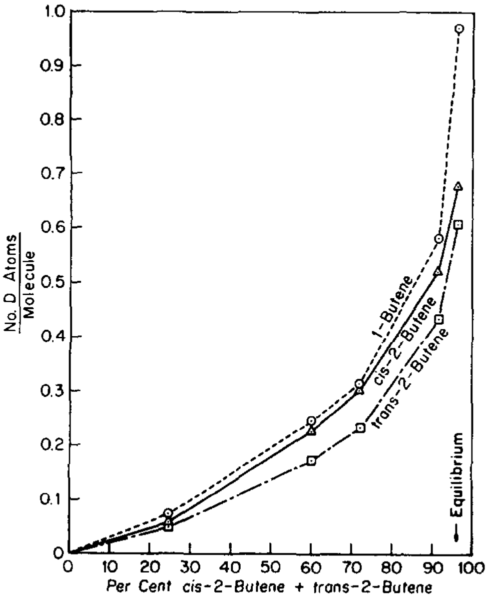


FIG. 1. Deuterium concentration in butenes during reaction of a 1-butene: D_2 = 101:400 torr mixture over 50 mg of GA-48 alumina in a static reactor at 25°C.

The percent conversions along the abscissas are simply the sum of the percentages of the isomerized product isomers. The highest possible conversion for each reactant isomer is 100 minus the percent of that isomer at equilibrium.

When 1-butene was the reactant hydrocarbon (Fig. 1), its deuterium content at all conversion levels was greater than that for either of the 2-butene products. Furthermore, the deuterium in the cis isomer always exceeded that in the trans. The zero conversion intercept for all species was zero.

In the case of *cis*-2-butene reactant (Fig. 2), the exchange into the product 1-butene was considerably greater than for the other isomers. The deuterium concentration in the cis isomer did not differ significantly from that in the trans.

The presence of D_2 affected neither the rate of 1-butene isomerization nor the initial cis–trans ratio; the isomerization reaction proceeded as though the D_2 were an inert diluent. The exchange rate was a function of the olefin: D_2 ratio, however, increasing relative to the isomerization as this ratio was decreased at constant temperature.

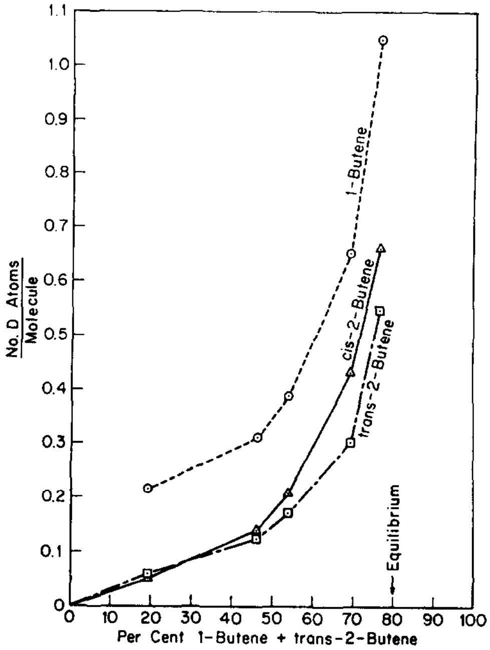


FIG. 2. Deuterium concentration in butenes during reaction of a *cis*-2-butene: D_2 = 100:400 torr mixture over 35 mg of GA-48 alumina in a static reactor at 24°C.

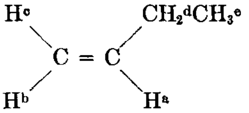
Finally, the rates of both the exchange and isomerization reactions of 1-butene were independent of whether the hydroxyl groups on the alumina were OH of OD. This was demonstrated by exchanging the OH groups with D_2 at 500°C (*5*) until no further HD appeared in the gas phase. Results with this catalyst were indistinguishable from those in Fig. 1. Moreover, it is known that most of the catalyst hydroxyl groups will not exchange with D_2 at this temperature (*5*) and that the rate of the H_2–D_2 exchange varies inversely with the extent of surface dehydroxylation (*6*). It is therefore clear that 1-butene exchanged with D_2 much more rapidly than did the other olefins and that neither exchange with D_2 nor isomerization involved a significant fraction of the catalyst hydroxyl groups.

