Mechanism of heterogeneous gas phase dehydration of 1-methylcyclohexanol catalysed by metal(IV) phosphates

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Abstract

The heterogeneous gas-phase dehydration of the tertiary alcohol, 1-methylcyclohexanol, and the secondary alcohol, cyclohexanol, over metal(IV) phosphate catalysts proceed at approximately equal rates. Under these conditions, cyclohexanol is known to react through a carbocationic mechanism. However, through use of deuterium-labelled substrates, it has now been shown that some of the major product (1-methylcyclohexene) from dehydration of 1-methylcyclohexanol arises by loss of hydrogen from the methyl group by a synchronous mechanism. The labelling results are consistent with either a synchronous or, more likely, a mixed synchronous/carbocationic mechanism. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gas phase dehydration of alcohols over acidic surfaces, such as alumina or metal(IV) phosphates, usually takes place by one or both of two mechanisms, as shown in Scheme 1 [1]. The first is a synchronous or concerted reaction similar to base-catalysed, liquid-phase E-2 elimination, in which the catalyst provides both an acidic site to react with the hydroxyl group and a basic site to abstract a proton (path *a* in Scheme 1) [2]. The second mechanism proceeds through a reaction similar to an E-1 elimination and involves the catalyst in providing an acidic site, which assists removal of the hydroxyl group to give a carbocation. Subsequent formation of alkenes is governed by Saytzeff's Rule (path *b* in Scheme 1) [3]. In some cases, there may be a third mechanism, in which there is synchronous 1,3-elimination of water (path *c*

in Scheme 1) [1]. This process usually plays only a small part in competition with the main synchronous mechanism.

Recently, it has been shown that cyclohexanol **1** is dehydrated in the gas-phase over zirconium phosphate by a carbocationic mechanism [4]. Substitution of a methyl group into the 4-position of **1** does not affect the mechanism of dehydration but a methyl substituent in the 2-position appears to skew the approach of the alcohol to the catalyst surface so that the hydrogen atom on C6 of the molecule is brought into close contact with the catalyst surface and reaction by a synchronous mechanism is observed. In this last case, hydrogen atoms, forced into contact with the catalyst surface by the presence of the 2-methyl group, are removed [4]. Thus, steric crowding around the hydroxyl group provides a favourable environment for a synchronous mechanism at the expense of the competitive carbocationic process.

To examine these steric effects on mechanism in greater detail, the dehydration of 1-methylcyclohexanol

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Concerted dehydration (*a*)
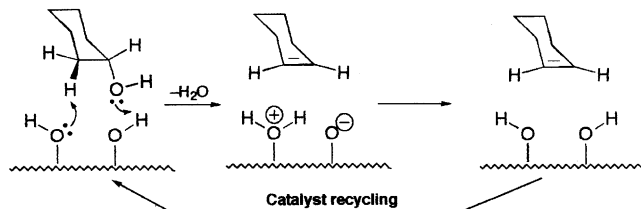
Non-concerted (carbocation) dehydration (*b*)
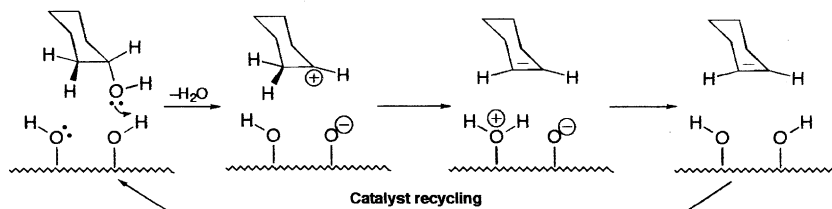
1,3-Elimination (*c*)
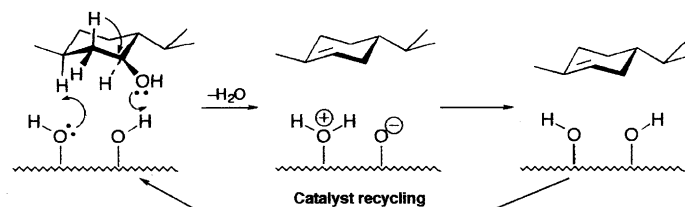
Scheme 1.

2 was examined because a methyl group attached to the same carbon as the hydroxyl group provides a significant increase in steric crowding near the reaction site, whilst at the same time, encouraging formation of a (tertiary) carbocation. The increase in steric crowding would be expected to affect the course of reaction in at least three ways:

(a) It should make bonding between the hydroxyl group and the catalyst surface somewhat more difficult and, hence, slow overall reaction.

