

## Reactions of Alkanes with Deuterium on Lanthana in the Temperature Range 570 to 720 K

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Reactions of methane, propane, *n*-butane, 2-methylpropane, and 2,2-dimethylpropane with deuterium have been studied on lanthana catalysts at 625 K and other high temperatures. The major products in all cases were the D<sub>1</sub>-alkanes and other lightly exchanged molecules formed by a stepwise exchange process. Two further reactions occurred with alkanes which could undergo direct dehydrogenation; these were the formation of small quantities of highly exchanged alkenes and the formation of highly exchanged alkanes. Deuterium NMR spectroscopy was used to analyse the products from some of the reactions; this technique confirmed the presence of alkenes and gave quantitative information on the amounts of deuterium in various positions and groupings in the hydrocarbons. Primary C-H exchanged more rapidly than secondary or tertiary bonds but the rates of reaction at 625 K did not vary substantially with the nature of the hydrocarbon. The results provided mechanistic information about the probable nature and relative reactivity of various adsorbed intermediates. Some self-poisoning was observed in all cases. © 1987 Academic Press, Inc.

### INTRODUCTION

Exchange reactions of alkanes with deuterium have been studied on a number of oxide catalysts. Several papers (1-6) have shown that  $\gamma$ -alumina is an active catalyst for such reactions at moderate temperatures. The mechanism is believed to involve carbanionic intermediates formed by heterolytic dissociation of the C-H bond, because activity increases with the acidity of the hydrocarbon and primary C-H bonds react more rapidly than secondary or tertiary bonds (6). The activity of  $\gamma$ -alumina depends on the pretreatment temperature, and a maximum rate of exchange of cyclopentane with deuterium was found for catalysts outgassed at 840 K (7). Magnesia (8) has been shown to be a less active catalyst than  $\gamma$ -alumina for reactions of alkanes with deuterium but the activity patterns were similar on the two oxides. Rutile (9) required even higher temperatures to bring about exchange, which was then accompanied by dehydrogenation to

form alkenes. The reaction of methane with deuterium over lanthana has been studied as part of an investigation of a series of oxides expected to show basic properties (10). A correlation was found between activity and the ionic radius of the cation, suggesting that reaction rate increased with the basic strength of the sites. The same study indicated that preferential exchange of primary hydrogen atoms in 2-methylpropane occurred at 573 K over lanthana but detailed results were not obtained.

The objective of the present work was to examine the exchange of a series of saturated hydrocarbons on lanthana to determine whether the pattern of activity was comparable to those found in earlier work with  $\gamma$ -alumina or magnesia. Preliminary experiments showed that temperatures of 570 K or greater were necessary to obtain reasonable rates of reaction and that for all the hydrocarbons studied, except methane and 2,2-dimethylpropane, dehydrogenation to alkene accompanied and contributed to the exchange of the alkanes. The technique of mass spectrometry was used to follow the reactions and in several cases supple-

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mentary information was obtained from analysis by deuterium NMR spectroscopy.

The lanthana catalysts examined were iden-

tical to those used recently to study exchange and addition reactions of alkenes (11, 12).

## EXPERIMENTAL

### Materials

Methane, propane (99%), *n*-butane, 2-methylpropane, and deuterium (99.5%) were obtained from Cambrian Chemicals Ltd., and cyclopentane (99.5%) was from Fluka A. G. The deuterium was purified by diffusion through a palladium-silver thimble and the hydrocarbons, except for methane, were vacuum distilled in the apparatus. The catalyst was prepared as the hydroxide by precipitation from an aqueous solution of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.999% from the Aldrich Chemical Co.) using ammonia. Pretreatment of individual catalyst samples consisted of heating about 95 mg of the hydroxide to 923 K under vacuum followed by outgassing for 3 h at the same temperature, which was selected because it had given maximum activity for the exchange of methane (10). The resulting oxide has a

surface area of  $16 \pm 1 \text{ m}^2 \text{ g}^{-1}$  measured by nitrogen adsorption (12).

