Dimerisation and Transannular Reactions of Cycloalkenes on H-Mordenite

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A series of cycloalkenes were adsorbed onto activated H-mordenite, and their transformations investigated with EPR. This technique monitors the catalytic transformations which occur, by detecting the radical cations formed from unsaturated intermediates with low ionisation potentials. Cyclopentene and cyclohexene were found to take part in dimerisation and ring enlargement reactions. Medium sized rings, cyclooctene and cyclodecene underwent transannular ring closure, as did cyclododecene, to form bicyclo[*n*.*n*.0]alkenes (*n* = 3, 4, 5).

Zeolite catalysts are most commonly used in the petrochemical industry, in catalytic cracking, but have also found some application in the synthesis of fine chemicals.[1,2] The catalytic activity of zeolites, with respect to the reactions of organic molecules, is usually attributed to Brønsted acid sites.[3] These sites are converted to Lewis acid sites by heating in air[4] to about 900 K at a rate of 100 K h^{-1}. The Lewis acid sites are believed to be responsible for the spontaneous generation of radical cations when organic molecules with sufficiently low ionisation potentials are adsorbed onto the high silica zeolite H-mordenite (H-MOR).[5] The generation of radical cations allows the behaviour of organic molecules in the zeolite to be investigated with EPR spectroscopy. As only molecules with low ionisation potentials lose an electron, the radical cation observed is not necessarily that of the major product, but this technique does allow some insight into the reaction mechanisms which occur in zeolites. The transformations which are observed can be the result of cationic reactions (due to the remaining Brønsted acid sites) or of radical cation reactions.

The long lifetime of most radical cations on H-MOR at room temperature makes this an ideal medium in which to study the EPR spectra over a wide temperature range. This persistence of the radical cation is probably due to a combination of factors including the restriction of movement in the zeolite channels. The radical cations of simple aliphatic alkenes formed in zeolites have attracted a large amount of attention, whereas little work has been carried out on the behaviour of cyclic alkenes.[6] The formation of 9(10)-octalin on adsorption of cyclopentene onto H-MOR has been reported.[7] We have investigated this reaction further, along with the reactions of other cycloalkenes in an attempt to deduce the mechanism of this reaction, as well as to study the conformations of cycloalkenes in H-MOR.

The H-MOR channels, which are elliptical with diameters[8] of 700 and 650 pm, impose restrictions on the reactions which take place. The reactant must be small enough to enter the channel, and the space requirements of the reaction transition state must be smaller than the channel. This shape selectivity of zeolites has been demonstrated in a number of catalysed reactions.[9] Rotation of organic radical cations is hindered by the size of the zeolite channel, and probably also by the zeolite framework which contains negatively charged oxygens. This leads to highly anisotropic spectra,[10] especially when α-protons are present. The separation of altering line width effects in the EPR spectrum due to the exchange of isotropic coupling constants in rings undergoing inversion or pseudorotation from those due to anisotropy is extremely difficult, if not unfeasible.[11] The geometry of cyclic alkene radicals cations can be approximately determined using the equation: $a(\mathrm{H}_\beta) = (A + B\cos^2\theta)\rho_{\mathrm{C}\alpha}$, which describes the relationship between the β-hydrogen coupling constants of cyclic radicals and radical cations and the dihedral angle θ between the C–H bond and the singly occupied 2p orbital. For radicals, A is small (*ca.* 0.1 mT) and B is about 5.4 mT. For radical cations these values are larger (0.5–0.9 and 5.5–6.0 mT respectively) leading to larger values for $a(\mathrm{H}_\beta)$ than observed for neutral radicals.[12]

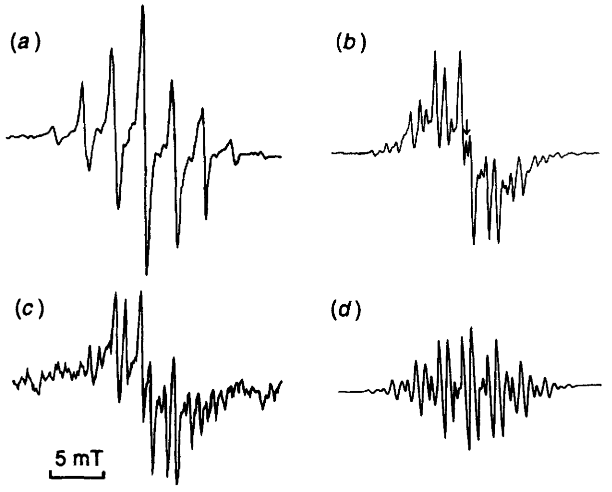
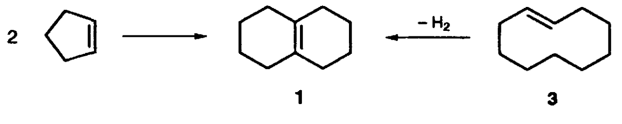


Fig. 1 (*a*) Spectrum measured at 210 K after adsorption of cyclopentene onto H-mordenite. (*b*) Spectrum taken at 294 K 20 min after adsorption, the arrow indicates the central line from the octalin radical cation. (*c*) Spectrum of 3-cyclopentylidenecyclopentene at 294 K adsorbed onto H-mordenite. (*d*) Isotropic simulation of (*c*) using data in text.