(b) Binding of the hydroxyl to the surface should force the methyl group itself close to the surface of the catalyst, thereby, favouring a synchronous reaction.

(c) As mentioned briefly above, it should favour the formation of a carbocation because the cation would be the more stable tertiary, rather than the secondary ion formed from **1**.

Data on rates of carbocation formation from alcohols in the gas phase are not available, but measurement of the rates of acid-catalysed oxygen exchange reactions in aqueous solution show [5] that the tertiary alcohol, 2,2-dimethylpropanol **3**, reacts faster [6] than does the secondary alcohol, 2-methylpropanol **4** by a factor of 5×10^3. Structurally, **2** may be regarded as analogous to **3** and **1** to **4**. Therefore, it is reasonable to assume that the rates of acid-catalysed dehydration of **2** and **1** in aqueous solution should differ by a similar factor.

2. Experimental

Monitoring of reactions and examination of product compositions were carried out by GC and GC/MS on, respectively, a Dani 3800 gas chromatograph using a 25 m × 0.3 mm capillary column coated with OV351

and a Fisons Trio 1000 mass spectrometer, using EI at 70 eV and the same GC column. It was not possible to separate 3- from 4-methylcyclohexene. Therefore, the latter two materials are reported here as a single GC peak. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ (SiMe$_4$ as internal standard), on a Varian Gemini 300 instrument, the former at 300 MHz and the latter at 100 MHz. Heteronuclear cross-correlation spectra were obtained from a Bruker AMX 400 spectrometer, ^{1}H spectra at 400 MHz and ^{13}C spectra at 100 MHz and homonuclear correlations were obtained on the Varian Gemini instrument.

2.1. Metal(IV) phosphates

Zirconium, titanium and tin(IV) phosphates were prepared by established methods [7] and have been described elsewhere [8]. The amorphous phosphates were precipitated by addition of an aqueous solution of a metal(IV) chloride or oxychloride to aqueous phosphoric acid; the precipitate was washed well with water and dried. These amorphous forms are denoted here as ZrPA, TiPA and SnPA. The amorphous forms were crystallised [9] by refluxing them for x h in aqueous phosphoric acid of concentration y mol; the crystalline phosphates are denoted as, for example, ZrPA(x:y).

2.2. 1-Methylcyclohexanol

Commercial material (Aldrich) was used without further purification. Its partial mass spectrum had peaks at m/z 115 (1.1%), 114 (13.8), 113 (1.4), 112 (0.1) and the ^{1}H NMR spectrum exhibited a very sharp singlet at δ 1.21 (3H, CH$_3$), with a broad multiplet at δ 1.1–1.7. Its ^{13}C spectrum is given in Table 1.

2.3. 1-Methylcyclohexene 5

Commercial material (Aldrich) was used without further purification. Its partial mass spectrum gave peaks at m/z 97 (3.0%), 96 (43.0), 95 (7.0), 93 (1.0), 92 (1.0) and 91 (3.0). ^{1}H NMR, δ 5.38 (2H, vinyl), 1.92–2.00 (2H, m), 1.86–1.92 (2H, br, t, J=12.1 Hz), 1.63 (3H, s, methyl), 1.56–1.66 (2H, m) and 1.48–1.56 (2H, m); H-coupled ^{13}C NMR, δ 134.1 (s, C1), 121.2 (t, C2), 30.0 (t), 25.3 (t), 23.9 (q, C7) and 22.4 (t). An H/C heteronuclear correlation spectrum shows that the peak at δ 30.0 carries the hydrogens at δ 1.86–1.92. The latter peak is a broad triplet, indicating that the peak at δ 30.0 must be due to C6 and that this is next to a quaternary carbon (C1). The peak at δ 25.3 corresponds to a carbon that carries the hydrogens at δ 1.56–1.66 and, similarly, the carbon at δ 23.0 carries the hydrogens at δ 1.92–2.00, and one carbon at δ 22.4 is associated with hydrogens at δ 1.48–1.56. An H/H homonuclear correlation spectrum indicates strong coupling between signals at δ 1.86–1.92 and 1.56–1.66 and between δ 1.86–1.92 and δ 1.86–1.92, 1.48–1.56. The spectra are summarised in Table 1.

2.4. Methylenecyclohexane, cyclohexanol and cyclohexene

These were commercial samples (Aldrich) and were used without further purification. NMR data appear in Table 1.