### Apparatus and Technique

The reactions were carried out in a static system connected via a capillary leak to a Vacuum Generators Micromass 601 spectrometer. The size of the reaction vessel was  $210 \text{ cm}^3$  and the usual charge of hydrocarbon for kinetic experiments was  $9.1 \times 10^{19}$  molecules with a 5:1 ratio of deuterium:hydrocarbon. Reactions were followed by recording the size of peaks in the relevant range of values of  $m/e$  in the mass spectrometer. The analyses were more complicated than those normally required for exchange reactions because of the formation of small amounts of alkenes which were found to be highly exchanged. Details of the electron voltages and the peaks used for the analyses are given in Table 1. The usual corrections were made for naturally occurring isotopes and for fragmentation of the parent ions and other ions used to determine the composition of the products. Calibration experiments were carried out using 50:50 mixtures of alkane:alkene to determine the relative sensitivity factors for the peaks used to estimate these com-

TABLE I  
Ionising Voltages and Ions Used for Mass Spectrometric Analyses

Compound	Electron voltage (eV)	Ion used <sup>a</sup>		Sensitivity factor <sup>b</sup> alkene/alkane
		Alkane	Alkene	
Methane	16	$\text{CX}_4^+$	—	—
Propane	12	$\text{C}_3\text{X}_8^+$	$\text{C}_3\text{X}_6^+$	2.14
<i>n</i> -Butane	20	$\text{C}_4\text{X}_{10}^+$	$\text{C}_4\text{X}_8^+$	2.78 <sup>c</sup>
2-Methylpropane <sup>d</sup>	15	$\text{C}_3\text{X}_7^+$	$\text{C}_3\text{X}_5^+$	0.61
Cyclopentane	25	$\text{C}_5\text{X}_{10}^+$	$\text{C}_5\text{X}_8^+$	0.84
2,2-Dimethylpropane	35	$\text{C}_4\text{X}_8^+$	—	—

<sup>a</sup> X represents H or D.

<sup>b</sup> The sensitivity factors were measured using 50:50 mixtures of alkane:alkene.

<sup>c</sup> *trans*-But-2-ene was used as the alkene.

<sup>d</sup> For reaction at 680 K, it was necessary to use the parent ions  $\text{C}_4\text{H}_7\text{D}_3^+$  and  $\text{C}_4\text{D}_8^+$  to estimate the contributions of alkane and alkene to the peak with  $m/e = 46$  ( $\text{C}_3\text{H}_4\text{D}_3^+$  and  $\text{C}_3\text{D}_3^+$ ).

TABLE 2  
Product Distributions for the Reaction of *n*-Butane with Deuterium

Expt	Temperature, <i>T</i>	Time, <i>t</i> (min)	Peak <i>m/e</i> : %	58	59	60	61	62	63	64	65	66	67	68
				83.40	11.75	1.42	0.21	0.34	0.30	0.98	0.09	0.38	1.04	
BUT 1				Alkane				Alkene				Alkane		
				D <sub>0</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	{ D <sub>7</sub> D <sub>8</sub> }	D <sub>7</sub>	D <sub>8</sub>	D <sub>9</sub>	D <sub>10</sub>	
BUT 1	625	40	Obs. <sup>a</sup>	84.21	11.90	1.43	0.14	(0.06) <sup>b</sup>	0.11	0.36	0.09	0.26	0.38	1.06
			Calc. <sup>c</sup>	83.69	13.09	0.92	0.04	0.00	—	—	—	—	—	—
BUT 2	721	42	Obs. <sup>a</sup>	55.9	23.6	12.2	5.3	(0.9) <sup>b</sup>	0.6	1.1	0.0	0.0	0.1	0.3

<sup>a</sup> Assuming that peaks with *m/e* = 63 and 64 are due to C<sub>4</sub>HD<sub>7</sub> and C<sub>4</sub>D<sub>8</sub> and that all other peaks are due to alkane.

<sup>b</sup> Values are less reliable because no allowance was made for a possible contribution from alkene to the peak at *m/e* = 62.

<sup>c</sup> A binomial distribution totaling 97.74% and based on a chance of deuterium in each position of *d* = 0.0154.

pounds. Details of the method for analysing for the small amounts of exchanged alkene in the presence of exchanged alkane are described later with reference to the reaction of *n*-butane.

