# Reactions of Alkenes and the Equilibration of Hydrogen and Deuterium on Zirconia

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The hydrogenation of various alkenes, the equilibration of  $H_2/D_2$  and the isomerisation of some  $C_6$ -alkenes have been studied over a range of temperatures on zirconia catalysts. Products from the reaction of some of the alkenes with deuterium were examined by <sup>2</sup>D n.m.r. spectroscopy. The rate of hydrogenation varied only to a small extent with the nature of the alkene, apart from some steric hindrance with some of the  $C_6$ -compounds, and the supply of hydrogen to the surface appeared to be rate-determining. Reactions of alkenes with deuterium below 400 K gave  $D_2$ -alkanes. As the temperature was raised, exchange of alkene was observed to an increasing extent, and the location of the deuterium atoms in the products provided evidence of possible mechanisms.

Zirconia has been studied as a catalyst for alcohol dehydration<sup>1-3</sup> and more recently for use with synthesis gas for the production of methanol<sup>4</sup> and the selective formation of 2-methlypropene.<sup>5, 6</sup> Several papers<sup>7-10</sup> have reported the hydrogenation of buta-1,3-diene to C<sub>4</sub>-alkenes either by using hydrogen or by transfer of hydrogen from cyclohexadiene to the C<sub>4</sub>-diene.

A number of techniques<sup>11</sup> have been used to examine the marked influence of pretreatment temperature on the development of acidic, basic, oxidising and reducing properties of the surface of zirconia. The maximum concentration of acidic sites  $(3.9 \times 10^{-8} \text{ mol m}^{-2})$  was found after pretreatment at 673 K but the maximum for basic sites  $(1.7 \times 10^{-7} \text{ mol m}^{-2})$  was associated with the higher temperature of 973 K. The isomerisation of but-1-ene, measured at 353 or 373 K, developed on outgassing the zirconia at 673 K and reached a maximum for pretreatment temperatures of 973 to 1073 K. Thus it appeared that basic sites were required for the isomerisation, and the evidence of intramolecular hydrogen transfer in the co-isomerisation of  $D_0$ - and  $D_8$ -but-1-ene provided support for the suggestion that allylic carbanionic intermediates were involved. Results obtained in a study of the acid-base and catalytic properties of a series of ZrO<sub>2</sub>-SnO<sub>2</sub> mixed oxides<sup>12</sup> were also consistent with the proposal that basic sites were involved in the isomerisation of but-1-ene. Halcom<sup>10</sup> in another study of this reaction confirmed the results obtained by the Japanese group.<sup>11</sup> Rates of isomerisation<sup>13</sup> of pent-1-ene and of 2-methylbut-1-ene at 473 K depended on the outgassing temperature and also showed maxima for pretreatment of zirconia at 973 K.

Some evidence is available on the reaction of hydrogen or deuterium with alkenes over zirconia. Yamaguchi and Hightower<sup>7</sup> stated that the reaction of deuterium with propene, 2-methylpropene or n-butene gave exclusively  $D_2$ -alkane at temperatures between 273 and 348 K, but detailed results were not presented. Halcom<sup>10</sup> confirmed that no exchange of but-1-ene and deuterium occurred below 373 K, but at 403 or 453 K some alkene exchange accompanied the formation of butane. A microwave spectroscopic study<sup>14</sup> of the products from the exchange of propene with deuterium at 433 K over a zirconia catalyst containing 9.1 wt% alumina and 0.36 wt% sulphur showed that replacement of the five hydrogen atoms on the end carbons had occurred

but the hydrogen at the central carbon was not exchanged. The results were consistent with a mechanism involving carbocations as intermediates. More recently, deuterium n.m.r. spectroscopy<sup>15</sup> has been used to examine the products from the reaction of 2-methylpropene over zirconia at 415 and 433 K. The main product at both temperatures was the  $D_2$ -alkane, but some exchange of alkene also occurred at about half the rate of the addition reaction, leading to products with deuterium randomly distributed in the 2-methylpropene.

The equilibration of hydrogen with deuterium at temperatures between 323 and 348 K was studied by Nakano *et al.*<sup>8</sup> on zirconia catalysts outgassed at various temperatures. Maximum activity was found for a pretreatment temperature of 873 K, and similar activity *vs.* temperature graphs were obtained for the  $H_2/D_2$  reaction and the direct hydrogenation of buta-1,3-diene. Evidence from infrared spectroscopy<sup>16</sup> demonstrated the reversible dissociative adsorption of hydrogen and deuterium on zirconia at room temperature, and the observed bands were interpreted in terms of Zr—H and Zr—H—Zr entities.

The main objective of the present work was to obtain a more comprehensive picture of the catalytic properties of zirconia for the exchange of alkenes with deuterium and for the conversion of alkenes into alkanes from studies with a range of alkenes. Results were also obtained on the rate of the  $H_2/D_2$  reaction, particularly in relation to the rates of hydrogenation of the alkenes. Some experiments were also planned on the isomerisation of 3,3-dimethylbut-1-ene (33DMB1), since this is a reaction which is known to occur on acidic oxides but not on basic oxides.<sup>17</sup> Some work on the reaction of 33DMB1 on zirconia has been reported,<sup>18</sup> but only at the rather high reaction temperature of 773 K. As the influence of pretreatment temperature had been extensively studied in the earlier work, most of the present results were obtained after out-gassing at 873 K, the value which had been reported<sup>8</sup> to give maximum rates for  $H_2/D_2$  exchange and for hydrogenation of butadiene.