2.5. 2,2,6,6-[²H]$_4$-1-methylcyclohexanol 2A

Cyclohexanone (25 ml) and deuterium oxide (99%; 25 ml) in 1,4-dioxan containing 4-toluenesulphonic acid (1 g) was refluxed for 2 h. The partially

Table 1
Positions of ^{13}C and ^{1}H NMR signals (δ) for unlabelled compounds

Compound[a]	δ (ppm) from tetramethylsilane						
	C1	C2	C3	C4	C5	C6	C7
2 (^{13}C)	69.9	39.5	22.7	25.6	22.7	39.5	29.5
5 (^{13}C)	134.1	121.2	25.3	22.4	23.0	30.0	23.9
(^{1}H)[b]	–	5.38	1.92–2.00	1.48–1.56	1.56–1.66	1.86–1.92	1.63
6 (^{13}C)	150.3	35.4	28.3	26.3	28.3	35.4	106.5

[a] The numbering of the carbon atoms is shown in the text.
[b] These hydrogens are attached to the carbons shown in the column headings.

Table 2
Abundances of ions in mass spectra of labelled 1-methylcyclohexanols (**2A**) and 1-methylcyclohexene (**5A**)

Compound	m/z values								
	95	96	97	98	99	100	116	117	118
2B									
Relative abundance[a]	1.8	5.4	17.8	31.9	27.8	4.0			
Corrected[b]	1.6	1.5	17.8	31.0	25.9	2.1			
Percentage of deuterium label[c]			d_1 24	d_2 41	d_3 35	–			
2A									
Relative abundance[a]							2.4	3.6	1.9
Corrected[b]							2.1	3.2	1.7
Percentage of deuterium label[c]							d_2 29	d_3 46	d_4 25

[a] Relative abundances measured from peak heights in mass spectrum.
[b] Peak heights corrected for ^{13}C isotopes and for the M-1 peak.
[c] Relative amounts (%) of deuteriated components.

deuteriated product was extracted continuously with pentane. After evaporation of the solvent from the pentane extract, the residue was again exchanged with fresh deuterium oxide (25 ml), as just described. Again, the product was extracted continuously with pentane, and after removing the pentane solvent from this second exchange, the resulting crude oil was immediately reacted with a twofold excess of methyl magnesium bromide, made from iodomethane (38 g) and magnesium (6 g) in diethyl ether. After 2 h, the resulting complex was decomposed by addition of water and filtered. The filtrate was dried (MgSO$_4$) and the solvent was evaporated under vacuum to give 2,2,6,6-[^2H]$_4$-cyclohexanol as an oil (16 g), bp 165–170°C (atmospheric pressure). The partial mass spectrum is given in Table 2. The proportions of d_4, d_3 and d_2 isotopic materials are shown in Table 2. The ^{13}C NMR spectrum was similar to that of the unlabelled material except that the peak at δ 39.5 had become a small complex multiplet. The ^1H NMR spectrum showed changes expected of the deuterium labelling at δ 1.4 and 1.7.

2.6. 7,7,7-[^2H]$_3$-1-methylcyclohexanol **2B**

Using a similar method to that described above, [^2H]$_3$-iodomethane (25 g; 0.18 mol; 99.5 atom%) was converted into [^2H]$_3$-methyl magnesium iodide in diethyl ether and was then reacted with cyclohexanone (17 g; 0.17 mol). After the usual work-up and distillation at atmospheric pressure, bp 165–170°C, the

required compound **2B** was obtained (15.9 g; 82% yield). The mass spectrum had a molecular ion at m/z 117 corresponding to the incorporation of three deuterium atoms and there were no peaks at m/z 114–116 that would have indicated loss of label through scrambling. In the ^{13}C NMR spectrum, a signal at δ 29.5 in unlabelled **2** had disappeared completely. As expected, the ^1H NMR spectrum had no signal corresponding to CH$_3$, which appears at δ 1.21 in an unlabelled sample.

2.7. 7,7,7,-[^2H]$_3$-1-methylcyclohexene **5A**

This labelled material was prepared by dehydration of the above labelled tertiary alcohol **2B**, which was heated with KHSO$_4$ in a reaction that was expected to minimise movement of the deuterium label [12]. Labelled alcohol **2B** (10 g; 0.09 mol) was mixed with finely ground KHSO$_4$ (5 g) and the mixture was heated in an oil bath maintained at 135°C for 2 h. The required **5** gradually distilled out from the reaction vessel and was collected (5 g; 58% yield). Its partial mass spectrum is shown in Table 2. Because of the presence of deuterium, the ^{13}C NMR spectrum contained no peak at δ 23.9 (CH$_3$) and, in comparison with unlabelled **5**, signals at δ 121.2 (C2) and δ 30.0 (C6) had been reduced by approximately 25%. In the ^1H NMR spectrum, the signal at δ 1.92–2.00 (H on C6) had been reduced by about 13% in comparison with unlabelled material. The data indicate that there had been some scrambling and loss of label during the dehydration process. From almost pure 1-[d$_3$]methylcyclohexanol,

the final **5** had 35% d_3, 41% d_2 and 24% d_1 label. Apart from the loss of label, the NMR and mass spectrometric results show that the acid-catalysed dehydration must also have led to some scrambling of the label into the C2 and C6 positions.