The mass spectrometric analyses were supplemented by deuterium NMR spectroscopy for three reactants: *n*-butane, 2-methylpropane, and 2,2-dimethylpropane. Reaction mixtures for experiments involving NMR samples contained a greater amount of hydrocarbon ( $1.4 \times 10^{20}$  molecules) in the reaction vessel, but with the usual 5:1 ratio of deuterium:hydrocarbon. After some 15% of exchange had occurred, the reaction mixture was expanded through a liquid nitrogen trap to condense the hydrocarbons which were subsequently transferred to an NMR sample tube containing 5% D-chloroform. The procedure for obtaining the spectra has been described (13).

## RESULTS AND INTERPRETATION

### *n*-Butane

The reaction between *n*-butane and deuterium took place at conveniently measurable rates at temperatures in the range 570 to 720 K. Results from the mass spectrum from a typical experiment taken after 40 min at 625 K are given in Table 2. Peaks in the range from *m/e* 59 to 61 were assumed to correspond to lightly exchanged alkane and those from *m/e* 65 to 68, to heavily exchanged alkane. Peaks with *m/e* from 62 to 64 were thought to arise mainly from the

heavily exchanged alkenes, C<sub>4</sub>HD<sub>7</sub> and C<sub>4</sub>D<sub>8</sub>. Analyses of the various isotopic products based on these assignments are given in the second row in Table 2 and the course of the reaction with time is shown in Fig. 1a. The assumption that some of the peaks were due to highly exchanged alkenes was confirmed by the shape of the curve for percentage alkene, which rose fairly quickly to a maximum of 0.45% of total hydrocarbon; the expected equilibrium value for dehydrogenation of *n*-butane to combined butenes was 0.68% under the conditions used at 625 K (14).

The curves in Fig. 1b show the results for the reaction of *n*-butane plotted according to the usual first-order reversible equations (15) which apply to exchange reactions. The first of these is

$$\ln(x_0 - x_\infty) = -k_0 t / (100 - x_\infty) + \ln(100 - x_\infty) \quad (1)$$

where  $x_0$  and  $x_\infty$  represent the percentage of light butene ( $D_0$ ) at time  $t$  and at equilibrium and  $k_0$  is the initial rate of exchange in  $\%(\text{time})^{-1}$ . The second is the corresponding equation for the rate of acquisition of deuterium by the hydrocarbon:

$$\ln(\Phi_\infty - \Phi) = -k_{\Phi} t / \Phi_\infty + \ln \Phi_\infty \quad (2)$$

Here  $\Phi$  is defined by

$$\Phi = \sum i D_i \quad (3)$$

where  $D_i$  represents the percentage of isotopic hydrocarbon with  $i$  deuterium atoms

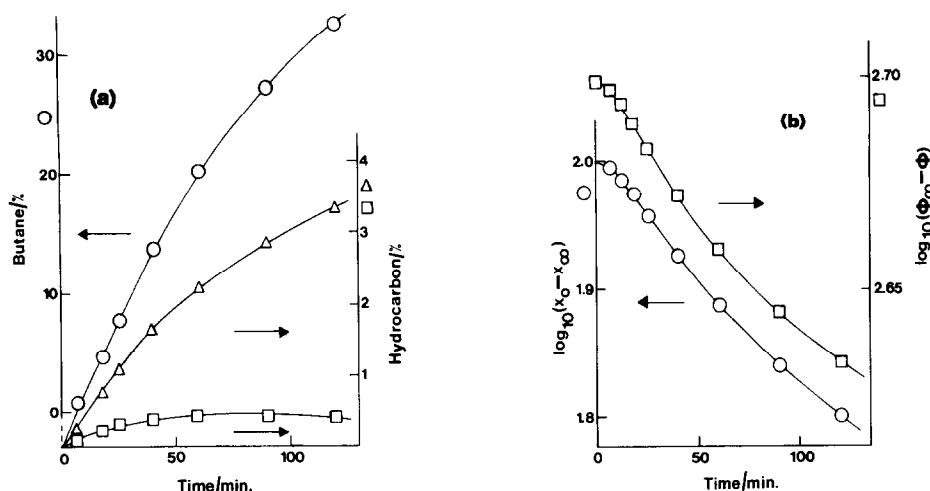


FIG. 1. (a) Course of reaction of *n*-butane with deuterium over lanthana at 625 K: ○, type I exchange ( $D_1$ -,  $D_2$ -, and  $D_3$ -products); Δ, type II exchange ( $D_9$ - and  $D_{10}$ -products); □, dehydrogenation. (b) Reversible first-order plots according to Eqs. (1) and (2) for the same reaction.

at time  $t$ . The  $k_\Phi$  value corresponds to the initial rate of acquisition of D atoms by 100 molecules of hydrocarbon in unit time and the ratio

$$M = k_\Phi/k_0 \quad (4)$$

gives the mean number of such atoms obtained by each reacting hydrocarbon molecule at the start of the reaction. Both plots were similar in shape and provided evidence for a short induction period followed by a rate of reaction that declined slightly with time.