## Experimental

## Materials

Ethene and propene (both CP grade) were obtained from Matheson and the dimethylbutenes (puriss) from Fluka AG; all were at least 99% pure and were distilled under vacuum before use. Deuterium (99.5%) from Matheson and hydrogen from BOC were diffused through a palladium-silver alloy thimble. Carbon dioxide used in some poisoning experiments was obtained as grade X from BOC and distilled under vacuum.

Zirconyl chloride,  $ZrOCl_2 \cdot 8H_2O$ , from Aldrich, was used to prepare the hydroxide following the procedure, described by Wang *et al.*,<sup>12</sup> which involved precipitation using aqueous ammonia. The zirconium hydroxide was calcined at 873 K and then allowed to rehydrate at room temperature. Weighed samples of the hydroxide (usually in the range 100–250 mg) were evacuated for 3 h at 873 K for the catalytic experiments. Two different samples of zirconyl chloride of 98 + % and 99.99 % purity were used as starting materials, and the resulting oxides are described as  $ZrO_2(I)$  and  $ZrO_2(II)$ ; the surface areas, determined by adsorption of nitrogen, were  $69 \pm 7$  and  $74 \pm 7$  m<sup>2</sup> g<sup>-1</sup>, respectively. Unless otherwise stated, runs were carried out using  $ZrO_2(I)$ .

#### Apparatus and Technique

Reactions involving isomerisation or hydrogenation of 33DMB1 were conducted in a greased-tap static system containing a silica reaction vessel in a closed volume of 180 cm<sup>3</sup>. All other experiments with alkenes were followed in a greased-tap recirculation system containing a silica vessel with a 1 cm diameter sinter, a liquid-nitrogen trap and a

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| reactant          | columnª | length/m | T/K | total<br>pressure <sup>b</sup><br>/kPa |
|-------------------|---------|----------|-----|--|
| ethene            | Α       | 2        | 293 | 177                                    |
| propene           | Α       | 2        | 348 | 308                                    |
| 33DMB1<br>23DMB2° | В       | 50       | 273 | 163                                    |

Table 1. Conditions used for gas chromatographic analyses

<sup>*a*</sup> A = 3% squalane on activated alumina; B = squalane capillary. <sup>*b*</sup> Nitrogen as carrier gas. <sup>*c*</sup> 23DMB2 is 2,3-dimethylbut-2ene.

connection through a three-way tap and a Carle valve to a Perkin-Elmer F11 gas chromatograph. The volume of the apparatus was  $355 \text{ cm}^3$  and recirculation was achieved with a Metal Bellows (240 V) pump and measured with a flow meter. The conditions used for the gas-chromatographic analysis are given in table 1.

Samples for analysis by deuterium n.m.r. spectroscopy were obtained by following the reactions to an appropriate conversion, determined by gas chromatography, and then condensing the hydrocarbons into the liquid-nitrogen trap and subsequently distilling them into an n.m.r. sample tube containing 5% D-chloroform. The procedure for recording and analysing the spectra has been described.<sup>19, 20</sup>

A pressure ratio of 5:1 hydrogen (or deuterium):alkene was used in the recirculating system with a hydrocarbon pressure of 2.4 kPa corresponding to a charge of ca.  $2 \times 10^{20}$  molecule. The isomerisation of 33DMB1 was followed using a pressure of 2.5 kPa ( $8 \times 10^{19}$  molecule).

#### Equilibration of Hydrogen and Deuterium

The equilibration of hydrogen and deuterium was followed in a static system (210 cm<sup>3</sup>) connected by a capillary leak to a Vacuum Generators MM601 mass spectrometer<sup>21</sup> using 22 eV electrons to ionise the molecules. The sensitivity of the apparatus for hydrogen and deuterium was calibrated using 1:1 mixtures of the gases. The sensitivity of the peak with m/e = 3 for HD was found by allowing a mixture of H<sub>2</sub> and D<sub>2</sub> to reach equilibrium over zirconia for 48 h at 293 K and choosing the calibration factor so that the equilibrium constant for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$
 (1)

agreed with the value given by Urey and Rittenberg.<sup>22</sup> This procedure was based on the work of Brookes<sup>23</sup> and gave the relative sensitivities for  $H_2:HD:D_2$  of 1.0:2.2:3.7. These values were independent of the temperature used for the reaction. It took 4 min to run the mass spectrum, and so in the kinetic experiments it was necessary to interpolate the observed peak heights in order to obtain sets of values for m/e = 2, 3 or 4 at the appropriate times.

For the catalytic experiments equal pressures of 3.5 kPa  $(1.7 \times 10^{20} \text{ molecule})$  of hydrogen and deuterium were admitted to adjacent sections of the vacuum line and allowed to mix overnight at room temperature. This storage in contact with Pyrex glass gave no increase in the 0.5% HD present as an impurity in the deuterium. However, blank experiments without zirconia showed a slow equilibration reaction in the silica reaction vessel which had been heated to 873 K for 3 h, *i.e.* the usual pretreatment procedure. Rates from such blank experiments were subtracted from the rates with catalyst present to give the net rate due to the zirconia.