In order to locate the deuterium atoms which exchanged into the 1-butene, a mixture of 1-butene and D_2 (40:400 torr) was allowed to react in the circulation system over 0.40 g of GA-48 at 23° until 48.6% of the 1-butene had isomerized. The olefins

TABLE 1
INTEGRATED AREAS UNDER NMR LINES FROM PARTIALLY DEUTERIUM-EXCHANGED 1-BUTENE

	24.5 cc NTP 1-Butene with 0.30 D/molec.	24.5 cc NTP 1-Butene reference		
Group of lines integrated	Rel. area of integral	Rel. area of integral	Normalized area	Normalized theoretical area
Methyl H^e	17.05	17.15	2.87	3.0
Methylene H^d	11.45	11.60	1.94	2.0
Terminal H^b & H^c	9.68	11.15	1.86	2.0
Vinyl H^a	5.98	5.98	1.00	1.0
Total	44.16	45.88		

were separated by semipreparative GLC, trapped, and distilled before mass spectral and NMR analyses. The mass spectral data indicated that the residual 1-butene contained 0.32 D atoms/molecule; the NMR data (Table 1) showed a concentration of 0.30 D atoms/molecule when the total integrated intensities of peaks (Fig. 3A) were compared with the total integrated intensities of corresponding peaks in an identical undeuterated sample (Fig. 3B) under the same instrumental conditions. The decrease in overall intensity was due primarily to a decrease in the lines associated with the H^b and H^c atoms (*7,8*) from the following nomenclature:



(2)

This means that the two terminal vinyl H atoms exchanged much more rapidly than did the remaining six H atoms. Furthermore, the decrease occurred about equally in the three groups of lines in the expanded A′ spectrum (Fig. 3), and this shows that H^b and H^c were equally labile.

Isobutene and D_2. Isobutene was reacted with D_2, and all eight H atoms exchanged at comparable rates. As with the *n*-butenes, double-bond migration could

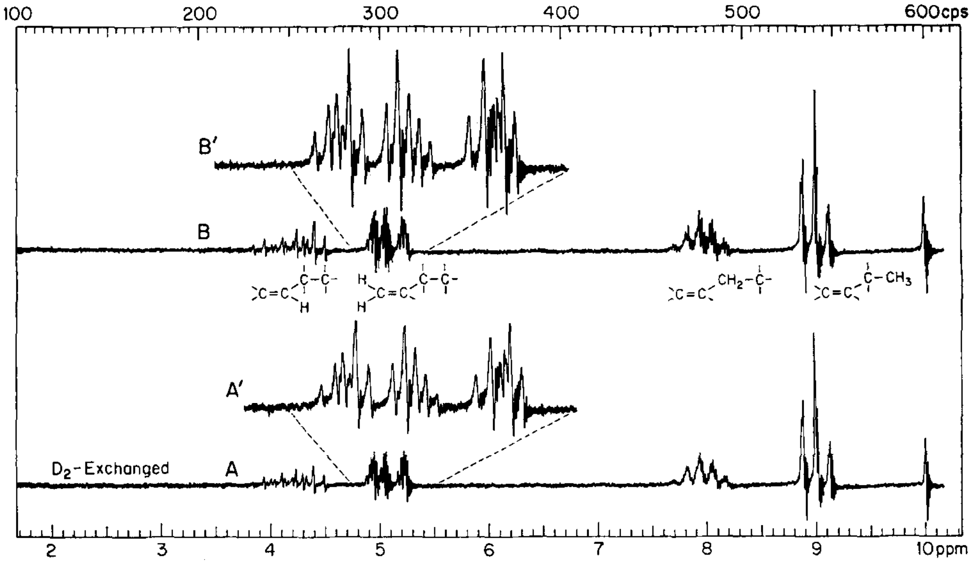


FIG. 3. NMR spectra of 1-butene and partially deuterium-exchanged 1-butene showing preferential incorporation of D atoms into the two terminal vinyl positions during reaction of a 1-butene: D_2 = 40:400 torr mixture over 0.40 g of GA-48 alumina in a circulation reactor at 23°C.

TABLE 2

NMR DATA SHOWING RELATIONSHIP BETWEEN DOUBLE-BOND MIGRATION AND D_2 EXCHANGE OF ISOBUTENE OVER ALUMINA

	Average deuterium concentration (D atoms/molecule)			
	at 23°C		at 60°C	
Location	Observed	Theoretical if all exch. equally	Observed	Theoretical if all exch. equally
In CH_3	0.78	0.89	0.80	0.85
In CH_2	0.41	0.30	0.33	0.29
Total	1.19	1.19	1.14	1.14
Mass spec. total	1.13	—	1.25	—
Ratio CH_3/CH_2	1.92	3.00	2.40	3.00

also occur in isobutene, but in contrast to the former, this would not result in a different isomer. Location of the exchanged atoms was accomplished with NMR, and the effect of temperature on the "exchange" and "isomerization" reactions was assessed from the corresponding NMR spectra. Two isobutene: D_2 = 40:400 torr mixtures were reacted at 23° and 60° over the same regenerated 0.40-g alumina sample used in the 1-butene experiments; the NMR results from the products are shown in Table 2. At both temperatures the exchange was carried to about 1.2 D atoms/molecule. In neither case was the deuterium equally distributed among the eight possible positions. A higher concentration of deuterium was found in the methylene group than in each of the methyls. Moreover, the ratio of deuterium atoms in the methyl to methylene groups increased from 1.92 at 23° to 2.40 at 60°; a value of 3.0 would have been observed had the atoms exchanged equally into all positions. Had double-bond migration always accompanied exchange, the ratio would have been greater than 3.0. The results are consistent with the view that exchange occurred only at the vinyl positions and that double-bond isomerization was an independent process having a higher energy of activation than the exchange reaction.