Results and Discussion

Cyclopentene and Cyclodecene.—Cyclopentene was adsorbed onto activated H-MOR at 210 K in the EPR cavity and the spectrum measured at this temperature. The spectrum obtained [Fig. 1(*a*)], which has already been assigned to 9(10)octalin[7] **1**, shows that the eight β-protons are equivalent. The ring inversion leading to this equivalence is more rapid than that observed for octalin in a solution of squalane and 3-methylpentane[13] at 205 K. In this case, the rate of inversion is given as 2.6 × 10^{-7} s^{-1}, and the axial and equatorial hydrogens are clearly distinguishable.[13] The large difference between the



Scheme 1

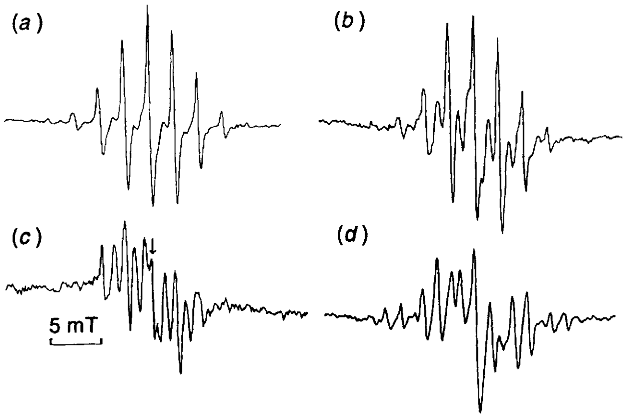
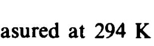


Fig. 2 (*a*) Spectrum measured at 294 K after adsorption of octalin onto H-mordenite. (*b*) Spectrum after 25 min. (*c*) Spectrum after 2 h, the arrow indicates the central line from the octalin radical cation. (*d*) Spectrum measured at 150 K immediately after adsorption of octalin.

solution spectrum and the zeolite spectrum is most probably a solvent effect, as the zeolite channel imposes no restrictions on the ring inversion whereas a solution may. The rapid inversion at relatively low temperature has been attributed to radical cations formed on the outer surface of the zeolite,[7] however, as the octalin molecule is small in comparison to the H-MOR channel it is unlikely that it sits on the surface. On warming the sample to room temperature (294 K), the spectrum of the octalin radical cation decayed and a second one built up [Fig. 1(*b*)]. Some features of this second spectrum are already visible at 210 K. After about 15 min at 294 K the second was the stronger, although the central line assigned to the octalin radical cation is still visible. The second spectrum was assigned to the radical cation of 3-cyclopentylidenecyclopentene **2**, and not to an octalin radical cation undergoing slower inversion as previously reported.[7] An authentic sample of the diene **2**, when adsorbed onto H-MOR, gave a very weak spectrum [Fig. 1(*c*)] which was essentially the same as that from cyclopentene. The spectrum was simulated [Fig. 1(*d*)] using the hyperfine coupling constants *a*(1 H) 0.8 mT, *a*(2 H) 1.3 mT, *a*(2 H) 2.1 mT, *a*(2 H) 2.15 and *a* (2 H) 3.0 mT. The smallest coupling constant of 0.8 mT was assigned to the α-hydrogen at C-1, the four β-hydrogens (2.1 and 2.15 mT) to positions 6 and 9 and the couplings of 1.3 and 3.0 mT were assigned to the hydrogens at 4 and 5 respectively. A coupling for the hydrogen at position 2 was not resolved. This assignment was based on the INDO calculation for an AM1 optimised structure, which predicts coupling constants of a_1(1 H) −0.72 mT, a_2(H) −0.07 mT, a_4(2 H) 1.13 and 1.34 mT, a_6(2 H) 2.31 and 2.84 mT, a_9(2 H) 2.30 and 2.80 mT, and a_5(2 H) 2.61 and 2.71 mT. The appearance of a broad background signal in the spectra measured from cyclopentene on H-MOR was indicative of the formation of a range of product radical cations. Small molecules, such as cyclopentene, can move relatively freely in the H-MOR channels and therefore take part in a variety of reactions, for example polymerisation, with greater ease than larger molecules. The radical cation of cyclopentene itself was not observed.