The course of the equilibration reaction with time followed the usual first-order reversible equation<sup>24</sup>

$$\ln\left(x_{\infty} - x\right) = -kt/x_{\infty} + \ln x_{\infty} \tag{2}$$

where x and  $x_{\infty}$  represent the percentages of HD present at time  $t(\min)$  and at equilibrium, and k is the initial rate of reaction in % min<sup>-1</sup>. The absolute initial rate of reaction was obtained from the relationship

$$r = 2kn_{\rm H_a}/(60 \times 100 \,Aw) \tag{3}$$

where A is the surface area, w the weight of zirconia,  $n_{\rm H_2}$  the charge of hydrogen and r the initial rate in molecule s<sup>-1</sup> m<sup>-2</sup>. The factor 2 was introduced to allow for the fact that with a 50:50 mixture of H<sub>2</sub>:D<sub>2</sub> only half of the exchanges will lead to observable product, neglecting isotope effects.<sup>25</sup>

# Results

#### Hydrogenation of Alkenes

Typical experiments for the hydrogenation of ethene are shown in fig. 1. At 273 K there was a small decrease in rate during a period of *ca*. 20 min, followed by a steady reaction. This behaviour was common to all alkene addition reactions in which < 15% of the reactant was converted. Rates were calculated from the steady region. At 325 K no initial fall in rate was detectable, but some decline occurred at conversions above 50%. This was attributed to a small kinetic dependence of the rate on the alkene pressure and confirmed by plotting the results according to eqn (2) of ref. (26). A good straight line was obtained assuming n = 0.2 for the order of the hydrogen reaction with respect to alkene pressure.

The rates of reaction at various temperatures of ethene, propene and 33DMB1 are given as Arrhenius plots in fig. 2, which also includes results from the previous work<sup>15</sup> with 2-methylpropene. There was good agreement between the results on  $ZrO_2(I)$  and  $ZrO_2(II)$ , and the derived Arrhenius parameters are reported in table 2. No isomerisation of 33DMB1 was detected at 378 K or below. The hydrogenation of 2,3-dimethylbut-2-ene (23DMB2) is reported in a later section.

# Hydrogen/Deuterium Equilibration

At 294 K the silica vessel contributed 10% of the total observed rate, and the net rate of equilibration on the zirconia was  $2.8 \times 10^{15}$  molecule s<sup>-1</sup> m<sup>-2</sup>. At 348 K the blank reaction contributed 15% and the net rate was  $6.6 \times 10^{15}$  molecule s<sup>-1</sup> m<sup>-2</sup>. These rates were only slightly greater than the rates of hydrogenation of ethene, as may be seen in fig. 2, and approximate values of the Arrhenius parameters for the equilibration derived simply from the two rates are included in table 2.

## Poisoning with Carbon Dioxide

The technique described by Brown *et al.*<sup>26</sup> was used to study the effect of doses of carbon dioxide on the rate of hydrogenation of ethene at 273 K. The steady rate of hydrogenation was measured for *ca.* 1 h, a known amount of carbon dioxide was released into the reaction line from a 4.2 cm<sup>3</sup> doser positioned upstream from the catalyst and then after an interval of *ca.* 15 min the new lower rate of reaction was obtained. Results are shown in fig. 3 as a percentage of the original rate against the amount of carbon dioxide caused a sharp reduction in rate consistent with the existence of some active but easily poisoned sites and then activity declined linearly with the volume of carbon dioxide admitted. Extrapolation of the linear section of the curve

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Fig. 1. The hydrogenation of ethene over 77 mg  $ZrO_2(I)$ :  $\Box$ , 273;  $\bigcirc$ , 325 K.



**Fig. 2.** Arrhenius plots for hydrogenation of alkenes and hydrogen/deuterium equilibration: open symbols  $ZrO_2(I)$ , filled symbols  $ZrO_2(II)$ ;  $\bigcirc$ , ethene;  $\square$ , propene;  $\triangle$ , 33DMB1;  $\bigtriangledown$ ,  $H_2/D_2$  equilibration. The dashed line is for 2-methylpropene from ref. (15).

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| reactant                     | temperature<br>range,<br>T/K | activation<br>energy,<br>E/kJ mol <sup>-1</sup> | frequency<br>factor,<br>log(A/molecule<br>$s^{-1} m^{-2})$ | rate at 300 K,<br>r/molecule<br>$s^{-1} m^{-2}$ |
|------------------------------|------------------------------|---|--|---|
|                              | h                            | vdrogenation                                    |  |   |
| ethene                       | 246-425                      | 18+1  | $18.3 \pm 0.2$   | $1.5 \times 10^{15}$                            |
| propene                      | 291-414                      | $16 \pm 1$                                      | $17.8 \pm 0.1$   | $1.0 \times 10^{15}$                            |
| 33DMB1                       | 294-378                      | $20 \pm 1$                                      | $18.1 \pm 0.2$   | $5.6 \times 10^{14}$                            |
| 23DMB2 <sup>a</sup>          | 329-426                      | $16 \pm 1$                                      | $16.3 \pm 0.3$   | $3.3 \times 10^{13}$                            |
| 2-methylpropene <sup>b</sup> | 273-432                      | $16\pm 1$                                       | $17.0\pm0.1$   | $1.6 \times 10^{14}$                            |
|                              |                              | equilibration                                   |  |   |
| $H_2/D_2$                    | 294 and 348                  | 14  | 17.9   | $2.9 \times 10^{15}$                            |
|                              | i                            | isomerisation                                   |  |   |
| 33DMB1                       | 410-528                      | $23\pm5$  | $16.1 \pm 0.5$   |   |