The  $k_0$ ,  $k_\Phi$ , and  $M$  values for *n*-butane corresponded to the total rate of reaction and it was appropriate to obtain values for the component processes, the reactions responsible for giving the lightly exchanged products (I) and the multiply exchanged products (II). The initial rates of these processes,  $k_1$  and  $k_2$ , were readily obtained from plots of the various products against time and so were the values of  $M_1$  and  $M_2$  corresponding to the degree of multiple exchange of reactions (I) and (II). An estimate of the initial rate of dehydrogenation,  $k_D$ , was obtained from the gradient of the curve for dehydrogenation in Fig. 1a. The values of the various rate parameters

for *n*-butane at 625 K are given in Table 3. An Arrhenius plot for  $k_0$  is shown in Fig. 2 and the derived parameters were  $E = 66 \pm 3 \text{ kJ mol}^{-1}$  and  $\log(A/\text{molecules s}^{-1} \text{ m}^{-2}) = 21.3 \pm 0.3$ . The comparison in Table 2 of the observed distribution of lightly exchanged butanes with the calculated binomial distribution, expected for stepwise exchange (15), shows that the dominant reaction was mainly but not completely stepwise. This conclusion was confirmed by the value of  $M_1$  in Table 3.

TABLE 3  
Rates of Reaction of Alkanes with Deuterium  
at 625 K

Reactant	Total $k_0(M)^b$	Exchange		Dehydrogenation $k_D$
		I <sup>a</sup> $k_1(M_1)^b$	II <sup>a</sup> $k_2(M_2)^b$	
<i>n</i> -Butane	6.1 (1.8)	5.3 (1.1)	0.6 (9.6)	0.16
2-Methylpropane <sup>c</sup>	2.7 (1.7)	2.2 (1.1)	0.3 (6.9)	0.09
Propane	3.1 (1.6)	2.6 (1.0)	0.3 (7.5)	0.04
Cyclopentane	1.8 (1.1)	1.6 (1.1)	0.02 (9.5)	0.05

<sup>a</sup> Type I exchange refers to the formation of lightly exchanged molecules, i.e., with up to four D atoms; type II exchange refers to the more heavily exchanged species.

<sup>b</sup> Values of  $M$ ,  $M_1$ , and  $M_2$  refer to the average numbers of hydrogen atoms replaced in the total, type I, and type II exchange processes, respectively. Rates/ $10^{15}$  molecules  $\text{s}^{-1} \text{ m}^{-2}$ .

<sup>c</sup> Exchange data based on the  $C_3X_7^+$  ions.

TABLE 4  
Analysis of NMR Spectrum from Reaction of *n*-Butane at 721 K

		But-1-ene			
		Chemical shifts, $\delta$ (ppm)		%D	
		5.89, 4.93, 2.01, 0.99		3.5	
		But-2-enes			
Grouping <sup>a</sup>		Chemical shift, $\delta$ (ppm)		%D	
CX <sub>3</sub> CD=		5.45		2.1	
CX <sub>2</sub> DCX=		1.57		7.4	
<i>n</i> -Butane					
Grouping	Chemical shift, $\delta$ (ppm)	Isotopic shift, $-\Delta\delta$ (ppb)			%D
		Components	Calc. <sup>b</sup>	Obs.	
Secondary D					
CH <sub>3</sub> CHDCH <sub>2</sub> —	1.2699	—	—	—	3.8
CH <sub>2</sub> DCHDCH <sub>2</sub> —	1.2625	$\beta$	8.0	7.4	4.1
CH <sub>3</sub> CHDCHD—					
CH <sub>3</sub> CD <sub>2</sub> CD <sub>2</sub> —	1.2083	$\alpha + 5\beta$	61.2	61.6	1.8
Primary D					
CH <sub>2</sub> DCH <sub>2</sub> —	0.8809	—	—	—	42.3
CH <sub>2</sub> DCHD—	0.8716	$\beta$	9.5	8.3	1.8
CHD <sub>2</sub> CH <sub>2</sub> —	0.8608	$\alpha$	20.0	20.1	23.0
CHD <sub>2</sub> CHD—	0.8516	$\alpha + \beta$	29.5	29.3	1.6
CHD <sub>2</sub> CD <sub>2</sub> —	0.8408	$\alpha + 2\beta$	39.0	40.1	4.5
CH <sub>3</sub> CH <sub>2</sub> —		$2\alpha$	40.0		
CD <sub>3</sub> CD <sub>2</sub> CD <sub>2</sub>	0.8193	$2\alpha + 2\beta + 2\gamma$	60.8	61.6	4.1
					100.0