2.8. Dehydration of 1 and 2 over metal(IV) phosphates

Dehydration reactions were carried out in a conventional continuous flow glass tube reactor (250×23 mm), in which the catalyst (0.1 g) was sprinkled over loosely packed glass wool [11]. The substrate (0.5 g) was heated to 150°C for **2** and 120°C for **1** in a 25-ml flask attached to the front of the reactor. The vapour of the alcohol was swept from the pre-flask and into the reactor by a stream of nitrogen ($0.2\ l\ min^{-1}$), giving a contact time of approximately 35 s. On emerging from the reactor, the product gases were cooled, first in a U-trap cooled in ice and then in a second U-trap cooled by liquid nitrogen. The contents of the U-tubes were combined and analysed by GC and by GC/MS.

3. Results and discussion

The compositions of the product mixtures obtained on dehydration of **1** and **2** in the gas phase over a range of metal(IV) phosphates are recorded in Tables 3 and

4. Dehydration of **1** gave almost entirely cyclohexene and no products from carbocationic rearrangement. Dehydration of **2** gave **5** as the major product, together with small amounts of 3- and/or 4-methylcyclohexene and, in some cases, some 1,5-dimethylcyclopentene resulting from carbocationic rearrangement. Both **1** and **2** were dehydrated most readily by tin phosphate, followed by zirconium and then titanium phosphates, a reactivity trend that parallels the order of decreasing acidity of catalyst [13]. The amorphous phosphates proved to be better catalysts than the crystalline varieties, probably because of their greater surface areas [10,14] and increased proportions of strongly acidic sites [13]. Unexpectedly, the ratios of unreacted secondary alcohol **1** to cyclohexene and of unreacted tertiary alcohol **2** to **5** were similar in the gas phase for any one catalyst over the range used, suggesting that the rates of dehydration were similar. There was a small bias towards more rapid dehydration of the tertiary alcohol, but this result is in complete contrast to the difference factor of 5×10^3 between secondary and tertiary alcohols in solution for carbocationic reaction [5,6]. The result indicates the existence of other rate determining factors for the gas phase dehydration.

For gas phase dehydration reactions on an acidic surface, it could be expected that the tertiary alcohol **2** might have greater difficulty in bonding to the surface compared with the secondary alcohol **1** because of the steric crowding induced by the methyl group on the

Table 3
Dehydration of cyclohexanol over metal(IV) phosphates

Catalyst[a]	Temperature (°C)	Composition of reaction mixture (%)[b]		
		Cyclohexene	Cyclohexanone[c]	Unreacted alcohol
ZrPA	270	44	1	56
ZrPA	350	95	3	2
ZrPC (11:126)	270	4	0	96
ZrPC (11:126)	350	4	5	91
TiPA	270	55	1	44
TiPA	350	80	3	17
TiPC (11:126)	270	7	0	93
TiPC (11:126)	350	29	1	70
SnPA	270	90	1	9
SnPA	350	97	2	1
SnPC (8:126)	270	30	1	69
SnPC (8:120)	350	74	2	24

[a] The nomenclature for the catalysts is described in the text.
[b] These percentages are based on relative GC peak areas.
[c] Probably caused by a small amount of oxygen in the nitrogen carrier gas to the reactor.

Table 4
Dehydration of 1-methylcyclohexanol over metal(IV) phosphates
Caused by carbocationic rearrangement.

| Catalyst[a]	Temperature (°C)	Composition of reaction mixture (%)[b]			
		3- and 4-methyl-cyclohexene	1-methyl-cyclohexene	unreacted alcohol	1,5-dimethyl cyclopentene
ZrPA	270	7	92	1	0
ZrPA	350	14	79	1	3[c]
ZrPC (11:126)	270	3	12	85	0
ZrPC (11:126)	350	5	25	70	0
TiPA	270	7	59	34	0
TiPA	350	10	54	35	1
TiPC (11:126)	270	6	51	43	0
TiPC (11:126)	350	6	53	41	0
SnPA	270	8	62	29	1[c]
SnPA	350	12	84	2	1
SnPC (8:126)	270	6	68	26	0
SnPC (8:120)	350	10	73	16	1