Table 2. Arrhenius parameters for reactions of alkenes and for  $H_2/D_2$  equilibration

<sup>a</sup> The alkene was rapidly converted to an equilibrium mixture of 23DMB2 and 23DMB1. <sup>b</sup> Results from ref. (15).



Fig. 3. Poisoning of ethene hydrogenation on 39 mg ZrO<sub>2</sub>(I) at 273 K by addition of carbon dioxide.

indicated that  $(1.0\pm0.2) \times 10^{18}$  molecule m<sup>-2</sup> of carbon dioxide eliminated the catalytic activity. If the cross-sectional area of the molecule is assumed<sup>27</sup> to be 0.22 nm<sup>2</sup>, this amount of carbon dioxide would have covered  $22\pm5\%$  of the zirconia surface.

The surface of the catalyst was black after poisoning with carbon dioxide. The coloration remained after degassing the catalyst for 3 h at 873 K, and little activity for hydrogenation of ethene ( $< 10^{13}$  molecule s<sup>-1</sup> m<sup>-2</sup>) was found at 273 K. However, removal of the hydrogen–ethene mixture and treatment for 3 h with 13 kPa of oxygen at 873 K removed the black colour and restored the normal activity ( $8.3 \times 10^{14}$  molecule s<sup>-1</sup> m<sup>-2</sup>) for the hydrogenation of ethene at 273 K.

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**Fig. 4.** Arrhenius plots for reactions of the dimethylbutenes on  $ZrO_2(I)$ : the dashed line refers to hydrogenation of 33DMB1, see fig. 2;  $\blacktriangle$ , deuteration of 33DMB1;  $\square$ , hydrogenation and  $\blacksquare$ , deuteration of 23DMB2 (and the isomer 23DMB1);  $\bigcirc$ , isomerisation of 33DMB1;  $\square$ , isomerisation of 23DMB2.

#### Further Results with Dimethylbutenes

Isomerisation of 33DMB1 to 23DMB2 and 23DMB1 was slow in the temperature range 410–528 K. Steady rates of reaction were found at the lower temperatures, but at 528 K a fall in activity was observed over 2 h even though the conversion had reached only 4%, well below the equilibrium value. This fall was attributed to self-poisoning, and the catalyst was black at the end of the experiment. Rates used for the Arrhenius plot in fig. 4 were taken from the initial part of the reactions, and the derived parameters are given in table 2. The product ratio R = 23DMB2/23DMB1 was 4.7 at 448 K but only 1.5 at 528 K.

Some experiments were carried out with 33DMB1 on catalysts pretreated at 723 K instead of the usual 873 K. Such catalysts had a surface area of  $143 \pm 10 \text{ m}^2 \text{ g}^{-1}$ . They gave a rate of isomerisation at 448 K of  $2.3 \times 10^{13}$  molecule s<sup>-1</sup> m<sup>-2</sup>, which was 20% faster than the rate on catalysts pretreated at 873 K. In contrast, the rate of hydrogenation of 33DMB1 at 325 K was only  $1.5 \times 10^{12}$  molecule s<sup>-1</sup> m<sup>-2</sup>, which was 70 times slower than the rate for the normal catalysts.

Some reactions were carried out with 23DMB2 and either hydrogen or deuterium, and a run at 430 K is shown in fig. 5. A fast isomerisation (>  $10^{16}$  molecule s<sup>-1</sup> m<sup>-2</sup>) to 23DMB1 was observed, but the rate declined rapidly as the equilibrium between the two alkenes was approached. Meanwhile, a slow but increasing rate of conversion to the alkane (23DMB) occurred, and the shapes of the curves suggested that the route to alkane was through the 23DMB1 isomer. Arrhenius plots for the addition reaction are shown in fig. 4 and the derived parameters are given in table 2. At the lower temperature of 328 K, the initial rate of isomerisation of 23DMB2 was  $5 \times 10^{14}$  molecule s<sup>-1</sup> m<sup>-2</sup> (see fig. 4).



Fig. 5. Reaction of 23DMB2 with deuterium at 430 K over 116 mg  $ZrO_2(I)$ :  $\bigcirc$ , 23DMB2;  $\square$ , 23DMB1;  $\triangle$ , 23DMB.

# Deuterium N.M.R. Spectroscopy

Deuterium n.m.r. spectroscopy was used to analyse the products from the reaction of four alkenes (ethene, propene, 33DMB1 and 23DMB2) with deuterium. In each case the reaction was followed by gas chromatography until ca. 15–25% of the alkene had been converted into alkane and the hydrocarbons were frozen and subsequently analysed.

