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# The mechanism of gas-phase dehydration of cyclohexanol and the methylcyclohexanols catalysed by zirconium phosphate and zirconium phosphite

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## Abstract

By means of deuterium labelling experiments, the mechanism of the gas-phase dehydration of cyclohexanol over a solid zirconium phosphate catalyst has been shown to involve a carbocation with a long lifetime. Product distribution studies have been used to show that the corresponding dehydrations of the 4-methylcyclohexanols also proceed through a carbocation mechanism, but have shown that the 2-methylcyclohexanols react partly by a carbocation mechanism and partly by a synchronous mechanism. Reactions catalysed by zirconium phosphite are slower, but give qualitatively similar products. Our results, and those of earlier workers, may be explained by consideration of the stereochemistry of the substrate absorbed on the catalyst surface; variations from the carbocation reaction result from orientations of the substrate adopted to relieve steric compression at the catalyst surface. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Cyclohexanol; Methyl cyclohexanol; Dehydration; Mechanism; Zirconium phosphate

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## 1. Introduction

Crystalline zirconium phosphate, $Zr(HPO_4)_2$, is composed of layers of zirconium atoms with bridging phosphate groups situated alternately above and below the zirconium atom plane [1]. Individual lamellae consist of three oxygen atoms of each phosphate group bonded to three different zirconium atoms, while the fourth phosphate oxygen atom carries an exchangeable proton. Zirconium phosphite, $Zr(HPO_3)_2$ has a very similar structure, except that the oxygen carrying the exchangeable proton in the phosphate is replaced by a hydrogen bonded directly to phosphorus in the phosphite [1–3]. In both zirconium phosphate and phosphite, the lamellae are held together by van der Waal's forces. It might therefore be supposed that only zirconium phosphate, with its Bronsted acid sites might be active as an acid catalyst. However, in the dehydration reaction of alcohols, both zirconium phosphate and phosphite show catalytic activity, suggesting that more than one mechanism could be operating [4].

Dehydration of cyclohexanol has proved to be a useful reaction for studies of the catalytic

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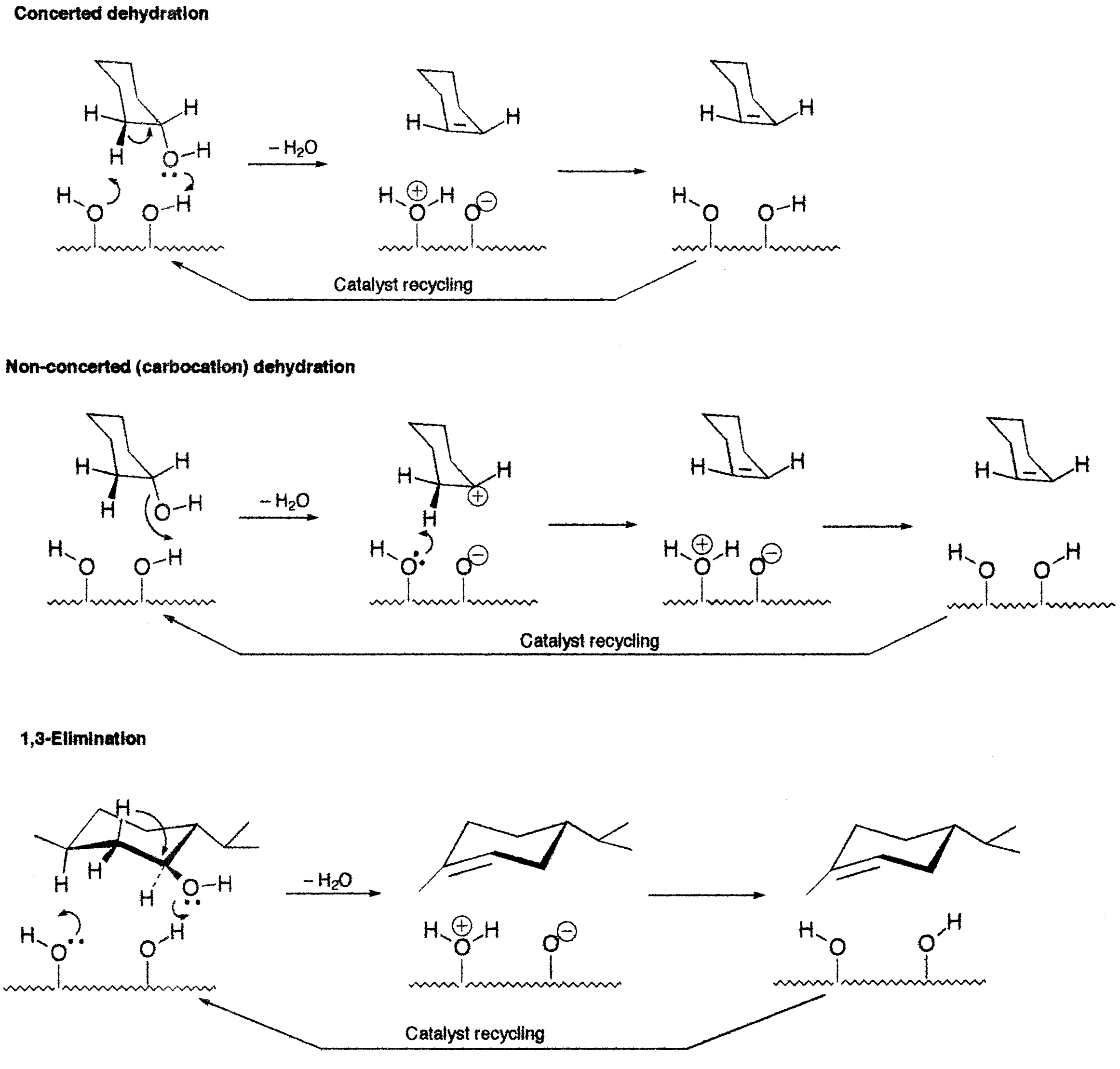
activity of zirconium phosphate. It has been used to show that catalytic activity depends on both intrinsic surface area [5] and acidity [6]. Attempts to relate this activity to crystal structure have not been successful [6,7]. These studies concern the surface activity of the catalyst, and did not consider the mechanism of the dehydration itself.