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For comparison, an authentic sample of octalin was adsorbed onto H-MOR at 294 K. The initial spectrum measured at 294 K about 7 min after adsorption is shown in Fig. 2(*a*). Again, the rapid ring inversion results in a spectrum assigned to eight equivalent hydrogens with a coupling constant of 2.5 mT. This is consistent with measurements in solution,[13] where the rate of ring inversion is 10^9 s^{-1} at 300 K. With time this spectrum also decays as a second one builds up. The spectra measured after 25 min and 2 h are shown in Fig. 2(*b*) and (*c*). The octalin radical cation does not decay completely, and the second spectrum could not be identified, although it is clearly different from the radical cation obtained from cyclopentene [Fig. 1(*b*)]. It could also not be assigned to an octalin radical cation in which ring inversion occurs more slowly. The EPR spectrum of the octalin radical cation was also measured at 150 K immediately after adsorption [Fig. 2(*d*)]. This had coupling constants of *a*(4 H) 3.6 mT and *a*(4 H) 1.4 mT, which are similar to those measured for the rigid radical cation in solution.[13] To confirm that very little reaction had taken place during, or before, the measurement of the low temperature spectrum, the sample was warmed rapidly to room temperature and a spectrum as shown in Fig. 2(*a*) was obtained.

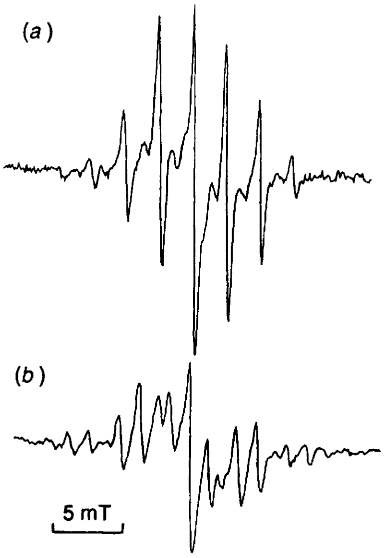
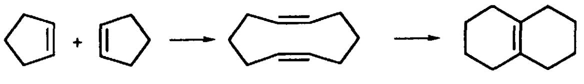


Fig. 3 (*a*) Spectrum measured at 294 K after adsorption of cyclodecene onto H-mordenite. (*b*) Spectrum at 150 K.

An EPR spectrum of the octalin radical cation was also obtained when cyclodecene (**3**, Scheme 1) was adsorbed onto H-MOR [Fig. 3(*a*)]. A weak background signal is apparent in the spectrum measured at 294 K which is identical to the background in the spectrum from an authentic sample of octalin [Fig. 2(*a*)]. However the spectrum of the octalin radical cation generated from cyclodecene decays slowly, over 4 to 5 weeks, and the background does not build up. The spectra obtained from cyclodecene at 294 K and 150 K [Fig. 3(*b*)] were identical to the spectra measured at the same temperatures shortly after adsorption of octalin, before decay occurs. They were also entirely consistent with the spectra obtained in solution,[13] and there can therefore be no doubt as to the assignment. The equivalence of the eight protons indicates that at 294 K the ring inversion is not hindered regardless of where the molecule sits. The stability of the octalin radical cation in H-MOR when generated from cyclodecene indicates that the species formed after adsorption of octalin and cyclopentene were not the products of reactions of this radical cation. In the case of cyclopentene, its behaviour in H-MOR can be interpreted in terms of two different reaction mechanisms. A cationic mechanism involving the addition of the cyclopentyl cation to cyclopentene followed by an elimination of hydrogen could have led to 3-cyclopentylidenecyclopentene **2**. This is similar to the mechanism proposed for the oligomerisation[14] of cyclopentene with BF_3 and would lead to other alkenes as well as polymerisation, explaining the broad background peak which was observed [Fig. 1(*b*)]. The octalin radical cation, formed by another mechanism and more rapidly, would then abstract an electron from the diene **2**, the latter having a lower ionisation potential. Likewise, the product of reaction of octalin on H-MOR, perhaps by elimination of hydrogen, had a lower ionisation potential than octalin itself and therefore transferred an electron. It could not be concluded that the product formed on reaction of octalin is not present in the cyclopentene sample. The absence of an EPR signal indicating its formation may have been due to a difference in ionisation potentials.