The results with ethene and 33DMB1 indicated that addition occurred without detectable exchange of the alkene. The rate of deuteration of ethene at 312 K was  $9.8 \times 10^{14}$  molecule s<sup>-1</sup> m<sup>-2</sup> (2.4 times slower than the rate of hydrogenation), and a sample containing 17% ethane gave a single resonance at  $\delta = 0.835$  ppm. This value corresponds to that expected<sup>19</sup> for the deuterium atoms in CH<sub>2</sub>DCH<sub>2</sub>D and showed that the reaction involved simple addition across the double bond of ethene. Rates of deuteration of 33DMB1 at 313 and 368 K are shown in fig. 4. The n.m.r. spectrum of a sample from the higher temperature after 20% conversion to alkane had two resonances of similar intensity with  $\delta = 1.193$  and 0.804 ppm. These values are assignable to the secondary and primary deuterium atoms in (CH<sub>3</sub>)<sub>3</sub>CCHDCH<sub>2</sub>D and again provide evidence for straight addition across the double bond. No evidence for exchanged alkene was found and 0.04 D per molecule would have been readily detected.

The deuteration of propene occurred at about half the rate of hydrogenation in the temperature range 298-433 K; the activation energy was  $13\pm3$  kJ mol<sup>-1</sup> and the frequency factor log  $A = 17.0\pm4$ . N.m.r. spectra were obtained on samples at three temperatures. The chemical shifts associated with the various groupings of deuterium atoms in propane and the distribution of deuterium between these groupings are given in table 3. The assigned values for the number of D atoms per molecule were based on the ratio of the peaks for primary D in CH<sub>2</sub>DCH<sub>2</sub>— and CH<sub>2</sub>DCHD—. For example,

| grouping   | chem. shift $\delta$ (ppm) | 305 K (12%) |                                | T (conversion to alkand<br>394 K (23 %) |                                | ne)<br>433  | e)<br>433 K (28%)              |  |
|--|----------------------------|-------------|--------------------------------|---|--------------------------------|-------------|--------------------------------|--|
|  |                            | D(%)        | D per<br>molecule <sup>b</sup> | D(%)                                    | D per<br>molecule <sup>b</sup> | D(%)        | D per<br>molecule <sup>b</sup> |  |
| CHD(CX <sub>a</sub> ) <sub>a</sub> <sup>a</sup>          | 1.2997                     | 49.9        | 1.00                           | 47.0                                    | 0.94                           | 47.0        | 0.90                           |  |
| CH <sub>2</sub> DCH <sup>2</sup><br>CH <sub>2</sub> DCHD | 0.8935<br>0.8839           | 50.1        | 1.00                           | 3.2<br>49.8                             | 1.06                           | 5.3<br>47.7 | 1.01                           |  |
| -  |                            | 100.0       |                                | 100.0                                   |                                | 100.0       |                                |  |

 Table 3. Groupings of deuterium in propane from the n.m.r. spectra for the reaction of propene with deuterium

<sup>a</sup> X represents H or D. <sup>b</sup> Values for secondary D are based on the relative amounts of the two types of primary D.

| 19.2 | 1.12                          |
|------|-------------------------------|
|      |                               |
| 15.3 | 0.89                          |
| 14.2 | 0.83                          |
| 51.3 | 3.00                          |
|      | 15.3<br>14.2<br>51.3<br>100.0 |

**Table 4.** Distribution of deuterium in propene from the n.m.r. spectrum for the reaction at 433 K (28% conversion to propane)

<sup>*a*</sup> Relative to  $-CH_2D = 3.00$ .

for the sample obtained from reaction at 394 K the relative percentages for these two types of primary D were 6 and 94%. Therefore it was assumed that each molecule contained 0.94 secondary D atoms.

No evidence for the exchange of propene was obtained from the n.m.r. spectrum of the products from reaction at 305 K, but small amounts of deuterium in the propenes were observed in the samples from the two higher temperatures. Results for the highest temperature, 433 K, are given in table 4. The chemical shifts were similar to those observed previously for propene exchanged over calcium oxide.<sup>20</sup> Deuterium was present in all possible positions in the molecule, including that on the central carbon atom. A comparison of the peak sizes for the propene was 0.08 D per molecule, assuming 1.91 D per molecule (see table 3) for the propane. Since this amount of exchange had occurred during the time required to convert 28% of the alkene to alkane, the addition reaction was *ca.* 3.5 times faster than exchange. A corresponding analysis of the sample from the experiment at 394 K showed 0.03 D per propene and a rate of addition 7 times faster than exchange.

