Reactions of Cyclopropane and Deuterium over Supported Metal Catalysts

Ronald Brown and Charles Kembali*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, UK

The reaction of cyclopropane and deuterium has been studied at low temperatures over a number of supported metal catalysts. The main reaction was normally ring-opening, yielding a mixture of isotopic propanes which were analysed mass-spectrometrically and by deuterium NMR spectroscopy. The patterns of isotopic propanes varied substantially with the nature of the metal and provided information about the types of adsorbed intermediates involved in the mechanisms of the reactions.

The reaction of propene and deuterium was also followed over supported platinum catalysts. In contrast to the results with cyclopropane, exchange of propene occurred and the propanes formed from propene were markedly different from those from cyclopropane, reflecting differences in the mechanisms of the reactions.

Evidence of dual-function catalysis was obtained using alumina-supported iridium with cyclopropane and deuterium; exchange took place on the support and ring-opening on the metal. Similar dual functionality was observed for reactions of methylcyclopropane or 1,1-dimethylcyclopropane with deuterium over the same Ir/AI_2O_3 catalyst. As a consequence of the present work, the high selectivity for the exchange of primary hydrogen atoms in various hydrocarbons over Ir/AI_2O_3 is now considered to be a function of the support rather than of the metal.

A number of reactions have been observed with cyclopropane and hydrogen or deuterium over metal catalysts. Exchange of the reactant does not usually occur but was found to take place in a stepwise manner over evaporated tungsten films.¹ The main reaction is ring-opening, sometimes termed hydrogenation or hydrogenolysis, and when deuterium is used the propanes formed may contain a number of deuterium atoms.^{2,3} With metals such as nickel or iron¹ more extensive breakdown of the molecule may occur, yielding ethane and methane. The cyclopropane-hydrogen system has often been used to investigate the properties of bimetallic catalysts such as silica-supported rhodium-iridium⁴ or nickel-copper,⁵ or the structure-sensitivity of the various possible reactions over a number of supported ruthenium catalysts.⁶ In some ways cyclopropane behaves similarly to propene, although it is less reactive and the kinetics for the formation of propane from the two reactants are not the same.^{2,3} The main objective of the present work was to use deuterium NMR spectroscopy to determine the groupings of deuterium atoms in the propanes produced from the reaction of cyclopropane and deuterium over a number of supported metal catalysts. It was hoped that the detailed information, so obtained, about the number and location of the labelled atoms in the product would give new information about the nature and reactivity of the adsorbed intermediates involved in the reaction. In one or two cases, the propene-deuterium reaction was studied on the same catalyst to provide comparative data, but no comprehensive investigation was made because detailed results for this system obtained through the use of microwave spectroscopy have been reported recently for various metal catalysts.7-10

The reactions of cyclopropane over oxide catalysts are significantly different from those over metals. Isomerisation to propene occurs over acidic oxides¹¹ and the corresponding formation of butenes is found with methylcyclopropane.^{12,13} In the presence of deuterium, exchange is the main process observed over basic oxides^{14,15} and little or no formation of saturated hydrocarbons takes place. These results indicated that the cyclopropane-deuterium system would be useful as a means of investigating the possible dual-function catalytic properties of an alumina-supported iridium catalyst. Ringopening to form propane would indicate catalysis by the metal, but exchange would suggest reaction on the support. Recent results¹⁶ with the Ir/Al₂O₃ catalyst gave evidence of preferential exchange of the primary hydrogens in a number of saturated hydrocarbons. The results were thought to arise from the activity of the metal, but a possible role of the support could not be excluded since exchange on γ -alumina tends to occur preferentially with primary C—H bonds.¹⁵ The second objective of this work was to use cyclopropane-deuterium as a test reaction to establish more clearly the catalytic properties of Ir/Al₂O₃. This part of the research was extended to include some experiments with methyl-cyclopropane.

Experimental

The preparation and pretreatment of most of the supported catalysts have been described previously and the details are given in Table 1. A silica-supported palladium catalyst was prepared by impregnation of 60–100 mesh silica (Sorbosil, Crosfield Chemicals) using 1% w/w of H₂PdCl₄ in 1 mol dm⁻³ HCl. After drying the catalyst for 4 h at 373 K it was reduced at 573 K for 2 h in flowing hydrogen and stored for subsequent use. Some experiments were carried out using Condea γ -alumina, STA 492, as catalyst after pretreatment in the same manner as the Ir/Al₂O₃.

Deuterium (99.5%), propane (99.5%) and cyclopropane (99%) were supplied by Matheson Gas Products. Methylcyclopropane, which contained as main impurities butane (1.0%), 2-methylpropane (0.2%) and butene (1.7%), was purchased from K and K Fine Chemicals, and 1,1-dimethylcyclopropane (97%) from Pfaltz and Bauer, Inc. The deuterium was diffused through a heated palladium-silver alloy thimble; the hydrocarbons were subjected to several freeze-thaw cycles before use.