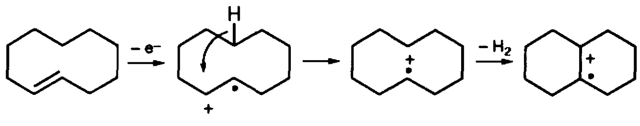
The proposed mechanism for the formation of octalin from cyclopentene (Scheme 2) involves initially a metathesis-type



Scheme 2

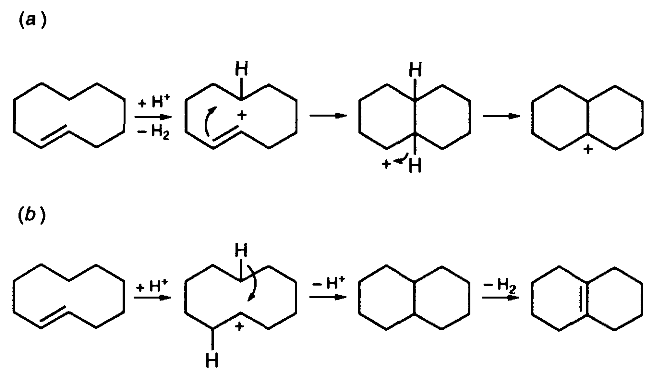
reaction forming cyclodeca-1,6-diene, the latter then undergoes transannular ring closure and hydrogen migration to form octalin. The cyclodeca-1,6-dienes are particularly susceptible to 1,5- and 1,6-transannular reactions as a result of their geometry. The preference for the formation of bicyclo[4.4.0]decene (octalin) as opposed to bicyclo[5.3.0]decene in H-MOR could be attributed to the greater ring strain in the latter.[15] The ring closure could have been the result of either a cationic or radical cation reaction as both Brønsted and Lewis acid sites are available.

It could be concluded that the octalin radical cation generated from cyclodecene was not formed *via* the neutral octalin molecule, as this would eventually lead to the same spectra from both compounds. The small background signal could be attributed to octalin formed either by another mechanism, or by reduction of the radical cation ($1^{\bullet+}$). The mechanism for the reaction of cyclodecene is shown in Scheme 3, and involves initially oxidation of cyclodecene. This is



Scheme 3

followed by a transannular 1,5-hydride shift generating the decalin radical cation which eliminates hydrogen. The two possible cationic mechanisms (Scheme 4) which have been

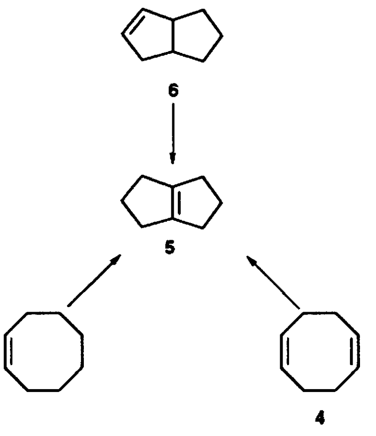


Scheme 4

proposed for the internal alkylation reactions observed in zeolites[3] can both be ruled out. Reaction (*a*) is highly unlikely as the zeolite cannot donate an electron to the resulting bicycloalkyl cation, and further loss of a proton leads to neutral octalin. In reaction (*b*) neutral decalin is formed. Although it has been shown that highly acidic zeolites can catalyse the elimination of hydrogen from unsaturated hydrocarbons, this was not observed in the activated H-MOR. After adsorption of *cis* and *trans* decalin onto H-MOR no EPR signal was observed.

As the EPR spectrum of the octalin radical cation did not differ from the solution spectra, it could be assumed that the zeolite channel exerted no, or very little, influence on the adopted conformation, or on internal reorganisation. In the spectra measured at 294 K [Fig. 2(*a*) and Fig. 3(*a*)] it is evident that the lines at higher magnetic field are narrower than those at low magnetic field. This anisotropy is consistent with the restricted rotation of the radical cation.[10] In an AM1 optimised structure of the octalin radical cation, in which the two rings adopted a half chair conformation, the equatorial and axial dihedral angles were 57°(θ_{eq}) and 7°(θ_{ax}). The EPR spectrum [Fig. 3(*b*)] at 150 K, where inversion no longer takes place, is consistent with coupling constants of a_{ax}(4 H) 3.6 mT and a_{eq}(4 H) 1.4 mT. This leads to reasonable[12] values for A and B of 0.9 and 6.4 mT respectively. For comparison, these values, when applied to the tetramethylethene radical cation with freely rotating methyl groups, give a coupling constant of a(12 H) 2.05 mT, which is not far from the experimental coupling constant of 1.72 mT.[16]