The mechanism of the gas-phase dehydration of cyclohexanol has proved difficult to study directly. Most available information on the dehydration has been obtained by examining the dehydration of methyl-substituted cyclohexanols. Investigations into the dehydration of the *cis*- and *trans*-2-methylcyclohexanols over alumina [8,9] or over hydroxyapatite [9] provided evidence for three simultaneous reactions (a–c):

(a) A synchronous reaction similar to E-2 elimination, in which alumina provides both an acidic site to attack the hydroxyl group



Scheme 1.

and a basic site to abstract a proton. The departing groups can be syn- or anti- to each other.

(b) A process similar to E-1 elimination in which reaction proceeds through initial formation of a carbocation. Product formation is then governed by Saytzeff's rule.

(c) A 1,3-elimination process similar to that observed during the dehydration of menthol [10]. This was found to be of limited importance [8,9], and appears to involve always less than 10% of the product distribution.

Putting a deuterium label on C-2 revealed that the *cis*-2-methylcyclohexanol formed 1-methylcyclohexene with loss of label. The *trans*-isomer was dehydrated to 1-methylcyclohexene without loss of label and without a deuterium isotope effect (Scheme 1).

To investigate the effect of different catalyst surfaces on the relative rates of these reactions, dehydration of the 2- and 4-methylcyclohexanols over zirconium phosphate and zirconium phosphite was studied. Because crystalline zirconium phosphate and phosphite have low specific surface areas, the dehydration was examined over amorphous materials, which have superior catalytic activity.

## 2. Experimental

### 2.1. Zirconium phosphate, ZrP

The preparation and characterisation of zirconium phosphate have been described [11]. Exchange of $H^+$ in zirconium phosphate for $Na^+$ was accomplished by stirring a suspension of the phosphate (1 g) with aqueous sodium hydroxide (100 ml 0.2 m) for 48 h at room temperature. The product was washed thoroughly with several changes of distilled water, and finally dried at 110°C. This sample is coded NaZrP. Exchange with copper sulphate has been described [11–13]; our sample was refluxed with copper sulphate solution for 16 h, and yielded a product in which 1 mol of zirconium phosphate exchanged 0.35 of a mole of copper (II). The sample was coded CuZrP.

### 2.2. Zirconium phosphite, ZrPi

This was prepared by a literature procedure [4]. The dried product was converted into its $H^+$ form by stirring it in an excess of aqueous $HNO_3$ (1 M) for 24 h. Solid state (MAS) $^{31}P$-NMR spectroscopy showed that the phosphite had not been oxidised during this procedure. After centrifugation, the $H^+$ exchanged zirconium phosphite was washed with distilled water until the wash water had a pH between 4 and 5, and then dried at 110°C.

### 2.3. Cyclohexanols

2- and 4-methylcyclohexanols and cyclohexanol itself were obtained commercially (Aldrich) and were used without further purification.

### 2.4. 2,2′,6,6′-[$^2H$]$_4$-Cyclohexanol

Cyclohexanone (25 ml) and deuterium oxide (99.9%, 25 ml) were dissolved in 1,4-dioxan (50 ml) containing *p*-toluenesulphonic acid

Table 1
Catalysis of the gas-phase dehydration of *cis*-4-methylcyclohexanol

| Catalyst | $T$ (°C) | Composition of reaction mixture (%) | | | | | A/B |
|---|---|---|---|---|---|---|---|
| | | 3- and 4-methyl-cyclohexene (A) | 1-methyl-cyclohexene (B) | 1,5-dimethyl-cyclopentene | 4-methyl-cyclohexanone | Unreacted alcohol | |
| ZrP | 270 | 62 | 25 | 1 | 1 | 9 | 2.5 |
| ZrP | 350 | 65 | 24 | 5 | 1 | – | 2.7 |
| ZrPi | 270 | 22 | 1 | – | 1 | 76 | 36 |
| ZrPi | 350 | 55 | 5 | – | 1 | 37 | 10 |

All data were recorded with a flow rate of 0.2 l $min^{-1}$.