<sup>a</sup> X represents H or D.

<sup>b</sup> Assuming isotopic shifts ( $-\Delta\delta$ , ppb) for primary deuterium of  $\alpha = 20.0$ ,  $\beta = 9.5$ , and  $\gamma = 0.9$ ; for secondary deuterium,  $\alpha = 21.2$  and  $\beta = 8.0$ .

A sample taken after reaction of *n*-butane at 721 K for 42 min was analysed by deuterium NMR spectroscopy. The mass spectrometric data for this sample are given in Table 2 and the results of the NMR analysis are shown in Table 4. The presence of the butenes was confirmed by the NMR technique and it was possible to determine the relative percentages of the total deuterium present in the butenes and in various groupings of primary or secondary deuterium in the isotopic butanes. The

calculated isotopic shifts were based on values for the  $\alpha$  (two-bond),  $\beta$  (three-bond), and  $\gamma$  (four-bond) shifts derived previously for propane (13). The good agreement between the observed and calculated shifts suggested that the individual values were similar for butane and propane.

Several points of interest are contained in the results in Table 4. Exchange of the terminal hydrogen atoms in butane was favored because the total amount of primary deuterium in the alkane was eight

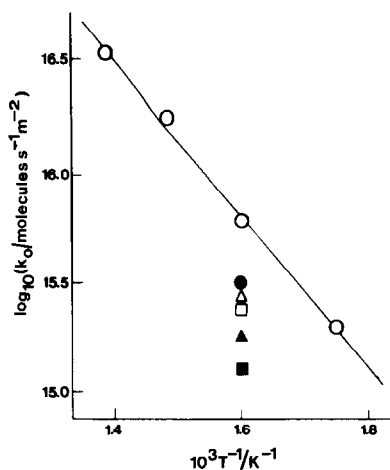


FIG. 2. Arrhenius plot for exchange of *n*-butane and rates of reaction of other alkanes: ○, *n*-butane; ●, propane; △, 2-methylpropane; □, 2,2-dimethylpropane; ▲, cyclopentane; ■, methane.

times the amount of secondary deuterium. A substantial fraction of the deuterium in the butane was present as isolated deuterium atoms, in agreement with the mass spectrometric results, and for these atoms the ratio of primary:secondary was even higher at 11:1. It was possible to estimate the average deuterium content of the alkenes by combining the data from the two techniques. The mass spectrometric evidence indicated that the 42.4% exchanged alkane contained an average of 1.68 D atoms/molecule and the NMR results gave the relative amounts of deuterium in the alkene and the alkane. The calculated value obtained was 6.3 D atoms/molecule for the 1.7% alkene present and this confirmed that most of the alkene was heavily exchanged, although the shapes of the resonances for the deuterium in the alkenes showed that a small part of the alkene was lightly exchanged. A slight preference for terminal deuterium in the but-2-enes was apparent, since the ratio of this kind of atom to deuterium on the central carbon atoms was 3.5:1.0 compared with a random ratio of 3.0:1.0. Some 27% of the deuterium in the alkenes was associated with but-1-ene whereas the equilibrium amount of this

alkene at 721 K was 21% of the total butene.