The experiments were carried out in an all-glass recirculation system similar to that described by Bird *et al.*²¹ The total volume of the system was normally 360 cm³. The usual pressure of cyclopropane was 2.7 kPa, corresponding to a charge of 2.3×10^{20} molecules with a 5:1 ratio of deuterium: hydrocarbon. The extent of conversion to alkane was

 Table 1
 The supported metal catalysts

metal	support	metal loading mole g ⁻¹ (support)	pretreatment	ref.
Pt	niobia	5.1×10^{-5}	H ₂ , 523 K, 2 h evac. 523 K, 0.5 h	17
Pt	silica	10-4	H ₂ , 673 K, 1 h evac. 723 K, 0.5 h	18
Rh	silica	10-4	as for Pt/SiO,	18
Pd	silica	9.4×10^{-5}	as for Pt/SiO_2^2	16
Pd	calcium aluminate	2.5×10^{-6}	as for Pt/SiO ₂	16
Ir	silica	10-4	as for Pt/SiO ₂	19
Ir	alumina	2×10^{-5}	H ₂ , 748 K, 4 h evac. 748 K, 0.5 h	20

determined by analysis of samples using a Perkin-Elmer F33 gas chromatograph fitted with a flame-ionisation detector. The C₃ hydrocarbons were separated on a column (2 m) containing 3% (by mass) squalane on activated alumina at 345 K using nitrogen as carrier gas at a pressure of 207 kPa. For runs with methylcyclopropane the temperature of the column was increased to 388 K. The C₅ hydrocarbons from reaction of 1,1-dimethylcyclopropane were analysed using a column (3.5 m) of n-octane on Porasil C operated at 333 K with a nitrogen carrier gas pressure of 138 kPa.

Some mass-spectrometric analyses were made during the course of the reactions but the main analyses were carried out after the required extent of reaction had occurred and the reaction mixture isolated from the catalyst. Low voltages, in the range 10–15 eV, were used for the ionising electrons in order to minimise fragmentation. With cyclopropane-propane mixtures the cyclopropane parent ion (m/z = 42) was typically between 3 and 7 times more sensitive than the propane parent ion (m/z = 44). In the absence of exchange of cyclopropane, minor corrections were made to the heights of the peaks at m/z = 43 and 44 to allow for natural isotopes in the cyclopropanes. The peaks from m/z = 44 to 52 were then

treated in the normal way for isotope and fragmentation corrections in order to obtain the amounts of the various isotopic propanes. The procedures used for other reactant mixtures are described in the appropriate sections below.

Results

Cyclopropane-Deuterium

Experiments using all the supported metal catalysts except Ir/Al_2O_3 are presented in this section. Results for typical experiments are shown in Table 2; no exchange of the reactant was observed but propane was formed at easily measurable rates over the platinum catalysts at 256 K and over the other metals at 296 K. There was some evidence for an initial rapid reaction over rhodium and to a lesser extent over platinum before a steady rate was observed. The mass-spectrometric analyses of the propanes are given in Table 3. All experiments with platinum, supported on silica or niobia, showed a pronounced maximum at the D₂-compound combined with a distribution which extended steadily out to the D₈-compound. The Ir/SiO_2 gave a maximum at D₂ and a

Table 2 Formation of propane from reactions of cyclopropane or propene with deuterium on supported metal catalysts

expt.	support	catalyst mass, w/mg	T/K	t/min	propane formed (%)	rate $r/10^{-3}$ molecule s^{-1} (metal atom) ⁻¹
			cyclopro	Dane		
Pt 1	SiO ₂	8.9	256	120	17.6	19
Pt 2 ^a	SiO ₂	8.7	255	110	18.2 ^a	314
Pt 3	Nb ₂ O ₅	58.0	256	12	15.7	29
Ir 1	SiO ₂	8.0	296	80	17.7	17
Pd 1	SiO ₂	11.4	296	34	23.7	39
Rh 1	SiO ₂	14.5	292	42	16.7	11
	-		proper	ne		
Pt 4	SiO ₂	9.1	236	12	40.0 ^b	410
Pt 5	Nb ₂ O ₅	54.7	234	89	16.2°	3.9

^a The ratio of D_2 : hydrocarbon was 1:1 compared with the usual 5:1 mixture. ^b 5.7% of the propene was exchanged. ^c 6.3% of the propene was exchanged.

Table 3 Mass-spectrometric analyses of the propane formed from cyclopropane and deuterium

percentages										
expt.	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	M_x^{b}
Pt 1	(0) ^a	9.0	39.7	17.7	10.1	6.3	5.2	5.1	6.9	3.36
Pt 2	1.0	15.2	34.0	15.6	9.4	7.3	6.0	5.7	5.8	3.26
Pt 3	0.8	6.4	38.1	11.1	13.2	8.7	4.7	4.7	10.3	3.70
Ir 1	(0) ^a	4.5	14.2	10.2	9.9	9.7	10.4	15.7	25.4	5.27
Rh 1	(0) ^a	3.4	2.3	6.4	7.4	7.0	13.2	22.2	38.1	6.31
Pd 1	(0) ^a	1.2	2.5	1.6	1.9	2.5	5.3	25.7	59.3	7.17

^a Amount too small to estimate. ^b M_x gives the mean deuterium content of the propanes.

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86

more prominent maximum at D_8 . Highly exchanged propanes were formed over Rh/SiO_2 and to an even greater extent over Pd/SiO_2 . A similar distribution of products was found for the palladium catalyst supported on calcium aluminate, although this experiment was run at 316 K partly because of the low metal loading.