***tert*-Butylethylene and D_2.** Since double-bond migration occurred with all of the butenes, it was not possible to investigate exchange without simultaneous isomerization. However, *tert*-butylethylene (TBE) cannot isomerize. Hence, exchange with the vinyl hydrogen atoms could be studied exclusively with this compound. A mixture of TBE and D_2 (20:500 torr) was reacted over the same regenerated 0.40-g alumina sample at 28° in the recirculation reactor. The exchange profile is shown in Fig. 4 as a function of time. The slow increase in the d_3 species indicates that two atoms exchanged considerably faster than did the third, and by analogy with 1-butene these were the two terminal vinyl atoms and the one nonterminal vinyl atom.

The exchange was allowed to continue

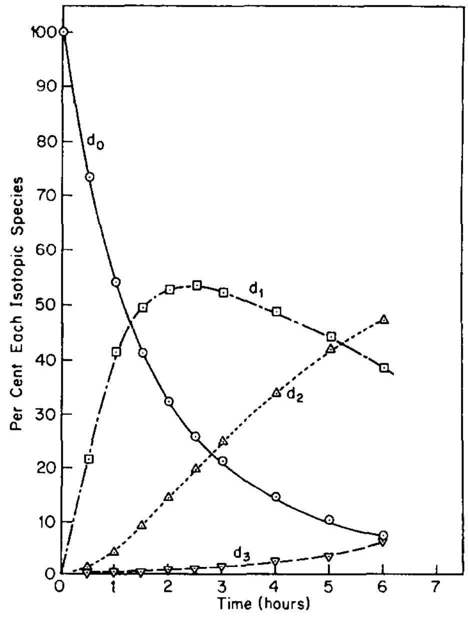


FIG. 4. Deuterium distribution in *tert*-butylethylene during exchange of a TBE: D_2 = 20:500 torr mixture over 0.40 g of GA-48 alumina in a circulation reactor at 28°C.

until the mass spectrum of the products showed 0.0%, 0.5%, 9.0% and 90.5% for the d_0, d_1, d_2, and d_3 species, respectively. No d_4 or higher species were observed. Gas-phase IR spectra (*9*) of this material, taken with a Beckman IR-12 spectrometer, showed unambiguously that the deuterium was exclusively localized in the three vinyl positions.

DISCUSSION

The experiments reported herein have shown that only the vinyl hydrogen atoms in noncyclic monoolefins undergo exchange with D_2 over a pure alumina catalyst at temperatures below 100°. This was most clearly demonstrated in the TBE–D_2 system, where no exchange occurred in the *tert*-butyl part of the molecule. Furthermore, not all the vinyl hydrogen atoms were equally susceptible to exchange with D_2, because those in terminal positions were much more labile than the methine hydrogen atom. Selectivity was also found with internal olefins; the vinyl hydrogens in *cis*-2-butene exchanged somewhat more rapidly than those on the trans isomer (Fig. 2), although this may have been due to the fact that 1-butene both exchanges more rapidly than either of the 2-butenes and isomerizes back to the cis isomer selectively. Even so, the observations stem from geometric effects. Peri (*10*) has suggested that defect "holes" are formed when adjacent hydroxyl groups are removed from the surface of γ-alumina by dehydration. Such holes could expose Al^{3+} ions which may serve as sites for the preferential exchange of the terminal vinyl hydrogen atoms of 1-butene, as the molecules approach the surface in an "end-on" configuration; presumably the holes would be too small to readily accommodate either of the 2-butenes which must approach from a "side-on" configuration to undergo exchange.