NMR analysis was also made of a sample of butane which was 13% exchanged at 571 K. The equilibrium amount of alkene at this temperature was only 0.05% and it was not possible to detect the deuterium in the alkene in comparison with the much larger amount in the exchanged alkane. Some 64% of the deuterium in the alkane was present as isolated atoms and the ratio of primary:secondary for these was 18:1. The deuterium present in the groupings corresponding to heavily exchanged molecules showed a ratio of 3.1:2.0 for primary:secondary which was close to the random ratio of 3.0:2.0.

#### *Other Alkanes Exchanging with Dehydrogenation*

2-Methylpropane, propane, and cyclopentane gave results that were broadly similar to those found for *n*-butane, i.e., a substantial amount of mainly stepwise exchange accompanied by a small amount of highly multiple exchange and some dehydrogenation to alkene. Overall rates of reaction at 625 K are shown in Fig. 2 and a detailed breakdown of the rates is given in Table 3. The maximum quantities of alkene formed, together with the possible amounts based on thermodynamic equilibrium, are reported in Table 5. Some decrease in the rate of reaction with time occurred with all systems and it was more noticeable at higher temperatures and in particular with cyclopentane, even at 625 K.

An experiment for NMR analysis was run with 2-methylpropane at 680 K and the results are given in Table 6. The chemical shifts for the resonances and also the values for the isotopic shifts were in accord with results reported previously for mixtures of 2-methylpropene and 2-methylpropane (11). There was an overlap between the resonances due to the  $-\text{CD}_3$  groups in the alkene and the tertiary D in the alkane. The amounts of the contributions to this peak were estimated assuming that the  $-\text{CD}_3$

TABLE 5  
Comparison of Maximum Percentages of Alkene  
with Calculated Amounts Corresponding to  
Equilibrium

Reactant	Temperature, $T$ (K)	% Alkene	
		Observed	Calculated <sup>a</sup>
<i>n</i> -Butane	625	0.47	0.68
	721 <sup>b</sup>	1.68	4.48
2-Methylpropane	625	0.56	0.58
	680 <sup>b</sup>	0.42	2.15
Propane	625	0.11	0.12
Cyclopentane	625	0.27	1.53
	721	0.29	22.0

<sup>a</sup> Using thermodynamic data (14).

<sup>b</sup> Obtained with the reactant mixtures used in the NMR experiment.

groups in the alkene contained three times the quantity of deuterium in the =CD<sub>2</sub> groups. The results from this experiment with 2-methylpropane were similar to those from the corresponding experiment with *n*-butane. The presence of a small amount

of highly exchanged alkene was demonstrated. The bulk of the deuterium in the alkane appeared in the grouping -CH<sub>2</sub>D and the amount of primary D was some 40 times the amount of tertiary D. A comparison of the proportions of deuterium in the alkene and the alkane, together with the mass spectrometric data, showed that the 0.42% alkene contained an average of 6.8 D atoms/molecule.

#### Alkanes Exchanging without Dehydrogenation

The exchange of methane was stepwise ( $M = 1.00$ ) at 625 K and the initial rate of reaction is given in Fig. 2. The rate declined by more than a factor of 2 before 10% of the methane had reacted. The exchange of 2,2-dimethylpropane also took place at 625 K without formation of alkene and the rate of reaction (see Fig. 2) decreased by a factor of 2 over a period of 2 h. The exchange was mainly stepwise since the value of  $M$  was only 1.02. The nature of the exchange was confirmed by running an NMR analysis on a sample from a reaction at 626 K. Using

TABLE 6  
Analyses of Products from Reaction of 2-Methylpropane with Deuterium for 160 min at 680 K

Mass spectrometric analyses							
% C <sub>3</sub> X <sub>7</sub> <sup>+</sup> ions from alkanes							
D <sub>0</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	D <sub>7</sub>
83.27	14.57	1.20	0.36 <sup>a</sup>	—	0.07	0.08	0.45
NMR results							
Alkene			Alkane				
Grouping	Chemical shift, $\delta$ (ppm)	%D	Grouping	Chemical shift, $\delta$ (ppm)	%D		
=CD <sub>2</sub>	4.6763	2.1	-CH <sub>2</sub> D	0.8862	71.1		
-CD <sub>3</sub>	1.68	(6.3) <sup>b</sup>	-CHD <sub>2</sub>	0.8650	5.7		
			-CD <sub>3</sub>	0.8280	12.6		
			≡CD	1.68	(2.2) <sup>b</sup>		

<sup>a</sup> There was also a contribution to the peak at  $m/e = 46$  from the 0.42% alkene present.