The NMR analyses gave resonances for the deuterium atoms in the propanes with similar chemical shifts to those described earlier.²² Secondary deuterium atoms gave broad peaks in the region $\delta = 1.29$ -1.23 ppm, but these could not be resolved by line-narrowing techniques. Primary deuterium atoms gave a series of peaks in the region from $\delta = 0.89$ to 0.83 ppm. Some of these results for the primary deuterium atoms are shown in Fig. 1 and 2. The separation of these peaks arises from the isotopic shifts associated with different groupings of primary and secondary deuterium atoms in the propanes. The values of these isotopic shifts were determined in the earlier work²² and are confirmed by the present results. The presence of the second deuterium atom on the same carbon atom in the grouping CHD₂CH₂- gives rise to a large α (two-bond) isotopic shift of -20 ppb. Likewise, the presence of a deuterium atom on the neighbouring secondary carbon atom in the grouping CH₂DCHD- shows a smaller β (three-bond) isotopic shift of the position of the resonance of the primary deuterium of -9 ppb. The detailed analyses derived from the NMR spectra for the reactions over the four silica-supported metals are given in Table 4.

Propene-Deuterium

The formation of propane occurred readily over the two supported platinum catalysts at 235 K and rates are given in Table 2. It was not possible to obtain a mass spectrum of the deuteropropenes without contributions from the deuteropropanes even by the use of low voltages for the ionising electrons because the relative sensitivity for the propene-propane parent ions was only about 3 for 10 eV electrons and did not vary much with electron voltage. The analyses obtained for



Fig. 1 NMR spectrum for the primary deuterium atoms in the propane formed from cyclopropane in experiment Pt 1. The interpretation of the resonances A–G are given in Table 4



Fig. 2 NMR spectra for the primary deuterium atoms in the propane formed from cyclopropane: upper curve, experiment Ir 1; lower curve, experiment Rh 1

the propene-propane mixtures are given in Table 5. The main problem of interpretation of the mass-spectrometric data was associated with the peaks at m/z = 44 and 45 which corresponded to D_2 - and D_3 -propenes and to D_0 - and D_1 -propanes as well as fragment ions. The allocation of these peaks to propenes and propanes was made using the results from gas chromatography for the percentage of propane and the NMR data on the relative amounts of deuterium in the alkenes and alkanes. Some confirmation that the figures derived in this way were valid was the observation that the ratio of D_0/D_1 propane was similar to the ratio of D_4/D_3 propane in both experiments.

The NMR spectrum of the products from experiment Pt 4 provided information about the deuterium in the propanes, given in the last column of Table 4, and good resolution was

 Table 4
 NMR analyses of the isotopic propanes from the reaction of cyclopropane over each of the silica-supported metals and from the reaction of propene over platinum

expt.:		Pt 1	Ir 1	Rh 1	Pd 1	Pt 4
$2^{\circ}D(\%):$ 1°D/2°D:		18.8 4 32	25.6 2.91	23.0 3.35	22.8 3 39	42.9
peaks	groupings of 1 °D	4.52	perce	entages of	`1°D	1.55
A B	CH ₂ DCH ₂ - CH ₂ DCHD-	32.7 11.5	7.7 6.8	2.4 2.7	2 1	8.4 44.4
С	$\left\{\begin{array}{c} CH_2DCD_2 - \\ CHD_2CH_2 - \end{array}\right\}$	7.3	5.0	3.8	_	7.3
D	CHD ₂ CHD−	9.6	7.6	5.9	2	15.5
Е	$ \left\{ \begin{array}{c} CHD_2CD_2 - \\ CD_3CH_2 \end{array} \right\} $	8.5	11.2	9.8	7	5.8
F G	$CD_{3}CHD$ $CD_{3}CD_{2}$ —	16.5 13.9	(20) (42)	(19) } (56) }	88	(14) (5)

Table 5 Mass-spectrometric analyses of the propenes and propanes formed from propene and deuterium

expt.	propenes propanes	D ₀	D1	${{\mathbb D}_2}^a {{\mathbb D}_0}^a$	$\begin{array}{c} {{\mathbb D}_3}^a \\ {{\mathbb D}_1}^a \end{array}$	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	M_x^{b}
Pt 4	∫ propenes	56.2	2.5	(0.9)	(0.4)								0.092
) propanes	7 0 <i>6</i>		(1.8)	(5.5)	21.7	6.0	2.5	1.0	0.7	0.5	0.2	2.28
Pt 5	propenes	/8.5	4.1	(0.9)	(0.3)	80	20		0.6				0.081
	(propanes			(0.0)	(2.2)	8.9	2.8	1.1	0.0		—	_	2.21

^a Values in parentheses are less accurate. ^b M_x gives the mean deuterium content of hydrocarbons.

obtained for the resonances corresponding to the various groupings of primary deuterium atoms as shown in Fig. 3. Detailed results on the distribution of deuterium in the exchanged propenes were also obtained from the same spectrum and these are given in Table 6. The chemical shifts for the various positions of deuterium in the propene molecule and the isotopic shifts for multiply exchanged molecules were in good agreement with the detailed results published already.²³ The isotopic compositions of the propanes and propenes formed in experiment Pt 5 using niobia as support were similar to those found for Pt 4 even though the rate of reaction was markedly slower, see Table 2.

Reactions over Alumina and Iridium/Alumina

Reaction of the standard mixture of cyclopropane and deuterium over 0.5 g alumina at 250 K gave stepwise exchange but neither isomerisation to form propene nor ring-opening were detected. Rates from experiments described in this section are given in Table 7. The mass-spectrometric analyses were carried out using 14 eV ionising electrons, and relatively small amounts of fragment ions were formed (10% loss of one hydrogen, 2.3% loss of two hydrogens) under these conditions.