[a] The nomenclature for the catalysts is described in the text.
[b] These percentages are based on relative GC peak areas from GC analyses.
[c] There was also a very small amount of an unidentified component.

tertiary alcohol. This effect would lead to a slower rate of adsorption onto reactive sites on the catalyst and, therefore, to a reduced rate of dehydration. Although **1** itself is known to dehydrate through a carbocationic mechanism [4], the existence of serious steric constraints means that the dehydration of **2** cannot be predicted with confidence. A carbocationic reaction could be expected to be favoured for the tertiary alcohol **2** because it could be expected to form an energetically favourable tertiary cation (reaction 1), followed by loss of a proton to give **5**. Alternatively, the tertiary alcohol **2** should also favour a synchronous mechanism, because steric effects draw H atoms on C2, C6 and C7 close to the catalyst surface. Hydrogen atoms on the three carbons (C2, C6, C7) next to that (C1) bearing the hydroxyl group are pulled close to the catalyst by the bonding of the OH group to the catalyst surface (reaction 2); hydrogens may be lost from positions C2 and C6 to give alkene **5** but loss of a hydrogen from the C7 atom would give methylenecyclohexane **6**, which would be expected to rearrange rapidly to **5**. Evidence that the dehydration product, **5** (reactions 1 and 2), might be formed at least partly from **6** comes from earlier work [15], which showed that 2-*d*-trans-2-methylcyclohexanol **7** can be dehydrated to **5**, whilst retaining 25% of its deuterium label, with-

out there being any kinetic isotope (H/D) effect (reaction 3). Similar reaction of the cis-isomer does exhibit a kinetic H/D isotope effect, but leads to complete loss of all of the label [15]. Thus, both carbocationic and synchronous mechanisms are expected to give **5**.

$$(1)$$

$$(2)$$

$$(3)$$
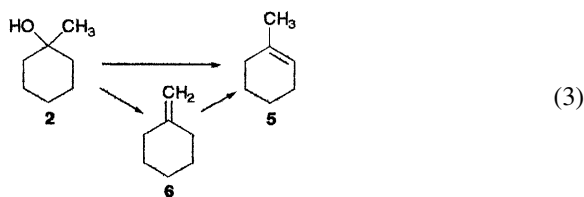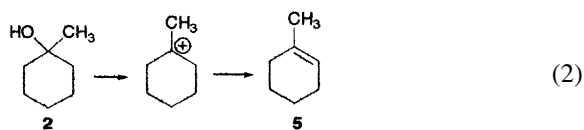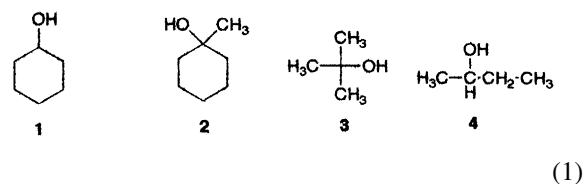
A means for distinguishing synchronous and carbocationic mechanisms in the dehydration of **2** is based on the above considerations and labelling studies. Reaction of **2A** is then expected to yield **5** by one or both of the two routes (carbocationic/synchronous; reactions 4 and 5). In the carbocationic mechanism, loss of a hydroxide anion would give a tertiary carbocation carrying four deuterium labels, but one of these must be lost as a proton to give the product d_3-labelled alkene **5B**. The carbocation might also give methylenecyclohexane **6A** by ejection of a proton from C7, but formation of this as the main product would be against all existing data known for the well-researched Saytzeff's rule [3]. The carbocationic mechanism must proceed with loss of at least one d-label to give a d_3-labelled **5**. Similarly, a synchronous elimination of OH with a d-label from C2 or C6 would again give a d_3-labelled **5** (**5B**, reaction 4). However, if synchronous reaction proceeds by loss of hydrogen from the C7 atom of alcohol **2A** with formation of **6** then 4 d-labels must be retained and formation of the observed product, **5** with four deuterium labels, requires only the favoured shift of one deuterium from C2 or C6 to C7. Hence, if dehydration of alcohol **2A** were found to give an alkene that retained all four deuterium labels, this would provide strong evidence for the operation of a synchronous process.