Table 2
Catalysis of the gas-phase dehydration of *trans*-4-methylcyclohexanol

| Catalyst | *T* (°C) | Composition of reaction mixture (%) | | | | | A/B |
|---|---|---|---|---|---|---|---|
| | | 3- and 4-methyl-cyclohexene (A) | 1-methyl-cyclohexene (B) | 1,5-dimethyl-cyclopentene | 4-methyl-cyclohexanone | Unreacted alcohol | |
| ZrP | 270 | 43 | 17 | 1 | 3 | 33 | 2.5 |
| ZrP | 350 | 65 | 23 | 2 | – | 8 | 2.8 |
| ZrPi | 270 | 12 | 1 | – | 4 | 82 | 9 |
| ZrPi | 350 | 59 | 3 | 1 | 6 | 34 | 18 |

All data were recorded with a nitrogen flow rate of 0.2 l min$^{-1}$.

(1 g). The mixture was refluxed for 2 h before being extracted with pentane, using a continuous flow extractor. The pentane was distilled off, and the exchange process was repeated with fresh deuterium oxide (99.9%, 25 ml). The mixture was again extracted with pentane. Evaporation of the solvent gave an oil which was reduced immediately with lithium tetrahydroaluminate.

The $^{13}$C-NMR spectrum of non-deuterated cyclohexanol has signals at δ69.7 (C-1), 35.2 (C-2,6), 24.1 (C-3,5) and δ25.4 (C-4). In our sample of 2,2′,6,6′-[$^2$H]$_4$-cyclohexanol, the signal at 35.2 has collapsed to a small, extensively coupled multiplet. The $^1$H-NMR spectrum of non-deuterated cyclohexanol shows four signals between δ1.0 and 2.0, plus a C*H*OH signal at δ3.57. On deuteriation, the signal at δ3.57 is sharpened by removal of the coupling of the H atoms on the 2 and 6 carbon atoms. From the diminution in the signal at δ1.66 after deuteriation, it was concluded that the cyclohexanol contained 96% of deuterium at the C-2 and C-6 positions.

## *2.5. 1,2,2′,6,6′-[$^2$H]$_5$-Cyclohexanol*

A sample of 2,2′,6,6′-[$^2$H]$_4$-cyclohexanone, prepared as above, was reduced with lithium tetradeuteroaluminate. The $^{13}$C-NMR spectrum of the product had sharp signals at δ24.8 and 23.6, plus a small sharp peak at δ66.2 and two extensively coupled multiplets at δ68.5 and 35.4. The $^1$H-NMR spectrum showed a single sharp signal at δ3.4 (residual C*H*OH) from which it was calculated that the hydrogen on C-1 was 82% of $^2$H and 18% of $^1$H.

## *2.6. Dehydration of cyclohexanol, and 2- and 4-methylcyclohexanol*

Dehydration reactions were carried out in a conventional continuous flow apparatus [11] us-

Table 3
Catalysis of the gas-phase dehydration of *cis*-2-methylcyclohexanol

| Catalyst | *T* (°C) | Composition of reaction mixture (%) | | | | A/B |
|---|---|---|---|---|---|---|
| | | 3- and 4-methyl-cyclohexene (A) | 1-methyl-cyclohexene (B) | 1,5-dimethyl-cyclopentene | Unreacted alcohol | |
| ZrP | 270 | 17 | 79 | 3 | – | 0.22 |
| ZrP | 350 | 22 | 69 | 10 | – | 0.32 |
| ZrPi | 270 | 10 | 46 | – | 44 | 0.22 |
| ZrPi | 350 | 17 | 64 | 1 | 18 | 0.27 |
| Alumina[a] | 250 | 16 | 84 | – | – | 0.19 |
| Alumina[a] | 350 | 20 | 80 | – | – | 0.25 |
| Hydroxyapatite[a] | 250 | 27 | 73 | – | – | 0.36 |
| Hydroxyapatite[a] | 350 | 21 | 79 | – | – | 0.26 |

[a] Data from Ref. [9].
All our data were recorded with a nitrogen flow rate of 0.2 l min$^{-1}$.