After 50 min reaction, the percentages of the various isotopic cyclopropanes were D₀ 70.4, D₁ 25.0, D₂ 4.2 and D₃ 0.4. This distribution is close to that expected (70.0, 25.7, 4.0, 0.3) for stepwise exchange. The NMR spectrum of this mixture is shown in Fig. 4. The chemical shift for singly exchanged molecules was 0.222 ppm. The main contribution to the peak at $\delta = 0.213$ ppm came from the deuterium nuclei in 1,2-dideuterocyclopropane so the β isotopic shift was -9.0ppb. The shoulder on this peak was thought to arise from the deuterium nuclei in 1,1-dideuterocyclopropane and its position suggested that the α isotopic shift was ca. -13.5 ppb. The small broad peak at $\delta = 0.2025$ ppm corresponded to nuclei subject either to $\alpha + \beta$ or 2β isotopic shifts. There was excellent agreement between the NMR results and values calculated for the relative sizes of the peaks from the massspectrometric data assuming a random distribution of

 Table 6 Distribution of deuterium atoms in the exchanged propenes formed over platinum

expt. grouping	chemical shift δ (ppm)	Pt	4	Pt 5
$\begin{array}{c} X - C - X \\ \parallel \\ CX_3 - C - D \end{array}$	5.855	19	19	30
<i>D</i> СН СХ ₃ С-Х	5.058	18	24	22
DCD	5.043	6)	24	23
H−C−D ∥ CX ₃ −C−X	4.965	26	37	26
$D-C-D$ \parallel CX_3-C-X	4.960	11)		20
-CH ₂ D	1.714	9		
$-CHD_2$	1.695	6	20	21
-CD ₃	1.676	5		
vinyl exchange/methyl	exchange	4.	0	3.8
D in alkane/D in alken	e	15.	1	5.3

Table 7 Rates of reaction of the cyclopropanes over alumina and alumina-supported irridium

reactant	catalyst	T/K	exchange, $r/10^{16}$ molecule s ⁻¹ g ⁻¹	ring-opening, $r/10^{-3}$ molecule (metal atom) ⁻¹ s ⁻¹
	(Al ₂ O ₃	250	6.5	
cyclopropane	$\left\langle Ir/Al_2O_3 \right\rangle$	258	19	9.3
	$(Al_2O_3 \text{ (ref. 15)})$	255	4.9	
methylcyclopropane	Ir/Al ₂ O ₃	255	9.7	4.4
	Al_2O_3 (ref. 15)	255	4.9	_
1,1-dimethylcyclopropane	Ir/Al ₂ O ₃	255	19	6.1



Fig. 3 NMR spectrum for the primary deuterium atoms in the propane formed from propene in experiment Pt 4



Fig. 4 NMR spectrum of the deuterium atoms in exchanged cyclopropane formed over γ -Al₂O₃ at 250 K

deuterium atoms in the products. The percentages of deuterium in the groupings contributing to the three NMR peaks with the calculated values in parentheses were 73.2 (72.3), 23.9 (24.3) and 2.9 (3.4). This agreement confirms that the exchange reaction was stepwise.

Results with cyclopropane and deuterium over aluminasupported iridium were different from those found with the silica-supported catalyst. Exchange occurred at about twice the rate of ring-opening to form propane. This behaviour indicated that Ir/Al₂O₃ was a dual-function catalyst with exchange catalysed by the support and ring-opening by the metal. The simultaneous occurrence of exchange and ringopening prevented an accurate analysis of the massspectrometric peaks for m/z = 44 (D₂-cyclopropane and D_0 -propane) or 45 (D_3 -cyclopropane and D_1 -propane). Despite these difficulties it was clear that the distribution of deuteropropanes was similar to that for Ir/SiO₂ reported in Table 3 with maxima for both D_2 - and D_8 -propane. The NMR spectrum of the products from this reaction confirmed that the exchange of the cyclopropane was stepwise and showed easily resolved resonances for the various groupings of primary deuterium atoms in the propanes broadly comparable to the results for Ir/SiO_2 in Fig. 2 and Table 4.

Evidence of dual-function catalysis was found with methylcyclopropane and deuterium over Ir/Al_2O_3 . Reaction over 160 mg of catalyst for 75 min at 255 K gave 24% exchange of the reactant and 18% of ring-opening with preferential formation of 2-methylpropane. The mass-spectrometric analysis showed that exchange was stepwise and that a spread of isotopic saturated C₄ hydrocarbons was formed with an average deuterium content of 3.3 D atoms molecule⁻¹. The information from the NMR spectrum of the products is summarised in Table 8.

Broadly similar results were obtained from the reaction of 1,1-dimethylcyclopropane and deuterium over Ir/Al_2O_3 . Reaction over 70.6 mg of catalyst at 255 K for 52 min gave 16% exchange and 8.8% ring-opening with preferential formation of 2,2-dimethylpropane. The results of the NMR analyses of the products are given in Table 9.