(4)

(5)
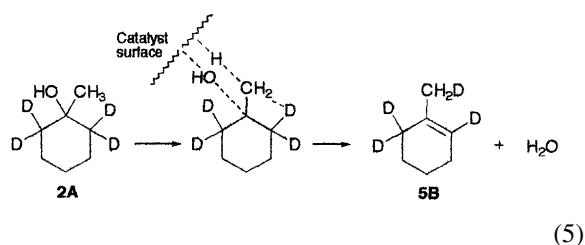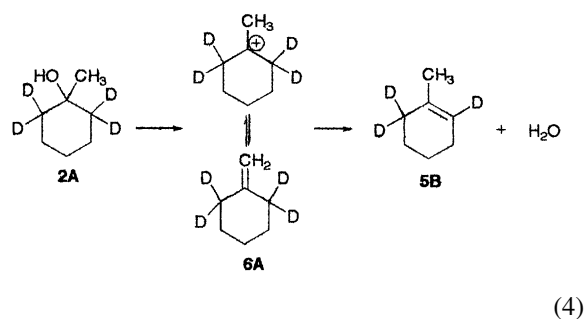
To test the above arguments, the d_4-labelled alcohol **2A** was dehydrated over ZrPA. After synthesis, the alcohol **2A** contained only 24% product having a d_4-label, the remainder being d_3, d_2 and d_1 (Table 2). On passage of this labelled alcohol over amorphous zirconium phosphate in the gas phase at 370°C, it gave **5** having the deuterium isotope composition listed in Table 5. Examination of this entry in Table 5 shows that there was still 8% of d_4-label from an initial 24% in the starting alcohol. Thus, the product alkene retained 33% of its original d_4-labelling. As outlined above, this result provides clear evidence that the d_4-labelled alcohol **2A** must have given a substantial proportion of d_4-labelled alkene **5B** (reaction 4), compatible with a synchronous, but not a carbocationic process.

The distribution of the four d-labels in the product alkene is important because scrambling of hydrogen over carbon atoms other than C2, C6 before dehydration could lead to retention of a d_4-label. An indication that intermolecular scrambling could not have occurred is provided by the observation that no d_5 or higher labelling was produced. The possibility of intramolecular scrambling was examined by NMR spectroscopy. Comparison of the ^{13}C NMR spectrum of **5** from the d_4-labelled alcohol **2A** with that of the same unlabelled alkene obtained from unlabelled alcohol **2** showed a significant reduction in the sizes of the signals at δ 23.9 (C7), 30.0 (C6) and 121.2 (C2). This result demonstrates the presence of both hydrogen and deuterium at each of these positions, the reduction in signal being caused by a reduced rate of spin relaxation because of the substitution of some hydrogen by deuterium. The analysis indicates that there is deuterium on C2, C6 and C7, but none at the other carbons. The ^{1}H NMR spectrum of **5** obtained from the labelled alcohol **2A** revealed that the signal at δ 1.86–1.92 (H6) had been reduced to less than half its size in the unlabelled authentic alkene. Similarly, the signal at δ 5.38 for the hydrogen on the double bond (H2) was reduced. No evidence for deuterium at C3, C4 or C5 was found.

These NMR spectroscopic results unambiguously confirm the operation of a synchronous mechanism because the d_4-labelled alkene could not have arisen by either inter- or intra-molecular scrambling of hydrogen from C2, C6 or C7 onto atoms C3, C4. The d_4-labelled alcohol **2A** gave d_4-labelled **5**, but a carbocationic

Table 5

Mass spectra of samples of 1-methylcyclohexene **5** isolated from dehydration of various deuterium-labelled samples of cyclohexanols and 1-methylcyclohexene **5**

Compound	m/z values						
	95	96	97	98	99	100	101
From 2A							
Relative abundance[a]	6.1	18.3	30.8	35.0	23.5	9.9	2.1
Corrected[b]	3.1	12.8	23.2	29.0	19.5	8.3	1.4
Percentage of deuterium label[c]		d_0 12.6	d_1 22.8	d_2 28.5	d_3 19.1	d_4 8.2	
From 2B							
Relative abundance[a]	2.0	4.6	11.4	26.5	46.6	5.0	
Corrected[b]	1.5	3.2	7.5	21.4	44.0	2.7	
Percentage of deuterium label[c]			d_1 10.3	d_2 29.3	d_3 60.3		
5 obtained by dehydration of 2B[d]							
Relative abundance[a]	4.8	23.8	23.2	27.7	10.5	1.8	
Corrected[b]	1.5	20.6	17.7	23.6	5.8	1.1	
Percentage of deuterium label[c]		d_0 30.4	d_1 26.1	d_2 34.8	d_3 8.6	–	

[a] Relative abundances measured from peak heights in mass spectrum.
[b] Peak heights corrected for ^{13}C isotopes and for the M-1 peak.
[c] Relative amounts of deuteriated components.
[d] 1-Methylcyclohexene was prepared by dehydration of 7,7,7-[^{2}H]$_3$-1-methylcyclohexanol with KHSO$_4$ and then passed through amorphous zirconium phosphate at 375°C (see text).

mechanism could give only a d_3-alkene. The reduction in the size of the ^{13}C NMR signal at δ 23.9 (C7) by approximately one third is consistent with an exchange of deuterium for hydrogen.