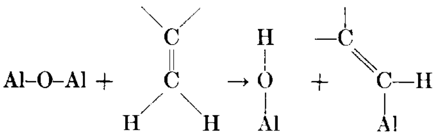
Isomerization did not involve exchange with D_2. If it had, the deuterium concentration in the 2-butene products in Fig. 1 would intially have exceeded the deuterium concentration in the unisomerized 1-butene, because initially each product molecule would necessarily contain one D atom. Thus, had each isomerization act involved exchange, the zero-conversion intercepts for the products would have been unity rather than zero. We (*4, 11*) have shown that the isomerization rate constants are such that the major fraction of *trans*-2-butene formed from 1-butene passes through the cis isomer as an intermediate. If *only* 1-butene underwent exchange and then isomerized without further exchange, the deuterium concentration curves in Fig. 1 would follow the observed order with 1-butene > cis > trans at all conversions. Probably the vinyl hydrogen atoms in the 2-butenes did undergo some subsequent exchange, but this was slow relative to exchange with the terminal vinyl atoms in 1-butene.

Further evidence that isomerization and exchange are unrelated stems from the activation energy differences for the two processes reflected in the NMR work with isobutene. Quantitative measurements (*12*) with cyclic olefins have shown that exchange of vinyl hydrogen atoms in cyclopentene with D_2 over the same catalyst has a temperature coefficient of about 5 kcal/mole. The activation energy for exchange of these noncyclic olefins is probably similar (particularly that for the *cis*-2-butene), and hence is considerably lower than the 13 kcal/mole (*4, 11*) activation energy for butene isomerization.

It is doubtful that the exchange took place by an *associative* mechanism. If deuterium were added to the molecule, double-bond migration would probably have accompanied the exchange. For example, suppose a deuteron from an OD group or from D_2 were added to the terminal carbon atom of 1-butene to form the $CH_2D^{\oplus}CHCH_2CH_3$ ion. Exchange could occur through loss of one of the two protons from the terminal carbon, but isomerization *also involving exchange* could occur if one of the two protons on the 3-carbon atom were lost. Furthermore, the two processes should have had very similar temperature coefficients, which was not the case. Peri (*10*) drew a similar conclusion from his infrared studies.

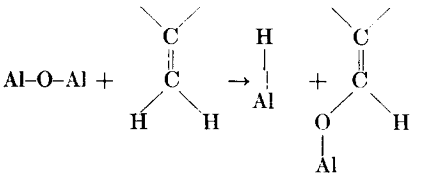
In comparing rates of exchange between cyclopentene with D_2 and deuterated cyclopentane with H_2 over the same catalyst (*12*), a large primary kinetic isotope effect ($k_H/k_D \sim 2.5$) was found, similar to that reported earlier (*4*b) for isomerization. Since the H_2–D_2 exchange was much faster than isomerization, it was concluded (*12*) that cleavage of a CH or a CD bond must occur in the transition state. This suggested that the exchange process was dissociative, rather than associative. Similar data for the exchange of methane with D_2 and the isotopic mixing between CH_4 and CD_4 over the same alumina catalyst were reported by Larson and Hall (*13*). Here too, an isotope effect was recorded which was attributed to more favorable cleavage of a CH than a CD bond in the transition state. The activation energy for these processes was also about 5 kcal/mole and the number of sites catalyzing the reaction, as judged from poisoning experiments with CO_2, was about $5 \times 10^{12}/cm^2$. The simplest explanation of these results was the supposition that methane, like H_2 and D_2, was dissociated by the catalyst. Olefins poisoned the methane exchange reaction, and it is possible that the olefinic parts of the molecules in the present experiments were so strongly adsorbed that they monopolized the active sites and thus prevented aliphatic C–H exchange.

The acid–base or ion-pair sites, which Peri (*14*) found reacted with ammonia to form $-NH_2$ and $-OH$ surface species, may also be involved in the exchange of the vinyl hydrogen atoms. These sites are probably strained Al–O–Al linkages (*15*) which can dissociate vinyl C–H bonds to form adsorbed olefinic species and OH groups, as illustrated for a terminal olefin by the scheme



(3)

or



(4)

Peri (*16*) used CO_2 as an indicator to find that 3–9×10^{12} sites/cm^2 of this nature were present. Earlier we suggested that an equivalent number of catalyst OH groups [$\sim$1% of the total present (*5*)] were involved in the methane exchange (*13*). New information (*17*) concerned with the H_2–D_2 exchange over this same catalyst now makes this seem unlikely. These data show that at 25°, the number of catalyst hydroxyl groups exchangeable with D_2 is very much smaller than the number of sites catalyzing the exchange reactions. If catalyst hydrogen is not involved, the Al–OH group of Eq. (3) (if indeed it exists) must differ in an important way from the remainder of the catalyst OH groups. Similarly, D_2 must adsorb in a way which prevents D atoms from reacting with the OH groups, yet still have ready access to the adsorbed vinyl groups. Presently, it is not clear how this may be accomplished, unless the reactions occur on areas of the catalyst surface which are very sparsely populated with OH. Equation (4) offers less difficulty, but does not appear to solve the problem.

ACKNOWLEDGMENTS

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