<sup>b</sup> The division of the 8.5% of D in the peak at  $\delta = 1.68$  ppm was estimated assuming a random distribution of D in the alkene.

TABLE 7

Products from Reaction of 2,2-Dimethylpropane with Deuterium for 215 min at 626 K

	% of C <sub>4</sub> X <sub>9</sub> <sup>+</sup> ions				
	D <sub>0</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>
Observed	82.04	15.73	2.03	0.20	—
Calculated <sup>a</sup>	81.33	17.00	1.58	0.09	—

<sup>a</sup> A binomial distribution corresponding to a chance  $d = 0.023$  of a D atom in each position, i.e., a deuterium content equivalent to that for the observed distribution.

previous results for the chemical shifts (13) it was possible to estimate the percentages of deuterium present in the groupings  $-\text{CH}_2\text{D}$  and  $-\text{CHD}_2$ . The mass spectrometric results for this sample are given in Table 7 and compared with a calculated binomial distribution with the same overall deuterium content as the experimental sample. The agreement between the two distributions shows that the reaction was mainly, but not completely, stepwise. This conclusion was confirmed by the NMR results because the observed percentages of deuterium in the groupings  $-\text{CH}_2\text{D}$  and  $-\text{CHD}_2$  were 92.8 and 7.2% whereas the calculated values for a stepwise process were 95.5 and 4.5%. More evidence of some contribution from multiple exchange was found for a reaction at 724 K which took place with an initial rate of  $1.64 \times 10^{16}$  molecules  $\text{s}^{-1} \text{m}^{-2}$  and a value of  $M = 1.24$ .

#### DISCUSSION

The dominant contribution to the exchange reaction with all hydrocarbons was a process which gave mainly the D<sub>1</sub> product, i.e., essentially a stepwise mechanism. Two other types of reaction took place with molecules that were able to undergo direct dehydrogenation: these were alkene formation and the related process of the production of highly exchanged alkanes. The latter

were observed as initial products only with reactants that showed dehydrogenation. The two main aspects of the results to be discussed are rates and mechanisms. This work provides further support for the evidence that lanthana behaves as a basic oxide catalyst for reactions of hydrocarbons. Rosynek and Fox (16) showed that the basic properties of the oxide were important for the low-temperature isomerization of butenes and a similar conclusion was reached by Utiyama *et al.* (10) in their comparative studies of methane exchange on various oxides.

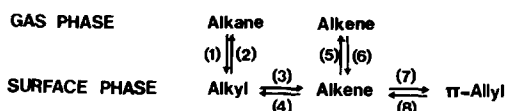
#### Rates

The rate of exchange found for methane at 625 K was 4.5 times faster than the rate of  $2.8 \times 10^{14}$  molecules  $\text{s}^{-1} \text{m}^{-2}$  reported by Utiyama *et al.* (10) at the lower temperature of 573 K. Since a change in temperature from 573 to 625 K gave an increase of rate by a factor of 3.2 for the exchange of *n*-butane, our result for methane is in accord with the earlier work. The variation in the rate of reaction with the nature of the hydrocarbon was not great; the results in Fig. 2 showed that there was only a factor of ca. 5 at 625 K between the rate for the least active hydrocarbon, methane, and that for the most active, *n*-butane. This behaviour with lanthana is similar to results reported earlier for exchange of alkanes on rutile (9) in which rates varying by only a factor of 10 at 750 K were obtained, with methane being the least reactive of the hydrocarbons studied. Certainly, the type of variation of rate with hydrocarbon acidity shown clearly at 289 K with  $\gamma$ -alumina, and, to some extent, with magnesia as well, is not apparent in the present work with lanthana. Nevertheless, we believe that the heterolytic dissociation of a C-H bond to form a carbanionic alkyl intermediate on the surface, as proposed by Utiyama *et al.* (10), is likely to be the initial step in the reaction. The correlation that they found between activity for methane exchange and ionic radius of the cation in



the oxide supported their suggestion. The present results show that lanthana is four times more active for the exchange of methane than magnesia (6) at 625 K and nearly 40 times more active for the exchange of *n*-butane. The higher rates of exchange of primary hydrogen atoms than of secondary or tertiary atoms, shown by the NMR evidence with *n*-butane and 2-methylpropane, provided confirmation that carbanionic alkyl intermediates are important, since such species are most readily formed by dissociation of primary C–H bonds. On the other hand, the possibility that preferential exchange in the terminal methyl groups results from steric factors controlling the ease of access of different parts of the molecule in the active sites on the catalyst cannot be excluded.

