

Mechanism of cyclohexanol dehydration catalysed by zirconium phosphate

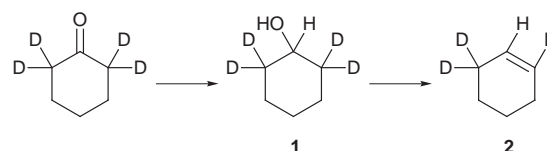
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Deuterium-labelling studies have shown that dehydration of cyclohexanol to cyclohexene over amorphous zirconium phosphate at 350 °C proceeds through a carbocation mechanism and not through a concerted process.

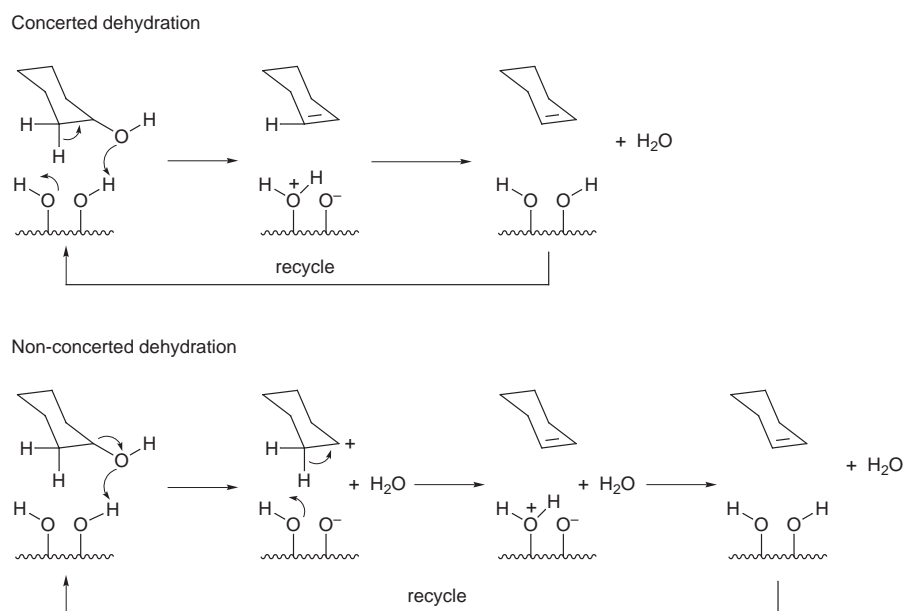
The dehydration of cyclohexanol to cyclohexene is often used as a model reaction to determine the catalytic efficiency of metal phosphates¹⁻³ even though the mechanism of the reaction is unknown. Studies of the dehydration of the 2-, 3- and 4-methylcyclohexanols, over alumina⁴ and over metal phosphates⁵ suggest that there are two mechanisms; one a synchronous mechanism, in which the OH and H are removed by the catalyst, possibly simultaneously, so that the reaction proceeds without any rearrangement, and the second a carbocation reaction which permits rearrangement. Any modification of the stereochemistry of the methylcyclohexanols which occurs during reaction is indicative of a carbocation reaction. In the absence of any such stereochemical change, the reaction is assumed to be synchronous. Both mechanisms have been observed⁴ (Scheme 1).

The symmetry of cyclohexanol precludes using a stereochemical probe. Therefore, in this work, the reaction has been studied by deuterium labelling. For a synchronous mechanism, dehydration of **1** should give a mixture of **2** and its mirror image in equal proportions. Dehydration of **1** via a carbocation would give an identical result, *only if* it took place without rearrangement. However, a shift of the carbocation centre from its initial position at C-1 would start a process of scrambling the deuterium label, so that a modified pattern of deuterium-



labelling would appear. Evidence that such shifts take place comes from work on the dehydration of methylcyclohexanols and from the behaviour of carbocations in superacids; migration of charge round a cyclohexane ring is so fast that the hydrogen atoms become equivalent on the NMR timescale.⁶ It is not known whether or not a cyclohexyl carbocation behaves similarly, since in superacid it rearranges rapidly to a methyl substituted cyclopentyl carbocation.⁷

Deuterium labelled cyclohexanol was prepared by exchange of the four labile protons of cyclohexanol with deuterium oxide, in the presence of an acid catalyst. Reduction of the exchanged ketone with lithium aluminium hydride gave cyclohexanol in which 94% of the hydrogens on C-2 and C-6 had been replaced by deuterium, as determined by ¹H NMR. ¹³C NMR confirmed the positions of the labels. Dehydration of the 2,2',6,6'-[²H₄]cyclohexanol over amorphous zirconium phosphate at 350 °C in the gas phase⁸ gave cyclohexene, containing 4.0% of methylcyclopentene. The ¹H NMR spectrum of the product contained three peaks, resulting from sets of equivalent hydrogen atoms on carbon atoms 1 and 2, 3 and 6, and 4 and 5. In unlabelled cyclohexene, these are in the ratio 1:2:2. If the reaction had been synchronous, the product should have shown peaks in the ratio of 1:2:4. Similarly,



Scheme 1

carbocation reaction *without* rearrangement would produce the same ratio, but migration of the carbocation centre would cause the ratio to approach 1:2:2. For the cyclohexene obtained in this work, the ratio was 0.93:2:2.48, which fits well with a reaction involving a highly mobile carbocation, but one which has not had sufficient time to randomise completely. The process of randomisation would in any case be slowed by isotope effects, which would cause hydrogen to move more rapidly than deuterium.

As a further test of this randomisation, the work was repeated except that the labelled cyclohexanone was reduced with lithium aluminium deuteride. This led to cyclohexanol, having 18% of H on C-1 and 82% of ^2H , as determined by ^1H NMR spectroscopy, and the position confirmed by ^{13}C NMR. The dehydration over amorphous zirconium phosphate at 350 °C was repeated. Reaction without rearrangement should give a ratio of peaks of 0.18:2:4, while a complete scrambling of the label should give a ratio approaching 1:2:2. The spectrum obtained showed a ratio of 0.76:2:2.46, indicating again that extensive scrambling of the label had taken place.

It could be argued that labelling the 2 and 6 positions of cyclohexanol with deuterium favours the carbocation reaction since the concerted reaction is slowed by the isotope effect introduced. This is true, but it is balanced by a similar slowing of the shift of a deuterium atom to C-1 relative to a hydrogen atom in the first step of migration of the carbocation from C-1. It could also be argued that randomisation of the label may have taken place after formation of cyclohexene; this is unlikely, since we have found that 4-methylcyclohexene is only 4% converted into 1-methylcyclohexene under our reaction conditions, despite having a methyl substituent which should favour reaction relative to the unsubstituted alkene.

Detailed pathways of deuterium scrambling are difficult to predict because of isotope effects. However, a concerted reac-

tion cannot scramble the label, so the extent of scrambling is irrelevant to this work. Any isotope effect on loss of H/D from the carbocation would favour *loss* of hydrogen from the double bond carbon atom, and hence reduce the observed scrambling; since extensive scrambling is observed, this effect can be ignored.

It is concluded that the dehydration of cyclohexanol over amorphous zirconium phosphate at 350 °C proceeds *via* a carbocation mechanism and involves charge migration around the ring. The speed of the reaction expected depends on the number of acidic sites in the catalyst, their acid strength, and the availability of the site to the OH group of cyclohexanol. Since this does not appear to be a concerted reaction, bonding of the whole substrate to the catalyst is probably not important. In this reaction, the catalyst is simply a solid acid.

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