Even at 433 K the exchange of propene contributed very little to the amount of deuterium detected in the propane. We assumed that the average D per propene was half

| compound            | (%)  | position <sup>a</sup>  | chemical shift, $\delta$ (ppm) | D (%)        | D per<br>molecule <sup>c</sup> |
|---------------------|------|--|--------------------------------|--------------|--------------------------------|
| 23DMB2              | 75.8 | CDX <sub>2</sub> —   | 1.640                          | 27.2         | 0.062                          |
| 23DMB1 <sup>b</sup> | 19.2 | $CDX_{2}C = (CDX_{2})CX(CX_{3}) - CX(CX_{3}) - CX(CX_{3}$ | 1.70<br>1.02                   | 2.6<br>5.5   | 0.069                          |
| 23DMB               | 5.0  | $\frac{\text{CD}(\text{CX}_3)_2}{(\text{CDX}_2)\text{CX}(\text{CX}_3)} - $   | 1.376<br>0.824                 | 29.2<br>35.5 | 1.00 <sup>c</sup><br>1.20      |
|                     |      |  | 100.0                          |              |                                |

Table 5. Distribution of deuterium in the products from reaction of 23DMB2 at 430 K

<sup>a</sup> X represents H or D. <sup>b</sup> No signals were detected apart from D atoms in the methyl groups. <sup>c</sup> Relative to an assumed value of 1.00 for the tertiary D in the alkane.

the final value of 0.08 and distributed as 0.01 on the central carbon and 0.03 on the terminal carbon atoms. Subtracting those values from the figures in the last column of table 3 gave 0.89 and 0.98 as the amounts of secondary and primary D acquired by the propane in the addition process.

Analysis of a sample from the reaction of 23DMB2 with deuterium shown in fig. 5 provided information on alkene exchange and the nature of the addition reaction. Deuterium was readily detected in the methyl groups of 23DMB2, all of which are equivalent; it was also found in the two types of methyl group of 23DMB1 in the expected 2:1 ratio but was not detected in the tertiary position or in the methylene group. Both alkenes had similar values for total D per molecule, and this showed that the isomerisation was mainly intramolecular. If there had been participation of deuterium in the formation of 23DMB1, it would have had a higher deuterium content than the reactant 23DMB2.

It was assumed that each alkane molecule (23DMB) had one tertiary deuterium atom in order to calculate the relative numbers of D per molecule given in the last column of table 5. Simple addition of deuterium across the double bond of 23DMB2 would lead to alkane with only tertiary deuterium, but simple addition to 23DMB1 would give alkane with equal amounts of primary and tertiary deuterium. Clearly, the experimental results agreed more closely with the latter alternative and confirmed that the route to alkane was through the isomer 23DMB1. The build-up of *ca.* 0.065 D per molecule in the alkenes during a period which gave 5% addition showed that for this system exchange was some 30 % faster than addition.

## Discussion

The catalysts used in this work can be compared with those used by Nakano *et al.*<sup>11</sup> Our catalysts had a greater surface area by factors of *ca.* 2; we found areas of 69 or 74 m<sup>2</sup> g<sup>-1</sup> for samples pretreated at 873 K compared with their value of 32.1 m<sup>2</sup> g<sup>-1</sup>. On the other hand, the amount of carbon dioxide,  $1.0 \times 10^{18}$  molecule m<sup>-2</sup>, needed to poison the hydrogenation of ethene at 273 K on one of our catalysts was lower than the amount,  $2.3 \times 10^{18}$  molecule m<sup>-2</sup>, which they reported for irreversible adsorption of carbon dioxide at 373 K. Likewise, the rate,  $2.6 \times 10^{16}$  molecule s<sup>-1</sup> m<sup>-2</sup>, of H<sub>2</sub>/D<sub>2</sub> exchange found by the Japanese group<sup>8</sup> for zirconia outgassed at 873 K was about four times greater than our rate at 348 K of  $6.6 \times 10^{15}$  in the same units; however, the details about conditions used in their work are not available to enable the two sets of experiments to be compared accurately.

The poisoning experiments which we carried out using carbon dioxide can only provide an upper limit to the number of catalytic sites because adsorption is likely to

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occur simultaneously on other sites. These considerations may explain why the amount of carbon dioxide needed to eliminate activity for the hydrogenation of ethene is an order of magnitude greater than the number of basic sites on zirconia  $(10^{17} \text{ m}^{-2})$ determined by the formation of diphenylnitroxide radicals from adsorbed diphenylamine.<sup>11</sup> Our results for poisoning of zirconia are not unlike those reported for zinc oxide,<sup>26</sup> for which  $2.3 \times 10^{18}$  molecule m<sup>-2</sup> of carbon dioxide were required to prevent the hydrogenation of ethene at 273 K. Assuming a cross-sectional area of 0.22 nm<sup>2</sup> for the molecule of carbon dioxide, some 50% of the zinc oxide was covered compared with 22% for zirconia.

#### Hydrogenation and Isomerisation of Alkenes

In this section the rates of reaction of the various alkenes on zirconia will be discussed and the catalytic behaviour of zirconia will be compared with some other oxides. More detailed consideration of probable adsorbed intermediates and possible mechanisms will be discussed in the following section.

The results in fig. 2 show that the rate of the  $H_2/D_2$  equilibration reaction is only slightly faster than the rate of the fastest hydrogenation (that of ethene) on zirconia. So it is possible that the ability of the catalyst to activate hydrogen, as measured by the  $H_2/D_2$  reaction, may be a controlling factor in relation to the activity of the catalyst for the hydrogen of alkenes. If the supply of hydrogen, either as molecules or dissociated, is the limiting step in the addition process, the similarity of the activation energies for the equilibration reaction and for the hydrogenation of the different alkenes (table 2) may be explained. The fact that the rates for all the alkenes studied (with the exception of the special case of 23DMB2 to be discussed later) show a spread of less than a factor of 10 is further support for a common rate-determining process which is not greatly influenced by the nature or the shape of the alkene molecule. It is also relevant to note that the rates of the direct hydrogenation of butadiene were found by Nakano et al.<sup>8</sup> to be ca. 25% of the rate of the  $H_2/D_2$  reaction (assuming that the two sets of data shown in their fig. 1 were obtained under comparable conditions). So with the diene as with the alkenes, the supply of hydrogen may be the controlling process for hydrogenation on zirconia.