Table 4
Catalysis of the gas-phase decomposition of *trans*-2-methylcyclohexanol

| Catalyst | *T* (°C) | Composition of reaction mixture (%) | | | A/B |
|---|---|---|---|---|---|
| | | 3- and 4-methyl-cyclohexene (A) | 1-methyl-cyclohexene (B) | Unreacted alcohol | |
| ZrP | 270 | 36 | 57 | 8 | 0.63 |
| ZrP | 350 | 36 | 64 | – | 0.56 |
| ZrPi | 270 | 5 | 11 | 83 | 0.47 |
| ZrPi | 350 | 35 | 46 | 19 | 0.76 |
| Alumina[a] | 250 | 85 | 15 | – | 5.6 |
| Alumina[a] | 350 | 80 | 20 | – | 4.0 |
| Hydroxyapatite[a] | 250 | 56 | 44 | – | 1.3 |
| Hydroxyapatite[a] | 350 | 54 | 46 | – | 1.2 |

[a] Data from Ref. [9].
All our data were recorded with a nitrogen flow rate of 0.2 l $\mathrm{min}^{-1}$.

ing a glass tube reactor ($250 \times 23$ $\mathrm{mm}^2$) in which the catalyst (0.1 g) was sprinkled over loosely packed glass wool. The substrate (0.5 g) was placed in a 25 ml two necked flask kept at 150°C (120° for reactions of cyclohexanol). The vapour of the alcohol was swept into a stream of nitrogen gas, which then passed over the heated catalyst. The flow rate for all reactions was 0.2 l $\mathrm{min}^{-1}$, giving a contact time with the catalyst of approximately 35 s. On emerging from the reaction tube, the products were cooled immediately, first in a U-tube surrounded by ice-water, and then condensed in a second U-tube surrounded by liquid nitrogen. The contents of the U-tubes were combined, and the reaction mixture was analysed by GC and GC/MS. Temperatures of reaction and product yields are reported in Tables 1–6.

The dehydration reactions of the methylcyclohexanols yield mixtures of 1-, 3- and 4-methylcyclohexene. Even using capillary GC it was not possible to resolve 3- and 4-methylcyclohexene, so that any of the two products are reported as a single peak.

Since interpretation of the present results depends on the stability of the product alkenes, which can protonate and rearrange to other alkenes with a Bronsted catalyst, the possibility of such rearrangement was examined. Each of the pure 3- and 4-methylcyclohexenes was put through the same reaction cycle at 350° as the substrate methylcyclohexanols. Any protonation

Table 5
Inhibition of catalysis of the gas-phase dehydration of *cis*- and *trans*-2-methylcyclohexanols

| Catalyst | Substrate | *T* (°C) | Composition of reaction mixture (%) | | | | A/B |
|---|---|---|---|---|---|---|---|
| | | | 3- and 4-methyl-cyclohexene (A) | 1-methyl-cyclohexene (B) | 1,5-dimethyl-cyclopentene | Unreacted alcohol | |
| ZrP | *cis* | 270 | 17 | 79 | 3 | – | 0.22 |
| ZrP | *cis* | 350 | 22 | 69 | 10 | – | 0.32 |
| NaZrP | *cis* | 270 | 10 | 53 | 1 | 35 | 0.19 |
| NaZrP | *cis* | 350 | 17 | 67 | 3 | 10 | 0.23 |
| CuZrP | *cis* | 270 | 14 | 57 | 3 | 24 | 0.25 |
| CuZrP | *cis* | 350 | 18 | 60 | 9 | 10 | 0.30 |
| ZrP | *trans* | 270 | 36 | 57 | – | 8 | 0.63 |
| ZrP | *trans* | 350 | 36 | 64 | – | – | 0.56 |
| NaZrP | *trans* | 270 | 33 | 47 | 4 | 14 | 0.70 |
| NaZrP | *trans* | 350 | 33 | 49 | 6 | 6 | 0.67 |
| CuZrP | *trans* | 270 | 18 | 77 | 4 | – | 0.73 |
| CuZrP | *trans* | 350 | 30 | 52 | 12 | – | 0.57 |

All data were recorded with a nitrogen flow rate of 0.2 l $\mathrm{min}^{-1}$.

Table 6
Catalysis of the gas-phase dehydration of cyclohexanol

| Catalyst | $T$ (°C) | Composition of reaction mixture (%) | | |
|---|---|---|---|---|
| | | Cyclohexene | Cyclohexanone | Unreacted alcohol |
| ZrP | 200 | 26 | 2 | 72 |
| ZrP | 270 | 44 | 1 | 56 |
| ZrP | 350 | 95 | 3 | 2 |
| ZrPi | 200 | 1 | 0 | 99 |
| ZrPi | 270 | 4 | 0 | 96 |
| ZrPi | 350 | 4 | 5 | 91 |
| None[a] | 350 | 0 | 0 | 100 |

[a] Only glass wool was used as a packing in the reactor tube.
All data were recorded with a nitrogen flow rate of 0.2 l min$^{-1}$.

of 3- or 4-methylcyclohexene would cause their rearrangement into the more stable trisubstituted alkene, 1-methylcyclohexene. In fact, there was only 4% rearrangement of 4-methylcyclohexene, and no rearrangement of 3-methylcyclohexene could be detected. Therefore, in subsequent discussions, the effect of double bond migration was considered to be small enough to neglect.

## 3. Instrumentation

Analyses of products were carried out on a Dani 3800 gas–liquid chromatograph with a flame ionisation detector, using nitrogen as a carrier gas, and a 25 m long capillary column with 0.3 mm internal diameter, coated with OV351. Mass spectra were measured on a Fisons Trio 1000 spectrometer, coupled to a Fisons 3800 gas–liquid chromatograph, using the same column as was used for analytical research.