Cyclooctene and Cyclooctadiene.—In general, relatively high-strain medium ring cycloalkenes commonly undergo transannular reactions as a result of the short distance between transannular carbons, which is approximately 300 to 330 pm.[17] Pseudorotation and inversion processes lead to geometries in which the unsaturated bond is in an ideal position for ring closure. This applies to, for example, (*Z*)-cyclooctene and (1*Z*,5*Z*)-cycloocta-1,5-diene. The twist-boat conformation of cyclooctadiene **4**, which was found to have the lowest energy in



Scheme 5

solution, has a C-1 to C-5 distance of only 327 pm.[18] The adsorption onto activated H-MOR of cyclooctene and cyclooctadiene resulted in identical EPR spectra [Fig. 4(*a*)]. The spectrum was simulated [Fig. 4(*b*)] using the coupling constants a(4 H) 3.5 mT and a(4 H) 1.5 mT, which were assigned to the axial and equatorial β-hydrogens of bicyclo[3.3.0]oct-1(5)-ene **5** respectively. As a neutral molecule **5** is probably energetically less favourable than the isomers (for example bicyclo[3.3.0]oct-2-ene **6** as a result of the ring strain. However oxidation of an isomer would ensure that rearrangement took place to form the bicycloalkene **5**, which is the more substituted, and therefore more stable, radical cation. To confirm this, bicyclo[3.3.0]oct-2-ene (**6**, Scheme 5) was adsorbed onto H-MOR. The EPR spectrum [Fig. 4(*c*)] observed was identical to those from cyclooctene and cyclooctadiene. At lower temperature (150 K) the EPR spectrum [Fig. 4(*d*)] shows some

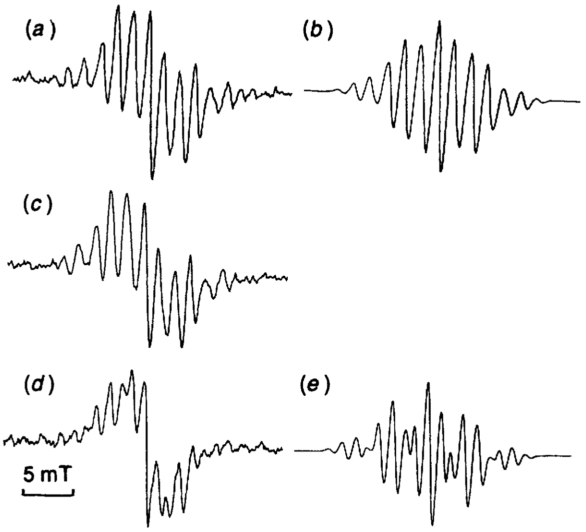
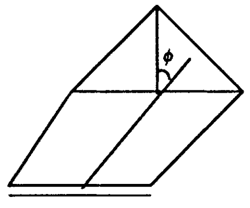


Fig. 4 (*a*) Spectrum measured at 294 K after adsorption of cyclooctene onto H-mordenite. (*b*) Isotropic simulation of (*a*) using data in text. (*c*) Spectrum measured at 294 K after adsorption of (*Z*)-bicyclo-[3.3.0]oct-2-ene onto H-mordenite. (*d*) Spectrum measured at 150 K. (*e*) Isotropic simulation of (*d*) using data in text.

changes, and the simulation [Fig. 4(*e*)] was carried out using the isotropic coupling constants a_{ax}(4 H) 3.61 mT and a_{eq}(4 H) 1.39 mT. Pseudorotation of the five membered ring is hindered by the presence of a fused ring, however the small change in the coupling constants indicates that the radical cation is, to some extent, flexible at 294 K. The rings probably exhibit a partial pseudorotation which is not rapid enough to average out the axial and equatorial couplings. An *ab initio* calculation of bicyclo[3.3.0]oct-1(5)-ene predicts a C_{2V} geometry,[19] in which both rings adopt an envelope conformation and the molecule has a small out of plane deformation of −3.6°. EPR studies of rigid ring systems have shown that the out of plane deformation can be decreased[20] on removing an electron from the neutral species, it therefore has little influence on the coupling constants in the radical cation of **5**. As the axial and equatorial coupling constants are very similar to those of octalin, the axial and equatorial dihedral angles must also be similar. The EPR spectrum of the radical cation of cyclopentene has been measured[16] at 77 K, and the angle (ϕ) between the two planes of the envelope form **7** estimated to be 5–10°. This is clearly not a large enough deviation from planarity to cause the coupling constants observed for the bicyclooctene **5** radical cation, as indicated by the near equivalence of the β-protons in cyclopentene[16] (5.3 and 4.85 mT). The neutral cyclopentene[21] molecule has an angle (ϕ) of 29°, from a molecular model of this the dihedral angles were estimated to be 6° (θ_{ax}) and 58° (θ_{eq}), which are in much better agreement with the measured coupling constants.