Table 8 NMR analysis of the products^{α} from the reaction of methylcyclopropane and deuterium over Ir/Al₂O₃ at 255 K

type of deuterium	chemical shift, δ (ppm)	(%)
3° in 2MP	1.674	12.1
2° in butane	1.27 to 1.22	7.7
1° in 2MP + butane	0.88 to 0.82	55.2
3° in MCP	0.648	1.7
trans D in MCP	0.38 to 0.37	12.1
cis D in MCP	-0.06 to -0.07	11.2
		100.0

^a Containing 79.2% methylcyclopropane (MCP) of which 24% had exchanged with deuterium, 16.9% 2-methylpropane (2MP) and 3.8% butane (1% present initially, 1.7% from rapid reaction of the butene impurity and 1.1% ring-opening of methylcyclopropane).

Table 9NMR analysis of the productsfrom the reaction of 1,1-dimethylcyclopropane and deuterium over Ir/Al_2O_3 at 255 K

type of deuterium	chemical shift, δ (ppm)	(%)
CH_2D - in 22DMP	0.9139	33.4
CHD_2 — in 22DMP	0.8930	3.2
1° D in 2MB ^b	0.855 to 0.801	15.2
2° D in DMCP	0.2064	48.2
		100.0

^a Containing 91.2% 1,1-dimethylcyclopropane (DCMP) of which 16% had exchanged with deuterium and 8.8% saturated C_5 -hydrocarbon resulting from ring-opening with 2,2-dimethylpropane (22DMP) as the major component. ^b No resonances were detected for 2° D or 3° D in 2-methylbutane (2MB).

Discussion

Interpretation of the NMR Spectra for Primary Deuterium Atoms in Propane

The peaks, A-G, shown in the spectra in Fig. 1-3 represent groupings of primary deuterium atoms in propane which were identified in earlier work²² and are listed in Table 4. Two groupings, CH_2DCD_2 with a 2β isotope shift of -18ppb and CHD_2CH_2 with an α isotope shift of -20 ppb may contribute to peak C. Likewise, the two groupings CH_2DCH_2 , is narrow and exhibits a linewidth of 0.25 Hz, present spectra for the propanes formed from cyclopropane over Pt/SiO₂ or Ir/SiO₂ reveal features which were not apparent in the previous work but are relevant to estimating the proportions of the two components of peaks C and E. The width of the peaks indicates whether or not the resonances for the primary deuterium atoms are broadened through D-D coupling with secondary deuterium atoms. Peak A in each spectrum, corresponding to the grouping CH_2DCH_2 , is narrow and exhibits a linewidth of 0.25 Hz, equivalent to 0.0045 ppm. Peak B, corresponding to the grouping CH₂DCHD— is always slightly broader than peak A to an extent consistent with the expected D-D coupling (unresolved) due to the secondary deuterium atom which produces a three-line spectrum (intensity ratio 1:1:1) with a separation between the lines of 0.17 Hz, equivalent to 0.003 ppm. Peak C in the spectrum for propane produced over Pt/SiO₂ is narrow, indicating that at least part of the resonance is due to CHD₂CH₂- because the grouping CH_2DCD_2 would give a broader peak due to the expected five-line spectrum (1:2:3:2:1) resulting from D-D coupling. On the same reasoning the narrow peak E must include a contribution from CD_3CH_2 and not solely from CHD₂CD₂.

Combination of the mass-spectrometric data in Table 3 with the NMR results in Table 4 leads to a comprehensive analysis of the deuterium in the propanes produced in each experiment. These analyses are brought together in Table 10. The values in the first two rows are derived in a simple way from the average deuterium content of the propanes and the ratio of primary/secondary deuterium from the NMR spectra. The remaining rows contain values calculated from the percentages of primary deuterium in the groupings given in Table 4. Assumptions have to be made in each case about the percentages of peaks C and E arising from the two relevant groupings. For simplicity we have assumed that the same percentage holds for the two peaks and selected a value to give results which are consistent with the other data. The success of the analyses is shown by the agreement between the values for the secondary deuterium per molecule derived independently from the groupings of primary deuterium, last row, and the corresponding values in the second row.

Mechanisms for the Reactions of Cyclopropane over the Silica-supported Metals, Platinum/Niobia and Palladium/Calcium Aluminate

The dominant reaction of cyclopropane over all these catalysts is ring-opening to form propane and no exchange of the reactant was detected. The mass-spectrometric analysis of the propanes, Table 3, suggests that ring-opening can occur by two processes. The first of these (a) gives a limited range of isotopic products, i.e. largely D₂-propane together with some D_1 - and D_3 -propane. The second (b) is a more complex process leading to a wider range of more highly exchanged products including perdeuteropropane. The metals differ significantly in the relative importance of the two processes. Platinum, whether supported on silica or niobia gives more (a) than (b). The proportion of (b) follows the sequence Pt < Ir < Rh < Pd, and as the contribution from (b) increases, the prominence of the maximum at the D_8 -propane rises and is most pronounced over palladium, supported on either silica or calcium aluminate.