The possible rate-determining role of hydrogen activation on zirconia is not unlike the situation which obtains on titanium dioxide (rutile) for the reactions of alkenes, except that much higher temperatures are needed to achieve appreciable rates with rutile catalysts. The  $H_2/D_2$  equilibration occurs at  $10^{15}$  molecule s<sup>-1</sup> m<sup>-2</sup> at 260 K on zirconia, but a temperature<sup>23</sup> of over 500 K was required for this rate on rutile. Again, even at 673 K the rates of hydrogenation<sup>24</sup> of ethene or propene on rutile were only  $10^{14}$  and  $10^{13}$  molecule s<sup>-1</sup> m<sup>-2</sup>, respectively, whereas rates of this magnitude were obtained on zirconia below 300 K (see table 2).

Comparisons can also be made between the rates of hydrogenation of ethene or propene on zirconia and corresponding data determined under similar conditions for the same reactions on zinc oxide<sup>26</sup> and on lanthana.<sup>28</sup> For zinc oxide the rates at 300 K for the hydrogenation of ethene or propene are  $2.7 \times 10^{15}$  or  $4.0 \times 10^{13}$  molecule s<sup>-1</sup> m<sup>-2</sup>, and for lanthana,  $2.2 \times 10^{18}$  or  $1.3 \times 10^{15}$  in the same units. So at 300 K zirconia and zinc oxide exhibit similar efficiency as catalysts for the hydrogenation of ethene, while zirconia and lanthana show comparable activity for the hydrogenation of propene rates at 300 K; these ratios are 1.5, 70 and > 1000 for  $ZrO_2$ , ZnO and  $La_2O_3$ , respectively. The high ratios on zinc oxide and lanthana have been attributed to the blocking of the sites needed for hydrogenation by the formation of adsorbed allyl species from propene. The absence of a high ratio on zirconia may be a consequence of the rate-limiting supply of hydrogen or of a lesser tendency for propene to dissociate to form allyl species.

Zirconia is not an efficient catalyst for the isomerisation of 33DMB1, as a temperature of around 570 K was needed to attain a rate of 10<sup>14</sup> molecule s<sup>-1</sup> m<sup>-2</sup>, and the ratio of hydrogenation/isomerisation was ca. 300 at 400 K (see fig. 4). Previous work<sup>17, 19</sup> has demonstrated that a catalyst must have acidic properties, which can involve Brönsted acidity or possibly Lewis acidity, in order to isomerise 33DMB1, and so it is not surprising that zirconia pretreated at 873 K is a poor catalyst for this reaction. In contrast to the results for hydrogenation of alkenes, rutile<sup>30</sup> is one of the more active oxides for the isomerisation of 33DMB1 as a rate of 10<sup>14</sup> molecule s<sup>-1</sup> m<sup>-2</sup> is attained at 350 K. The same rate can be achieved at ca. 400 K on alumina.<sup>29</sup> On the other hand, zinc oxide and lanthana, like zirconia, are not effective catalysts for the reaction. A temperature of 520 K was needed to give a rate of 10<sup>14</sup> molecule s<sup>-1</sup> m<sup>-2</sup> on zinc oxide,<sup>31</sup> and no appreciable reaction was detected on lanthana<sup>28</sup> at 510 K. The use of temperatures in excess of 500 K with the alkene/oxide systems can lead to selfpoisoning, as observed in the present work with 33DMB1 on zirconia at 528 K. The fact that the isomerisation was marginally faster on zirconia outgassed at 723 K rather than 873 K is consistent with the earlier work<sup>11</sup> which indicated that acidic properties were associated with lower outgassing temperature, preferably around 673 K.

The relative rates of isomerisation and addition with 23DMB2 are shown in fig. 4 and they contrast markedly with those for 33DMB1. The isomerisation was a rapid reaction on zirconia at 328 K but addition took place 10 times more slowly. The evidence from the deuterium n.m.r. experiment with 23DMB2 showed that the route to the alkane was through the isomer 23DMB1, and indicated the probability of considerable steric hindrance for the direct hydrogenation of 23DMB2.

# **Exchange Results and Possible Mechanisms**

For the discussion of the results on the exchange of the alkenes with deuterium and the evidence from n.m.r. spectroscopy about the distribution and groupings of deuterium atoms in the products, it is helpful to relate the behaviour of individual alkenes to the possible reactions set out in scheme 1. This shows the main routes by which alkene

gas alkene alkane  
(2) 
$$| (1)$$
 (7)  $| (8)$   
surface (A) vinyl (3) (4) alkene (5) alkyl  
(B) allyl (4) Scheme 1.

exchange may take place, the possible steps in the formation of alkane and includes the intermediates which are likely to be involved in the isomerisation reactions as well. The scheme is simplified by the omission of reference to any charges or partial charges on the adsorbed intermediates, but such charges may have an important bearing on what is likely to happen with some reactants, particularly on the more highly ionic oxides. In general, exchange may occur through reversible dissociation either to vinyl or allyl species or by reversible association to alkyl species. The position of deuterium atoms in the product molecules formed at low conversions can be a useful guide to likely mechanisms, but equally the absence of exchange of a particular type is just as valuable as an indication of the reactions which do not contribute.