NMR spectra were recorded on a Bruker AMX 400 spectrometer, $^1$H spectra at 400 MHz and $^{13}$C spectra at 100 MZ. Spectra were recorded in $CDCl_3$, with $SiMe_4$ as internal standard.

## 4. Results and discussion

The products of dehydration of the *cis*- and *trans*-4-methylcyclohexanols catalysed by zirconium phosphate are listed in Tables 1 and 2, and offer a useful insight into the mechanism of the reaction. A synchronous reaction, simultaneous abstraction of a proton and a hydroxyl group, could give only 4-methylcyclohexene by a 1,2-elimination and 3-methylcyclohexene by a 1,3-elimination. However, initial formation of a carbocation at the hydroxyl position would be expected to lead to rapid H migration with the formation of 1-, 3-, and 4-methylcyclohexenes. The observation of significant amounts of 1-methylcyclohexene from dehydration of both *cis*- and *trans*-4-methylcyclohexanol clearly indicates that a carbocation mechanism is involved in both reactions. Confirmation of this conclusion is supplied by the observation that both *cis*- and *trans*-4-methylcyclohexanols yield on dehydration similar ratios of 1-methylcyclohexene to 3- and 4-methylcyclohexene, since both isomeric alcohols yield the identical carbocation. A synchronous reaction would have yielded different proportions of alkenes. It is therefore concluded that the dehydration reactions of *cis*- and *trans*-4-methylcyclohexanols proceed through a carbocation mechanism.

Dehydration of the isomeric 4-methylcyclohexanols over zirconium phosphite proceeded much more slowly than the corresponding reaction over zirconium phosphate. The products of dehydration, listed in Tables 1 and 2, include small amounts of 1-methylcyclohexene, but the main products are the 3- and 4-methylcyclohexenes; the product ratios differ substantially. We conclude that the main reaction is synchronous, though there is also a small amount of a carbocation reaction. These dehydration reactions also yield 4-methylcyclohexanone, probably as a result of the presence of traces of oxygen in the gas stream; the slower dehydration reaction over the phosphite favours observation of the competing oxidation.

The dehydration reactions of *cis*- and *trans*-2-methylcyclohexanol catalysed by zirconium phosphate are reported in Tables 3 and 4. For convenience of comparison, we have included earlier results [9] in which these alcohols were dehydrated over alumina and over hydroxyapatite catalysts. These latter results closely match the results of an even earlier investigation [8]. Our results are in good qualitative agreement with earlier results, even though different catalysts were used. Our data, and both sets of earlier data, all show that the *cis*- and *trans*-isomers of 2-methylcyclohexene yielded different mixtures of alkenes on dehydration, so the reaction products cannot be formed from a single common intermediate [8].

The isomeric 2-methylcyclohexanols can be dehydrated to 1-methylcyclohexene through a carbocation or a synchronous reaction. Saytyeff's rule prevents formation of 3-methylcyclohexene in any but trace amounts from the carbocation generated on dehydration, but a synchronous reaction can form the 3-methyl alkene. The other isomer, 4-methylcyclohexene, can be formed only by a 1,3-elimination.

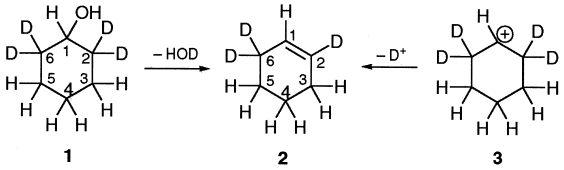
Our results, and earlier results, are not so easily interpretable as those obtained for 4-methylcyclohexanol dehydration. It is certain that to some extent a synchronous process is operating, since both isomers yield 3-methylcyclohexene on dehydration. However, both isomers also yield 1-methylcyclohexene as the main product of dehydration over zirconium phosphate, so we conclude that a carbocation mechanism also occurs. Otherwise, the synchronous reaction on the more sterically hindered side of the hydroxyl group would have to be the main dehydration process. Exactly the same arguments apply to dehydration catalysed by zirconium phosphite, except that the reaction is much slower.

The above results reveal an unexpected enhanced synchronous reaction when the carbon atom next to that carrying a hydroxyl group has a methyl substituent. It proceeds in the direction *away* from the methyl substituent. To examine this feature in greater detail, the dehydration of the unsubstituted parent alcohol, cyclohexanol, was studied. The products of dehydration of cyclohexanol are reported in Table 6. As would be expected, the main product is cyclohexene, together with a little cyclohexanone resulting from oxidation by oxygen in the nitrogen stream. Zirconium phosphate is again a more effective catalyst than zirconium phosphite. Since all three dehydration mechanisms discussed above would yield cyclohexene, the results offer no clue as to the reaction mechanism for the parent cyclohexanol.