The NMR spectra in Fig. 1 and 2 confirm the relative contributions of processes (a) and (b) to the formation of propane over the different metals and also provide evidence about the nature of the products from process (a), particularly over platinum. The spectrum in Fig. 1, with the large peak A and small peak B indicates that most of the D₂-propane must be $CH_2DCH_2CH_2D$ rather than $CH_2DCHDCH_3$. A simple calculation shows that if all the 9% D₁-propane is assumed to be $CH_2DCH_2CH_2D$ and all the 39.7% D₂-propane $CH_2DCH_2CH_2D$ these two compounds would account for only 90% of the observed size of peak A. So the grouping CH_2DCH_2- must be present in some of the more highly exchanged molecules, *i.e.* some of the D₃-propane must be $CH_2DCH_2CH_2$. The deductions in the preceding section,

 Table 10
 Analyses of deuterium in the propanes

expt.	Pt 1	Ir 1	Rh 1	Pt 4 ^a
from combined	MS/NM	R data		
1° D/molecule	2.73	3.92	4.86	1.30
2° D/molecule	0.63	1.35	1.45	0.98
from groupi	ngs of 1°	D		
resonances C and E assumed to be $CX_{1}CD_{2} = (%)$	50	80	50	80
1° D per exchanged methyl	1.47	2.06	2.52	1.32
exchanged methyls per molecule	1.86	1.90	1.93	0.98
2° D per molecule	0.63	1.28	1.46	1.00

^a Experiment with propene as reactant.

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86

based on the linewidth, that peaks C and E arise partly from the groupings CHD_2CH_2 — and CD_3CH_2 — reinforce these conclusions. There must be mechanisms which lead to further exchange of the hydrogen atoms on the terminal carbon atoms of propane without replacement of either of the secondary hydrogen atoms during the ring-opening reaction of cyclopropane over platinum.

The prominent peak A for propane formed over iridium shown in Fig. 2 and the related data in Table 4 confirm that this metal is second to platinum in promoting the simple ring-opening reaction. The results in Table 10 show that, as expected, both methyl groups in the propanes formed from cyclopropane contain deuterium, and the degree of methyl group exchange naturally follows the proportion of reactions occurring by process (b), *i.e.* Pt < Ir < Rh.

The possible intermediates involved in the reactions of cyclopropane over the metals are shown in Fig. 5. Species V is drawn as a planar π -bonded intermediate but could equally well be depicted with sp³ hybridisation and two σ -bonds to the surface. The absence of cyclopropane exchange and the nature of the propanes, revealed by mass-spectrometric or NMR analysis, formed in the ring-opening reaction enable a number of comments to be made about the role and reactivity of the various intermediates.

(1) If I is formed, the reaction must be irreversible and further breakdown perhaps to IV must occur rather than desorption to exchanged cyclopropane.

(2) The main mode of adsorption of the reactant is likely to lead to II and thus ring-opening is again largely irreversible.

(3) Interconversion between II and III can provide a means of further exchange at the terminal carbon atoms in propane, leading to the presence of the observed groupings CHD_2CH_2 — and CD_3CH_2 — in the products. The same results might be achieved by interconversion between II and IV, or by interconversion between III and VII.

(4) The fate of III is probably a major factor in controlling the nature of the overall reaction. The possibilities include dissociation to form II, V or VII, or desorption to yield propane. The more readily III is desorbed the greater will be the proportion of moderately exchanged propanes. Thus, the fate of III probably determines the relative contributions from process (a) and process (b).

(5) There must be some chance of acquisition of hydrogen atoms in steps such as II to III, or III to propane because D_1 -propane is formed. However, this chance must be small otherwise D_8 -propane would not be observed.



Fig. 5 Possible adsorbed intermediates involved in the reactions of cyclopropane over the metal catalysts

(6) The extensively exchanged products resulting from process (b) probably involves interconversions between III and V, and between V and VI.

There are a number of parallels between the behaviour of the four metals with cyclopropane and the types of reaction which occur in the exchange of saturated hydrocarbons with deuterium on the same metals. Platinum is known 16,22,24 to produce twin-peaked or U-shaped distributions of exchanged products, *i.e.* substantial amounts of the D₁-alkane together with a maximum at the perdeutero product as well. The conventional explanation of this behaviour has assumed that on some sites the adsorbed alkyl species, equivalent to species III, undergoes little interconversion with other species before being desorbed whereas on other parts of the surface substantial interconversion occurs. Similar factors appear to operate with cyclopropane as reactant. Hegarty and Rooney²⁵ have recently proposed a more detailed explanation of the two mechanisms on platinum. In contrast, palladium gives very highly exchanged initial products with most alkanes and pronounced maxima for the perdeutero compounds. This is believed to reflect the very efficient interconversion in the palladium surface of adsorbed alkyl, alkene and probably also allyl species. Clearly the same kind of mechanisms operate with the present system. Rhodium tends to behave like palladium, but the exchange is generally not quite so extensive with most hydrocarbons and similar behaviour is found with cyclopropane. There was one minor difference between the propanes formed from cyclopropane and those from exchange of propane over rhodium.^{16,26} With cyclopropane, substantially more D_8 - than D_7 -propane was formed, but with the exchange of propane at temperatures of 311 or 331 K there was more D_7 - than D_8 -propane. This behaviour with propane was interpreted as evidence for a significant contribution to multiple exchange by mechanisms involving $\alpha\gamma$ absorbed species such as II and IV in addition to the more usual alkyl-alkene interconversion process. The results in Table 10 confirm that $\alpha\gamma$ -species are important in rhodium since 50% of resonances C and E are attributed to the groupings CHD₂CH₂- and CD₃CH₂, respectively. Some of these groupings are also present in the propanes formed over iridium, which is known to have some ability to cause multiple exchange with compounds like 2,2-dimethylpropane by mechanisms involving interconversion between absorbed alkyl species and either $\alpha\alpha$ - or $\alpha\gamma$ -diadsorbed species.^{16,27,28}