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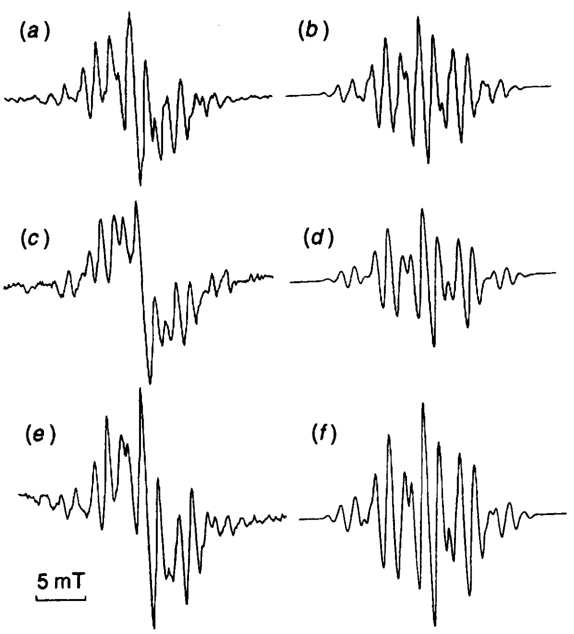
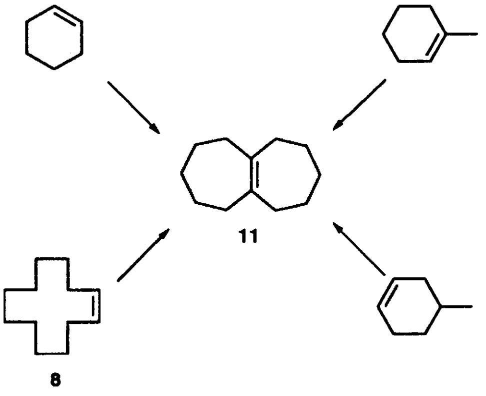
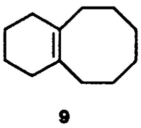


Fig. 5 (*a*) Spectrum measured at 294 K after adsorption of cyclododecene onto H-mordenite. (*b*) Isotropic simulation of (*a*) using data in text. (*c*) Spectrum at 120 K. (*d*) Isotropic simulation of (*c*) using data in text. (*e*) Spectrum measured at 294 K after adsorption of 1-methylcyclohexene onto H-mordenite. (*f*) Isotropic simulation of (*e*) based on data in text.



Scheme 6

Cyclohexene and Cyclododecene.—Cyclododecene **8** is the smallest of the large alicyclic rings which have considerably lower strain energy than the medium-sized rings. The EPR spectrum observed at 294 K after adsorption of cyclododecene onto H-MOR is shown in Fig. 5(*a*) with the simulation [Fig. 5(*b*)] obtained with the coupling constants *a*(4 H) 3.44 mT and *a*(4 H) 1.45 mT. The signal could not be observed until approximately 5–6 h after adsorption. The spectrum measured at 120 K [Fig. 5(*c*)] has coupling constants of *a*(4 H) 3.52 and *a*(4 H) 1.37 mT, which are not greatly different from the coupling constants at 294 K. The spectrum was assigned to bicyclododecene, and the small change in coupling constants at lower temperature indicated a slight decrease in the flexibility of the two rings. Bicyclo[6.4.0]dodec-1(8)-ene **9** could be ruled out as the six membered ring would be expected to undergo rapid ring inversion at 294 K (*cf.* octalin) leading to four equivalent β-hydrogens with a coupling constant of approximately 2.5 mT, and the low temperature spectrum would be



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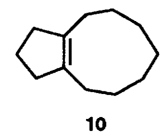

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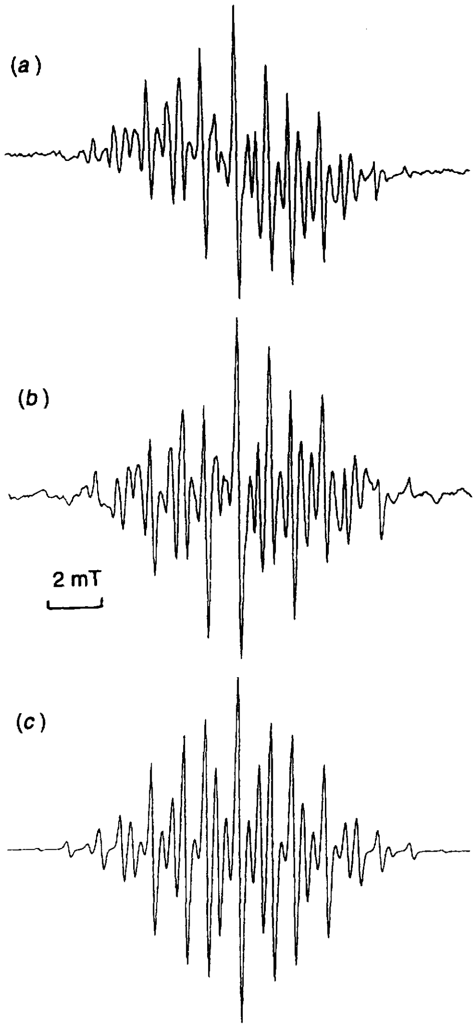