To resolve this problem, we made use of the fact that only the carbocation mechanism can involve rearrangement of the substrate; all synchronous mechanisms exclude rearrangement. It is known that a carbocation centre can move rapidly round a carbocyclic ring [14–16] and in order to detect this, a deuterium-labelled cyclohexanol was prepared. After dehydration, scrambling of the label was investigated in the cyclohexene product.

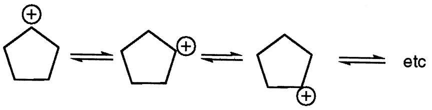
The first step in making the labelled substrate was to prepare 2,2′,6,6′-tetradeuterocyclohexanone by acid-catalysed H/D exchange in $D_2O$. The tetradeutero ketone was reduced to 2,2′,6,6′-tetradeuterocyclohexanol, which was then dehydrated over zirconium phosphate to yield deuterium-labelled cyclohexene.

If the dehydration of (**1**) had followed a synchronous mechanism at carbons 1 and 2, the resulting cyclohexene should have the labelling pattern shown in structure (**2**).

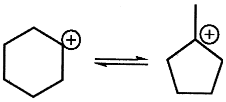


**1** **2** **3**

Similarly, loss of water through a synchronous reaction at carbon atoms 1 and 6 would yield a product chemically identical to structure (**2**). If the dehydration of cyclohexanol (**1**) proceeded through the carbocation (**3**), then provided that no shift of the carbocation centre occurred, the product would have a labelling pattern identical to that produced during the synchronous reaction. However, any shift of the carbocation centre, either by hydrogen (deuterium) shift or carbon shift, would start a process of scrambling of the deuterium label. This process would ultimately distribute the deuterium equally over all the carbon atoms. Evidence for such shifts comes from studies on cycloalkyl carbocations in superacids at low temperatures [14–17]. For example, migration of a positive charge around a cyclopentyl ring is so rapid at −70°C that the various hydrogen atoms cannot be distinguished on the time-scale of $^1$H-NMR spectroscopy.

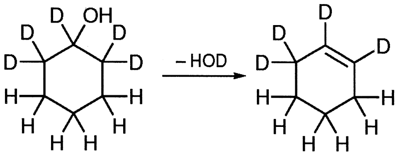


Additionally, it is known that a cyclohexyl carbocation can scramble deuterium labels through its equilibration with a methylcyclopentyl carbocation.



The $^1$H-NMR spectrum of cyclohexene consists of three broad singlets at δ5.66 (hydrogens on C-1 and C-2), δ1.98 (hydrogens on C-3 and C-6) and δ1.61 (hydrogens in C-4 and C-5) with peak areas in the ratio 1:2:2. Allowing for the presence of deuterium, a synchronous elimination of water from labelled cyclohexanol (**1**) would result in cyclohexene (**2**) in which these peak areas are in the ratio 1:2:4. In contrast, a long-lived carbocation would randomize the label and produce peak areas in the ratio 1:2:2. We therefore measured the $^1$H-NMR spectrum of the cyclohexene produced by dehydration of labelled cyclohexanol (**1**) over zirconium phosphate and found the peak areas to be in the ratio 0.9:2:2.5. This distribution of label precludes the synchronous reaction mechanism, and strongly supports the view that the reaction proceeds through a carbocation having a relatively long lifetime.

As a further test of the carbocation mechanism, the experiment was repeated except that the pentadeuterio-labelled cyclohexanol (**4**) was used, having deuterium at C-1 as well as at C-2 and C-6. Because only 82% of the hydrogen at C-1 had been replaced by deuterium, dehydration of labelled cyclohexanol (**4**) by a synchronous mechanism should yield cyclohexene (**5**) in which the $^1$H-NMR peak areas are in the ratio 0.18:2:4. In contrast, dehydration proceeding through a long-lived carbocation should produce a scrambled label with $^1$H-NMR peaks in the ratio of 1:2:2. After dehydration of (**4**), the cyclohexene had a $^1$H-NMR spectrum with peak areas in the ratio 0.8:2:2.5, in keeping with a long-lived carbocation mechanism and confirming the earlier result obtained with tetradeuterio-labelled cyclohexanol (**1**).



**4** **5**

Two possible caveats to this experiment can be advanced. Firstly, the scrambling of the deuterium label might have occurred after the product cyclohexene had been formed. To examine this possibility, 4-methylcyclohexene and 3-methylcyclohexene were each passed through the reactor. Any carbocation-induced rearrangement of these disubstituted alkenes would produce the more stable trisubstituted 1-methylcyclohexene. In fact, the recovered alkene from heating 4-methylcyclohexene to 350° over zirconium phosphate contained less than 4% of 1-methylcyclohexene; a similar experiment with 3-methylcyclohexene revealed no rearrangement. It is concluded that there can be little or no carbocation-type rearrangement of the product alkenes during cyclohexanol dehydration. The second caution concerns neglect of the H/D isotope effects on the loss of $H^+(D^+)$ from the carbocation. Such an effect would be expected, but since it would mean a preferential loss of $H^+$, it would serve only to increase the proportion of deuterium on the double bond of the product cyclohexene. The effect of this would be to reduce the apparent degree of scrambling of the label, particularly during dehydration of pentadeuteriocyclohexanol. Despite this possible H/D isotope effect, a large amount of scrambling of the D-label has been clearly demonstrated. The existence of scrambling is proof of the carbocation mechanism. A preliminary report of this work has been published previously [18].