The absence of any detectable exchange with ethene and 33DMB1 shows that these molecules do not readily undergo reversible dissociation to adsorbed vinyl species. Furthermore, if we accept that alkane formation occurs by the stepwise route through

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reactions (5) and (7), the alkyl reversal reaction (6) must be slow compared with (7). Behaviour of this kind was found for the reaction of ethene<sup>32</sup> and cyclopentene<sup>33</sup> on zinc oxide, and for these systems the rate-determining step in the addition process was reaction (5), the formation of adsorbed alkyl. However, for zirconia we should not exclude the possibility that the addition reaction takes place by a one-step process, not shown in the scheme, involving the addition of a molecule of hydrogen or deuterium. This suggestion would be in keeping with the facts, *i.e.* that no alkene exchange occurs and that each alkane formed has two deuterium atoms in the expected places, and has been put forward as a possible mechanism for ethane formation on zinc oxide.<sup>34</sup> An alternative to the concept of direct molecular addition is stepwise reactions involving the two hydrogen or deuterium atoms which are to be added being held on pair sites in the surface.<sup>32,33</sup> Activation of hydrogen or deuterium by adsorption on a pair site would enable the addition reaction to occur without accompanying either exchange of the alkene or the H<sub>2</sub>/D<sub>2</sub> equilibration reaction.

The results with propene are important as a guide to possible mechanisms. Exchange was not detected at 305 K, but at 433 K it occurred at *ca*. 25% of the rate of the addition reaction. The interesting feature was that the hydrogen atom on the central carbon was exchanged just as readily as the remaining five hydrogen atoms (see table 4). This behaviour is in marked contrast to results for propene exchange on calcium oxide or alumina,<sup>20</sup> both of which gave negligible exchange on the central carbon, and on lanthana,<sup>28</sup> which gave little such exchange.

The replacement of the hydrogen atom on the central carbon of propene cannot be achieved by reversible formation of either allyl or prop-2-yl adsorbed species but must involve either vinyl or prop-1-yl species. When a vinyl mechanism occurs, e.g. on alumina,<sup>20</sup> exchange of the terminal methylene group is more rapid than the replacement of the hydrogen on the central carbon. Steric factors may be responsible for this difference in rate, since the linking of a propen-2-yl species to the surface may be more difficult than the corresponding process with a propen-1-yl intermediate. Since preferential exchange of the methylene hydrogen atoms was not found with zirconia a vinyl mechanism is less likely than a process involving prop-1-yl intermediates. It follows that there must be a limited amount of alkyl reversal at temperatures of 400 K or above. The slightly greater degree of exchange of the hydrogen on the central carbon suggests that reversible formation of prop-1-yl occurs more readily than the same process with prop-2-yl. This suggests that the alkyl species is unlikely to be cationic in character because a positive charge would facilitate the formation of the 2-yl species rather than 1-yl. The type of propene exchange observed in the present work with pure zirconia contrasts with earlier results for the reaction carried out on a sulphur-treated zirconia or zirconia-alumina catalysts.<sup>14</sup> Those results showed exchange limited to the five terminal hydrogen atoms and were consistent with acidic type catalysis *via* secondary carbocationic alkyl species.

While alkyl reversal would be a sufficient mechanism to account for the exchange of all hydrogen atoms of propene, it is not possible to exclude a contribution from a  $\pi$ -allyl mechanism to the exchange of the five terminal hydrogen atoms, but it is clearly not the dominant mechanism on zirconia. The importance of  $\pi$ -allyl mechanisms on zirconia may increase with the size of the alkene. For 2-methylpropene<sup>15</sup> which showed exchange at 433 K at about half the rate of the addition reaction, the results were consistent with a  $\pi$ -allyl mechanism since the deuterium was randomly distributed in the alkene. The isomerisation which took place with 23DMB2 relatively rapidly compared with either exchange or formation of alkane was essentially an intramolecular process because the product isomer, 23DMB1, contained no more deuterium than the reactant. The most likely mechanism for this reaction on zirconia is hydrogen transfer through the reversible formation of  $\pi$ -allyl intermediates, although for more acidic surfaces an associative route through tertiary carbocationic alkyl species could be important.

The principal conclusions about mechanisms of alkene reactions with deuterium on zirconia are: (1) Alkane formation occurs in such a manner that the products contain two deuterium atoms in the expected positions. Adsorption of deuterium on pair sites may be involved. (2) The extent of alkene exchange only becomes significant at temperatures of 400 K or above. The reaction must involve some degree of alkyl reversal with propene. (3) The reversible formation of  $\pi$ -allyl intermediates contributes to exchange and isomerisation to an extent which varies with the nature of the alkene. Even in the presence of deuterium, isomerisation tends to involve intramolecular reaction as shown by the present results with 23DMB2 and previous work with but-1-ene.<sup>10,11</sup>

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