Fig. 6 (*a*) Spectrum measured at 294 K after adsorption of 1,3-dimethylcyclohexene onto H-mordenite. (*b*) Spectrum measured at 294 K after adsorption of 1,4-dimethylcyclohexene. (*c*) Simulation using data in text.

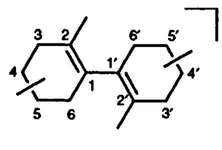
very different from the room temperature spectrum. This leaves two possible assignments, bicyclo[7.3.0]dodec-1(9)-ene **10** and bicyclo[5.5.0]dodec-1(7)-ene **11**. Transannular ring closures of 12-membered rings are relatively rare as they lead to an increase in the strain energy. However, they have been induced, for example, with H_2SO_4 [22] and by catalysis (Cp_2TiCl_2–$LiAlH_4$).[23] The bicyclododecene **10** is produced on photolysis of both *cis* and *trans* cyclododecene in solution.[24] Where ring closure does occur it is usually between the 1 and 5 or 1 and 6 positions.[22] The five and seven membered rings do not have significantly different strain energies[25] (29 kJ mol^{-1} for cyclopentene and 31 kJ mol^{-1} for cycloheptene) whereas cyclononene has a higher strain energy (48 kJ mol^{-1}), therefore the zero bridge double bond makes **11** energetically more favourable than **10**. The long time delay between adsorption of the alkene and the appearance of a signal indicates that the cycloalkene was not easily accommodated into the H-MOR channels. It is conceivable that as the ring interconverted from one conformation to another, only those with a sufficiently small space requirement passed into the zeolite. Therefore, the reaction in the zeolite is not entirely comparable to the reactions of cyclododecene in solution. In analogy to the reaction of cyclopentene, it was expected that cyclohexene would also undergo a ring enlargement reaction to produce bicyclododecene.

An identical spectrum to that obtained from cyclododecene on H-MOR was observed when cyclohexene was adsorbed, although in this case there was no time delay before the appearance of the signal. This was to be expected as cyclohexene is easily accommodated into the zeolite channels. Unlike cyclopentene, the spectrum from cyclohexene on H-MOR persisted over a number of weeks. Assuming that the same mechanism as that proposed for cyclopentene (Scheme 1) applies to cyclohexene, it can be envisaged that cyclododeca-1,7-diene is formed with a conformation in which the two double bonds are in close proximity. Parallel transannular ring closure would lead to bicyclo[6.4.0]dodecene **9** and a cross transannular reaction would give bicyclo[5.5.0]dodecene **11**. As already discussed, bicyclo[6.4.0]dodecene is not compatible with the observed spectrum. The equivalence of the spectra measured from samples of cyclohexene and cyclodecene strongly suggests that the species formed is the same and most probably bicyclo[5.5.0]dodecene **11**. The topography and ring strain of the large ring cycloalkenes are not significantly different from those of the corresponding cycloalkane. The preferred structure of cyclododecane[26] is almost square and, including the covalent bond radii for the hydrogens, is only slightly larger than the zeolite channel. A small reduction in the width of the molecule would allow it to enter the zeolite channel without causing a large increase in strain energy (this operation causes an increase in ecliptical strain). We propose that such a conformation leads to the formation of bicyclo[5.5.0]dodecene **11**. A small axial dihedral angle (θ) in **11** is not consistent with either the chair or the boat form, which are the preferred conformations of cycloheptene.[27] The boat form of cycloheptene exhibits a pseudorotation process which passes through the twist form. This twist form has axial and equatorial dihedral angles which are consistent with the observed coupling constants (θ_{ax} was estimated to be 10° from a molecular model). As with bicyclooctene, pseudorotation is restricted by the presence of a fused ring, thus the β-hydrogens do not exchange rapidly enough to cause averaging of the axial and equatorial couplings at 294 K.