The d-labelling results indicate that the minimum amount of reaction proceeding by loss of hydrogen from C7 (synchronous reaction) is about 33% since this proportion of d_4 labelled alkene was formed from the d_4 labelled alcohol. If **2** lies almost immobilised on the catalyst surface then, as an approximation, positions C2, C6 and C7 would be equally likely to lose H/D and, overall, 66% of deuterium and 33% of hydrogen would be lost. However, if **2** can flex on the catalyst surface so that all hydrogens at C2, C6 and C7 can be involved in the reaction, then, statistically, 57% of deuterium and 43% of hydrogen would be lost. If an isotope effect operates, loss of hydrogen becomes easier than loss of deuterium and the range (66–57%) must fall accordingly. The observed loss of 67% of deuterium label suggests that **2** is largely immobilised on the catalyst surface during the dehydration step.

To explore the dehydration of **2** in greater detail, the differently labelled isomer, **2B**, was prepared and

passed over heated ZrPA, as for the d_4-labelled alcohol **2A** (Scheme 2). With this labelling pattern, a carbocationic reaction should yield **5A** directly, such that all three deuterium atoms on the methyl group are retained (path *a*, Scheme 2) or it could involve synchronous loss of deuterium from the methyl by initial formation of methylenecyclohexane **6B**, followed by rearrangement to the product alkene **5D** (path *b*, *c*; Scheme 2). Therefore, in this case, retention of all three deuterium atoms in the product alkene would indicate direct formation of **5** via ei-
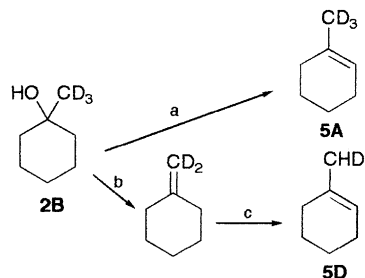
Scheme 2.

ther a carbocationic or a synchronous mechanism. Alternatively, loss of deuterium label would indicate an indirect synchronous formation of **5** via **6**. When **2B** was dehydrated over ZrPA at 350°C, the resulting **5** gave the deuterium isotope distribution shown in Table 5 (entry 2). The results reveal that only about 60% of the product alkene retained all three deuterium atoms present in the starting alcohol. Thus, direct formation of **5** must occur at least to this extent by loss of hydrogen from C2 or C6, through a cationic mechanism or a synchronous mechanism. The 40% loss of *d*-label on dehydration suggests this level of synchronicity following abstraction of a deuterium atom from the methyl position together with OH. As above, the distribution of the *d*-label in the product is important and was examined by NMR spectroscopy.

The ^{13}C NMR spectrum of **5** derived by dehydration of the alcohol **2B** had only a very small peak at δ 23.9 (C7), consistent with a large amount of deuterium at this position leading to slow spin relaxation. The peaks at δ 30.0 (C6) and 121.2 (C2) were somewhat reduced, indicating mostly the presence of hydrogen accompanied by some deuterium. The ^{1}H NMR spectrum of the alkene had only a small peak at δ 1.64 (CH$_3$), confirming the presence of only a small proportion of hydrogen. The complex peak at δ 1.86–1.92 (H6) had been reduced, again indicating some loss of hydrogen and gain of deuterium at C6. The NMR and mass spectrometric results are consistent in showing that the methyl group in **5** resulting from the dehydration of the d_3-alcohol **2B** must retain a significant fraction of the original deuterium, but also, that it loses about 40% of the deuterium originally present. The remaining 60% of hydrogen must have come from positions C2, C6 in alcohol **2B**, and statistically, would be expected to be about 66%. The deuterium distributions in the **5** resulting from dehydration of d_4-**2A** and d_3-**2B** are self-consistent and consistent with a considerable degree of synchronicity in the process.