The dehydration of cyclohexanol over zirconium phosphite is too slow to be studied by a similar scrambling experiment, but the products of zirconium phosphite catalysed dehydrations throughout this work have been qualitatively similar to those of zirconium phosphate catalysed dehydrations, suggesting a mechanistic similarity. However, the dehydration of alcohol by zirconium phosphate is clearly the result of the acidity of the O–H bond, and such a bond is absent in the phosphite. To reduce the effect of this Bronsted catalysis, we exchanged 35% of the acidic protons of zirconium phosphate for copper ions. When this exchanged phosphate was used as a dehydration catalyst, the results given in Table 5 were obtained. The dehydration of *cis*-2-methylcyclohexanol is slowed without significant change in the product ratios, but dehydration of the *trans*-isomer proceeds more rapidly. Clearly, another reaction is involved. We then tried to exchange the acidic protons with $Na^+$; dehydration of both *cis*- and *trans*-isomers of 2-methylcyclohexanol proceeds more slowly than with the unexchanged catalyst, and give similar product ratios. Detailed results are given in Table 5. It appears unlikely that we can entirely eliminate Bronsted catalysis from the reactions of zirconium phosphate.

The dehydration reactions of zirconium phosphite give products qualitatively similar to those obtained by dehydration with the phosphate catalyst. The possibility that the observed reaction over zirconium phosphite could result entirely from traces of zirconium phosphate in the phosphite can be eliminated, since the relative amounts of substrate dehydrated in separate reactions using these catalysts are not simply related to each other (Tables 1–6).

The activity of zirconium phosphite as an alcohol dehydration catalyst has been recorded earlier [4], when it was observed that zirconium phosphite catalysed the dehydration of ethanol. The infrared spectrum of zirconium phosphite does show weak –OH frequencies, but these have been shown [19] not to bond to added ethanol, suggesting that they are deep inside the zirconium phosphite structure. Since catalysis of dehydration by both catalysts gives qualitatively similar results, it has been suggested that the observed catalysis involved polar P–H bonds, activated by the highly electronegative oxygen atoms around the phosphorus atom [19]. It has not, however, been possible to find any adequate precedents for this suggested behaviour of a P–H bond. Although the present results confirm that dehydrations catalysed by zirconium phosphite parallel those catalysed by Bronsted acids, they do not rule out Lewis acid catalysis of the reactions.

## 5. Conclusion

We have shown that cyclohexanol and the 4-methylcyclohexanols are dehydrated over zirconium phosphate by a carbocation reaction, but that dehydration of the 2-methylcyclohexanols also involves a parallel synchronous reaction. Earlier workers [8–10] have obtained similar results for 2-methylcyclohexanol dehydration, and have also shown [8,10] that *trans*-2-alkylcyclohexanols yield the corresponding 4-alkylcyclohexenes, while the *cis*- do not. It has been shown that when 2-deuterio-*cis*-2-methylcyclohexanol is dehydrated, unlabelled 1-methylcyclohexene is formed with a normal kinetic deuterium isotope effect while dehydration of 2-deuterio-*trans*-2-methylcyclohexanol yields labelled 1-methylcyclohexene whose formation shows no kinetic isotope effect [9].

All these observations may be rationalised by consideration of the stereochemistry of the reaction on the catalytic surface. When an alcohol approaches a catalyst surface, it may approach with the C–O bond approximately perpendicular to the catalyst surface or approximately parallel. The latter approach is suitable to carbocation, synchronous 1,2-anti-, synchronous 1,2-syn- or 1,3-elimination reactions; the perpendicular approach does not permit 1,2-anti-elimination. In cyclohexanol, the C–O bond is equatorial [20], and steric factors favour a perpendicular approach to the surface rather than a parallel approach. With a perpendicular approach of an equatorial hydroxyl group, the rest of the cyclohexanol molecule is at some distance from the catalyst surface so it is not involved, and reaction consists of cleavage of the C–O bond to yield a carbocation, which is not necessarily involved with the catalyst surfaces. A similar situation is involved in the reaction of *trans*-4-methylcyclohexanol; both substituents are equatorial [20], so the molecule approaches the catalyst with the C–O bond perpendicular to the catalyst surface and the rest of the molecule is not involved with the catalyst, resulting in a carbocation reaction. The *cis*-4-methylcyclohexanol exists as a rapidly equilibrating mixture of two conformations [20]; one has the hydroxyl group equatorial and the methyl group axial, while the other has the hydroxyl group axial and the methyl group equatorial. Steric hindrance to approach of the axial –OH to the catalyst surface would then result in reaction taking place entirely through the conformation with an equatorial hydroxyl group, giving rise once again to a carbocation reaction, as was observed. In reactions of the 4-methylcyclohexanols, the methyl substituent thus has a negligible effect on the course of the reaction.