It is not surprising that some measure of self-poisoning was observed in the exchange of all the hydrocarbons because of the relatively high temperatures needed to study the reactions. The breakdown of alkenes on lanthana to form strongly adsorbed surface carboxy entities and adsorbed water has been suggested as a cause of declining rates of reaction with time over this oxide (12). The present results show that similar although lesser extents of self-poisoning occurred with all the alkanes. The greatest evidence of self-poisoning was associated with dehydrogenation at the higher temperature and the allied production of multiply exchanged alkane. The results in Table 5 show that equilibrium amounts of dehydrogenation were achieved for all alkanes, except cyclopentane, at 625 K but not at the higher temperatures. The potential for self-poisoning with cyclopentene on lanthana was noted in the earlier study on alkene reactions (12). A comparison of the product distributions for *n*-butane given in Table 2 shows how the contribution of the multiple exchange was smaller at the higher temperature and the course of the reaction with time suggested that this was due to self-poisoning.



SCHEME 1. General scheme for alkane reactions on lanthana.

### Mechanisms

It is convenient to relate the mechanistic information that can be deduced from the results to the general scheme for alkane/alkene reactions on lanthana. As already indicated, the main process contributing to the reactions of the alkanes with deuterium is essentially stepwise exchange. This involves the reversible formation of the adsorbed alkyl intermediates by steps 1 and 2. The results in Table 3 show that the other reaction, i.e., multiple exchange and dehydrogenation, amounted to 10% or less of the overall reaction and so 90% or more of the adsorbed alkyl species returned to the gas phase (as D<sub>1</sub> product) by reaction 2, which was in general 10 or more times faster than reaction 3. This evidence on the relative rates of reactions 2 and 3 is consistent with the belief that the rate-determining step for conversion of alkene to alkane on lanthana (11, 12) is reaction 4, which is rapidly followed by reaction 2. The same behaviour has been established for the addition reactions of ethene (17) and of cyclopentene (18) on zinc oxide.

Once alkene intermediates are formed by the minor reaction, 3, there are a number of different possible consequences. Some desorption occurs by reaction 5 to form the small amount of lightly exchanged alkene for which there was NMR evidence, but the bulk of the adsorbed alkene becomes substantially exchanged through the relatively rapid and reversible reactions 7 and 8. There are two routes by which this highly exchanged adsorbed alkene is converted to product: (i) conversion to highly exchanged alkane by reactions (4) and (2), and (ii) desorption as highly exchanged alkene by

reaction 5. The data in Table 3 indicate that the latter is the minor route for systems other than cyclopentane/lanthana. A similar reaction scheme was suggested earlier (9) for high-temperature reactions of alkanes on rutile, but the results now available for NMR analyses on products formed over lanthana provide much stronger evidence for the scheme proposed. The high rates of reactions 7 and 8 are consistent with the ability of lanthana to exchange, at temperatures below those used in the present work, those alkenes that can dissociate to  $\pi$ -allyl species. The fact that no alkene was observed to form from 2,2-dimethylpropane is evidence that lanthana is not an effective catalyst for the isomerization of this molecule to other C<sub>5</sub>-alkanes which would have undergone dehydrogenation in the same way as the C<sub>4</sub>-alkanes.

The significant percentage of the deuterium present in the grouping CHD<sub>2</sub>CH<sub>2</sub>- in the sample from the reaction of *n*-butane at 721 K (Table 4) is interesting. It confirms the tendency for preferential exchange of the primary hydrogen atoms but it does not require a mechanism for multiple exchange of a methyl group. Since over 42% of the alkane had exchanged before the sample was taken (Table 2), an appreciable percentage of the molecules would have acquired two or three deuterium atoms by successive reaction, leading to the formation of compounds such as CHD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CHD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>D as well as CH<sub>2</sub>DCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>D.

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