Comparison of the Reactions of Propene and Cyclopropane over Supported Platinum

The results in Table 2 show that propene was more reactive than cyclopropane over Pt/SiO2, in agreement with earlier work,^{2,3} but little difference in activity was observed with Pt/Nb₂O₅. The analyses in Tables 4, 5 and 10 show major differences in the nature of the propanes formed from the two reactants. Whereas the D2-propane formed from cyclopropane was CH₂DCH₂CH₂D, the dominant product from propene was the CH₂DCHDCH₃ compound, giving rise to the large resonance B in the NMR spectrum in Fig. 3; a similar peak was found in the reaction over Pt/Nb₂O₅. Some redistribution of hydrogen and deuterium atoms also occurs during the addition process, forming appreciable amounts of the D_1 - and D_3 -propanes and to a lesser extent more highly exchanged products, see Table 5. The results for experiment Pt 4 in Table 10, show that an average of only one methyl group in the propanes is exchanged, but some degree of multiple exchange is found in that group and 20% of resonances C and E arise from CHD₂CH₂- and CD₃CH₂-, respectively.

3821

Our evidence for some exchange of the alkene accompanying the formation of propane is in agreement with previous work by Hirota and Hironaka²⁹ and, more recently, by Naito and Tanimoto.⁸ The distribution of deuterium in the alkene given in Table 6 agrees more closely with results obtained by microwave spectroscopy in the older work²⁹ using a platinum black catalyst than with the data reported for reaction at 198 K over platinum silica.⁸ However, all of the investigations show preferential exchange of hydrogen atoms in the vinyl positions, relatively less exchange of the methyl group and clear evidence that there is not sufficient double-bond movement to make the two ends of the molecule equally exchanged. A major advantage of the NMR technique is the information which it provides about the groupings of deuterium atoms in the alkenes. Although the extent of the exchange of the alkene was limited to a few per cent, Table 5, a significant proportion of the exchanged propenes contained two or more deuterium atoms, as shown in Table 6. The results now presented for the reaction of propene are broadly similar to those obtained recently in a detailed study of the reactions of 2-methylpropene.¹⁷ In both cases, the main mechanism of exchange involves reversible dissociation to adsorbed vinyl species. The limited amount of methyl group exchange probably results from some doublebond movement. The work with 2-methylpropene established that there was a route from vinyl species to alkyl species which led to enhanced exchange of one methyl group of the alkane.

The same kind of mechanism probably operates with propene, giving rise to the multiple exchange located mainly in a single methyl group of the propane formed as indicated by the results in Table 10 and the evidence in Table 4 that some 30% of the primary deuterium in the propane is found in the groupings CHD₂CHD— and CD₃CHD—.

Reactions over Alumina or Alumina-supported Iridium

The data in Table 7 show that all the rates of exchange are within a factor of two of 10^{17} molecule s⁻¹ g⁻¹ with all three reactants over the various catalysts at ca. 255 K. The nature of the aluminas used as catalysts in the present work, by Robertson et al.¹⁵ and as support for the iridium²⁰ was similar but not identical and so the agreement between the rates for exchange is remarkable. The NMR results with methylcyclopropane establish clearly the selectivity of the exchange process which had been established in the earlier work¹⁵ solely from kinetic measurements. The four hydrogen atoms of the unsubstituted CH₂ groups of the molecule react ca. 10 times faster than the hydrogen on the substituted group and the hydrogens in the methyl groups do not exchange at low temperatures. Likewise with 1,1-dimethylcyclopropane, exchange is confined to the hydrogen atoms in the CH₂ groups of the ring.

It is clear that Ir/Al_2O_3 differs from Ir/SiO_2 and shows two kinds of activity. The ability to bring about exchange must be associated with the support, whereas the ring-opening occurs on the metal. These results throw doubt on the interpretation which was given for recent results¹⁶ on the exchange of various hydrocarbons over Ir/Al_2O_3 . A high selectivity for the exchange of primary hydrogen atoms was attributed to the nature of the catalysts by the metal, although in the discussion John³⁰ raised the possibility that the alumina support might be the cause of the selectivity. In Table 11 we compare the rates of exchange of three hydrocarbons over Ir/Al_2O_3 with rates calculated for the same temperatures from the earlier work¹⁵ with γ -Al₂O₃. Both propane and 2methylpropane react faster by a factor of *ca.* 10 over the supported metal, but with n-butane the reaction over the

		$r/10^{16}$ molecule s ⁻¹ g ⁻¹			
reactant	T/K	Ir/Al ₂ O ₃	$Al_2O_3^a$		
propane	335	18	1.2		
n-butane	334	1.9	3.3		
2-methylpropane	372	92	7.1		

[&]quot; Ref. 15.

alumina is faster. The new evidence for the dual-function character of the alumina-supported iridium suggests that it was wrong to ignore the contribution from catalysis on the support which is now considered to be responsible for the preferential exchange¹⁵ of primary hydrogen atoms with Ir/Al_2O_3 .