This situation does not continue when we consider the 2-methylcyclohexanols. Consider first the *trans*-isomer. The *trans*-diequatorial conformation dominates over the *trans*-diaxial [20], so approach with the C–O bond perpendicular to the catalyst surface is to be expected. However, this would cause severe steric compression between the neighbouring methyl group and the catalyst surface. This can be relieved in either of two ways mentioned below.

(1) The 2-methylcyclohexanol molecule can tip sideways on to the catalyst surface, lifting the methyl group away from the surface, as in Diagram 1.

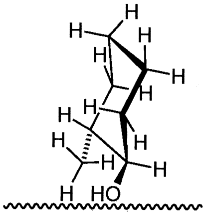


Diagram 1.

This would have the effect of pushing the equatorial hydrogen on C-6 close to the surface of the catalyst, which would favour a synchronous 1,2-syn-elimination reaction, as shown in the scheme, yielding 3-methylcyclohexene. The axial hydrogen on C-2 would be well away from the catalyst, so could not be involved in a synchronous reaction directly. However, the hydrogens of the methyl group are now close to the catalyst surface, so a synchronous 1,3-elimination is now possible, by either of two routes.

(A) The hydroxyl group is removed from C-1, simultaneously with a shift of the hydrogen of C-2 to C-1 and loss of a methyl proton to give methylene cyclohexane, as shown in Diagram 2. Methylene cyclohexane would then rearrange to form 1-methylcyclohexene [9].

(B) The hydroxyl group is removed from C-1 simultaneously with loss of a hydrogen from the methyl group. The hydrogen on C-2 would move to the methyl group immediately, forming 1-methylcyclohexene directly, as in Diagram 3.

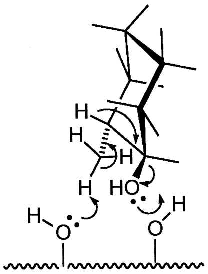


Diagram 2.

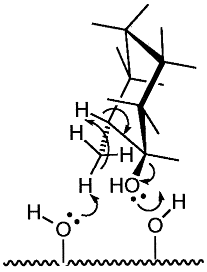


Diagram 3.

In both cases, replacement of the hydrogen on C-2 by deuterium would result in formation of 1-methylcyclohexene retaining the label transferred to C-1 or the methyl group. No kinetic isotope effect would be observed.

(2) The 2-methylcyclohexanol molecule could relieve steric compression on the methyl group by flipping to put the methyl group equatorial and the hydroxyl group axial, as in Diagram 4.

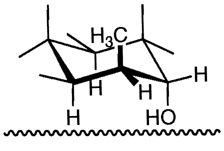


Diagram 4.

This removes the methyl group from the surface completely, but puts the axial hydrogen atoms on C-3 and C-5 close to the catalyst surface, which would favour formation of 1-methylcyclohexene and of 4-methylcyclohexene by synchronous 1,3-elimination reactions as described in 1(B) above.

The energy barrier to (2) is much greater than that involved in (1), so the first mechanism is expected to dominate.

The *cis*-isomer of 2-methylcyclohexanol exists as an equilibrating mixture of conformations, one with an axial hydroxyl group and an equatorial methyl group and the other with an equatorial hydroxyl group and an axial methyl group [20]. As with *cis*-4-methylcyclohexanol, reaction is expected to proceed entirely through the conformation with an equatorial hydroxyl group. When this approaches the catalyst surface, the axial methyl group suffers less steric compression than the equatorial group in the *trans*-isomer, but will still tip the molecule sideways to permit synchronous syn-elimination of the hydroxyl group and the C-6 equatorial hydrogen atom to give 3-methylcyclohexene. This reaction is less favoured than in the *trans*-isomer, as observed. The equatorial hydrogen atom on C-2 is also close to the catalyst surface, so is removed in a synchronous 1,2-syn-elimination. Its replacement by a deuterium atom thus, gives a substrate which yields 1-methylcyclohexene in a reaction which has a kinetic isotope effect, and yields unlabelled product, as observed. The orientation of the molecule should place this atom further from the surface than the corresponding hydrogen on C-6, but experimental evidence shows that the reaction does, in fact, take place.

Flipping of the cyclohexene ring is not an option for release of strain in the *cis*-isomer when it is bonded to a catalyst surface, as it would put the methyl group between the cyclohexane ring and the catalyst surface during the flipping process, creating impossible steric compression. Thus, formation of 4-methylcyclohexene is not possible, as observed.

It is not possible to exclude the possibility that the 1,3-elimination reactions follow from bonding to the catalyst surface of a molecule with an axial hydroxyl group. This would, however, permit easier 1,3-elimination in the *cis*-2-alkylcyclohexanols, as the maximum steric compression occurs during flipping of the ring; the flipped ring is more easily accommodated. Since this elimination is not observed, flipping of the bonded molecule is considered to be more likely.

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