The evidence for synchronicity in the dehydration of **2** suggests that **6** could be an intermediate in the reaction. Alternatively, the dehydration to **6** and its reversion to **5** might take place rapidly and consecutively on the catalyst surface before the most thermodynamically stable alkene is released. If there is such a reversion, it can only occur through hydrogen scrambling amongst positions C2, C6 and C7. If scrambling does occur, then the deuterium labelling results obtained

above must be regarded as residual amounts, indicating the minimum degree of synchronicity and not a maximum. Accordingly, it was decided to examine the effect of passing **6** and a labelled 1-methylcyclohexene over the ZrPA catalyst.

When an authentic sample of methylenecyclohexene was passed over ZrPA catalyst at 350°C at about the same flow rate as was used for the alcohols **2**, **2A** and **2B**, it was found that 64% of the alkene was converted into **5**. Methylenecyclohexene was not observed during dehydration of **2** and it must be concluded that this alkene **6** cannot be a 'free' intermediate in the formation of **5**, but may contribute to a 'transition state' form, which rapidly reverts to **5** whilst still on the surface of the catalyst.

To investigate the possibility of hydrogen scrambling on the surface of the catalyst, 1-methylcyclohexene **5B** was prepared from **2B** by liquid phase dehydration promoted by KHSO$_4$. The resulting **5** showed scrambling even in this process to the extent that the alkene retained 35% of the original d_3-label, with d_2 (41%) and d_1 (24%). A sample of this alkene was passed once over ZrPA at 350°C. The resulting alkene was found to have retained d_3 (9%), d_2 (35%) and d_1 (26%) (Table 5). Thus, **5** can lose a significant amount of label on the surface of the catalyst after dehydration has occurred and indicates that the earlier results for the degree of synchronicity must be regarded as minima. NMR spectra are consistent with scrambling amongst C2, C6 and C7. ^{13}C NMR spectroscopy shows an increase in the size of the signal at δ 23.9 (C7; more hydrogen present leading to faster relaxation of spins) compared with the alkene before reaction over ZrPA and there are reductions in the sizes of the peaks at δ 121.2 and δ 30.0 (C2, C6; more deuterium present leading to slower relaxation of spins). Confirmation of this labelling pattern is found in the ^{1}H NMR spectrum, which reveals a relative reduction in the size of the peak at δ 5.38 (H on C2) by 9% and a fall of some 14% for the peak at δ 1.86–1.92 (H on C6).

4. Conclusions

The rates of dehydration of acyclic secondary and tertiary alcohols in solution differ by some 5000 times. These reactions are known to proceed through a

carbocationic mechanism and the greater rate of dehydration of the tertiary alcohol is ascribed to the known greater stability of a tertiary over a secondary carbocation. For the two alcohols considered in the present experiments, **1** and **2**, a similar rate difference would be expected for a carbocationic dehydration mechanism in solution. In complete contrast, when these last alcohols were dehydrated in the gas phase over amorphous zirconium phosphate, the rates of dehydration were found to be almost the same. It was expected that steric effects would be important for adsorption of **2** onto the catalyst surface and that these might lead to at least a partial change in mechanism from carbocationic to synchronous, in which elimination of H and OH occur simultaneously. Labelling experiments in the dehydration of d_n-1-methylcyclohexanol have shown that synchronous loss of water must occur and that a purely carbocationic elimination mechanism cannot explain the observed results. When examined by mass and ^{13}C and ^{1}H NMR spectroscopy, the patterns of retention or loss of d-label respectively in d_4-and d_3-1-methylcyclohexanol following dehydration over zirconium phosphate are self-consistent and also consistent with a direct synchronous loss of water to give **5**. The formation of small amounts of 3- and/or 4-methylcyclohexene indicated the existence of some carbocationic content.

Synchronicity implies formation of methylenecyclohexene as either a true intermediate or as a transition state-like entity of fleeting existence. Passage of methylenecyclohexene over ZrPA catalyst was found to lead to about two thirds conversion to the more thermochemically stable **5**. The rate at which 1-methylcyclohexanol **2** was passed over the amorphous catalyst of moderately high surface area was such that there was ample time for all molecules to reach the surface. This is confirmed by the observation of almost complete dehydration of **2**. It must be concluded that methylenecyclohexene could not have been a 'free' intermediate at any stage because none was observed in the reaction products. The likelihood of it never being released from the catalyst surface as

an intermediate follows from the observed scrambling of deuterium and hydrogen found in d-labelled **5**. Because of these scrambling effects, the approximately 33% of synchronicity observed in the dehydration of **2** must be regarded as a minimum, the true value probably being much greater. Additionally, the existence of a synchronous reaction of hydrogen at C7 immediately indicates at least a similar level involving hydrogens at C2 and C6. Conservatively, this raises the likely degree of synchronicity to about 70–80%.

Acknowledgements

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