The ring-opening process with both methylcyclopropane and 1,1-dimethylcyclopropane tends to occur preferentially at the bond between the unsubstituted carbon atoms. The results in Table 9 show that the process with 1,1-dimethylcyclopropane involves a simple 1,3-addition of deuterium to form $(CH_2D)_2C(CH_3)_2$ as the major product, in line with earlier work by Chevreau and Gault,³¹ who studied the reaction over a number of metals. Some of the deuterium in the product was present in the grouping CHD_2 , but the amount of this, equivalent to 8.7% of the total deuterium, can be explained by addition of deuterium to exchanged reactant. At the end of the experiment the percentages of the isotopic 1,1-dimethylcyclopropanes were 84.3% D₀, 14.6% D₁, 0.9% D_2 and 0.1% of D_3 and D_4 . These values show that the extent of the exchange at the end of the experiment was 0.171 D atom per molecule. If we assume that the average Dcontent during the course of the experiment was half this value, i.e. 0.09 D per molecule the calculated percentage of deuterium as CHD_2 — in the 2,2-dimethylpropane from ringopening is 8.6%, in good agreement with the experimental value. The mechanism must involve the formation of species of types II and III in Fig. 5 followed by desorption without other interconversions on the iridium surface.

We acknowledge the skilful assistance of Dr. I. H. Sadler who obtained the NMR spectrum using the S.E.R.C. high-field facility at Edinburgh. C.K. holds a Leverhulme Emeritus Fellowship.

References

- 1 J. R. Anderson and N. R. Avery, J. Catal., 1967, 8, 48.
- 2 G. C. Bond and J. Sheridan, Trans. Faraday Soc., 1952, 48, 713.

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86

- 3 G. C. Bond and J. Turkevich, *Trans. Faraday Soc.*, 1954, 50, 1335.
- 4 T. C. Wong, L. F. Brown, G. L. Haller and C. Kemball, J. Chem. Soc., Faraday Trans. 1, 1981, 77, 519.
- 5 T. S. Cale and J. T. Richardson, J. Catal., 1985, 94, 289.
- 6 J. Schwank, J. Y. Lee and J. G. Goodwin Jr, J. Catal., 1987, 108, 495.
- 7 S. Naito and M. Tanimoto, J. Catal., 1986, 102, 377.
- S. Naito and M. Tanimoto, J. Chem. Soc., Faraday Trans. 1, 1988, 84, 4115.
 S. Naito and M. Tanimoto, J. Chem. Soc., Faraday Trans. 1,
- 1988, **84**, 4115.
- 10 S. Naito and M. Tanimoto, J. Catal., 1989, 119, 300.
- 11 J. G. Larson, H. R. Gerberich and W. K. Hall, J. Am. Chem. Soc., 1965, 87, 1880.
- 12 H. R. Gerberich, J. W. Hightower and W. K. Hall, J. Am. Chem. Soc., 1968, 90, 851.
- 13 J. W. Hightower and W. K. Hall, J. Am. Chem. Soc., 1968, 90, 851.
- 14 J. G. Larson, J. W. Hightower and W. K. Hall, J. Org. Chem., 1966, 31, 1225.
- 15 P. J. Robertson, H. S. Scurrell and C. Kemball, J. Chem. Soc., Faraday Trans. 1, 1975, 71, 903.
- 16 R. Brown, C. Kemball and I. H. Sadler, Proc. 9th Int. Congr. Catal., The Chemical Institute of Canada, Ottawa, 1988, vol. 3, pp. 1013-1019.
- 17 R. Brown, C. Kemball and I. H. Sadler, Proc. R. Soc. London, Ser. A, 1989, 424, 39.
- 18 T. C. Wong, L. C. Chang, G. L. Haller, J. A. Oliver, N. R. Scaife and C. Kemball, J. Catal., 1984, 87, 389.
- 19 T. C. Wong, L. F. Brown, G. L. Haller and C. Kemball, J. Chem. Soc., Faraday Trans. 1, 1981, 77, 519.
- 20 A. C. Faro Jr, M. E. Cooper, D. Garden and C. Kemball, J. Chem. Res., 1983, (S) 110; (M) 1114.
- 21 R. Bird, C. Kemball and H. F. Leach, Proc. R. Soc. London, Ser. A, 1986, 408, 249.
- 22 R. Brown, C. Kemball, J. A. Oliver and I. H. Sadler, J. Chem. Res., 1985 (S) 274; (M) 3201.
- 23 R. Brown, C. Kemball, I. McGillivray and I. H. Sadler, Proc. R. Soc. London, Ser. A, 1986, 406, 183.
- 24 C. Kemball, Adv. Catal., 1959, 11, 223.
- 25 B. F. Hegarty and J. J. Rooney, J. Chem. Soc., Faraday Trans. 1, 1989, 85, 1861.
- 26 J. A. Oliver, C. Kemball, R. Brown and E. W. Jamieson, J. Chem. Soc., Faraday Trans. 1, 1985, 81, 1871.
- 27 A. C. Faro Jr and C. Kemball, J. Chem. Soc., Faraday Trans. 1, 1986, 82, 3125.
- 28 R. Brown and C. Kemball, J. Chem. Soc., Faraday Trans. 1, 1989, 85, 2159.
- 29 K. Hirota and Y. Hironaka, Bull. Chem. Soc. Jpn., 1966, 39, 2638.
- 30 C. S. John, Proc. 9th Int. Congr. Catal., The Chemical Institute of Canada, Ottawa, 1988, vol. 5, p. 356.
- 31 T. Chevreau and F. G. Gault, J. Catal., 1977, 50, 124.

Paper 0/02579H; Received 11th June, 1990