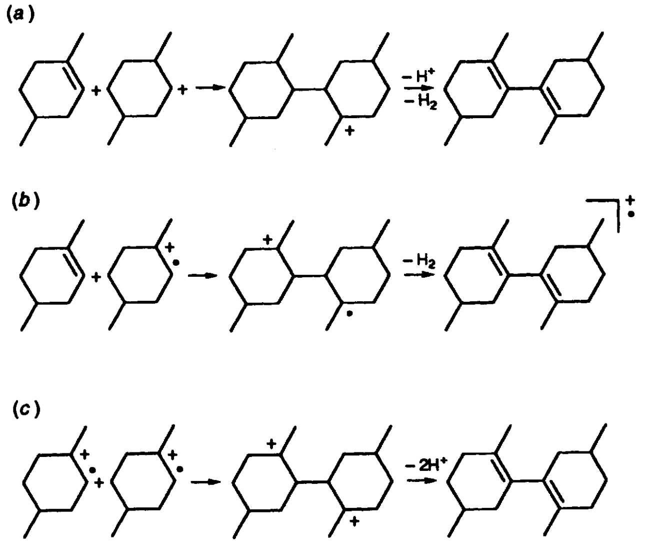
In order to determine the effect of substituents, 1-methyl and 4-methylcyclohexene were adsorbed onto H-MOR. The spectra [Fig. 5(*e*)] are identical to each other and very similar to the spectrum observed after adsorption of cyclododecene. At 294 K the coupling constants [Fig. 5(*f*)] were *a*(4 H) 3.56 mT and *a*(4 H) 1.44 mT. The anisotropy in the spectra obtained after adsorption of cyclododecene [Fig. 5(*a*)] and 1-methylcyclohexene [Fig. 5(*e*)] is much clearer than in the spectrum of bicyclooctene [Fig. 4(*a*)], especially at the outer lines, thus the simulations were carried out using an average line width. The ring enlargement reaction, and the small effect of the remote methyl group, of 4-methylcyclohexene could be predicted. However, the formation of the same radical cation from 1-methylcyclohexene was unexpected. The most likely explanation is that the double bond migrates prior to dimerisation, a proton catalysed reaction commonly observed in zeolites.[28] The methyl groups are not shown in **11** in Scheme 6 as it was not possible to assign exact positions, although it is clear that they do not occupy β-positions.

It should be pointed out that small differences in coupling constants, of about 0.05 mT, are not easily determined as a result of the large line width, but are apparent in the total spectrum width, and in differences in line shapes. At 294 K the spectra of the radical cations generated from cyclodecene, cyclooctene and cyclododecene were very different, and all were perfectly reproducible. At low temperature the coupling constants are more alike but the spectra are still visibly different. In a freon matrix at 77 K the species might no longer be distinguishable because of lower spectral resolution, which can lead to a false interpretation.

1,3- and 1,4-dimethylcyclohexene when adsorbed onto H-MOR produced spectra [Fig. 6(*a*) and (*b*) respectively] which were identical to each other but entirely different from the spectra measured from samples of the other cycloalkenes. That the radical cation had no α-protons was clear from the small line width. The simulation [Fig. 6(*c*)] was carried out using the coupling constants *a*(6 H) 1.17 mT and *a*(4 H) 1.94 mT, which were assigned to the six methyl hydrogens and four ring β-hydrogens respectively of 2,2′-dimethyl-1,1′-bicyclohexenyl species **12**. The spectrum shows some contamination from a second radical cation. The absence of a coupling constant for the four protons at positions 6 and 6′ is unanticipated but may be due to a twisted structure which causes a high spin density at the 2 and 2′ positions. 1,3,5-Trimethylcyclohexene, when adsorbed onto H-mordenite, gave a weak EPR spectrum which was clearly different to that from the dimethylcyclohexenes. It is therefore unlikely that 1,3-dimethylcyclohexene dimerises in the 2-position, but instead the double bond migrates so that the reaction takes place at C(6). That bicyclododecene was not formed cannot be ruled out, although it can be expected that the extra strain energy imposed on each ring by the presence of two methyl groups makes its formation unfavourable. There are three possible mechanisms for the formation of the dicyclohexenyl (Scheme 7). Reaction (*a*) is improbable as the proton would be expected to add to the other end of the double bond, generating the more substituted alkyl cation. Both radical cation mechanisms are possible, although in the highly acidic conditions of the zeolite the dimerisation of two radical cations is more favourable.[29]



12



Scheme 7

Conclusions

Metathesis reactions are usually associated with metal–carbene complexes formed with catalysts such as rhenium oxide or molybdenum chloride. Studies on silica–aluminas loaded with rhenium catalysts have shown that the activity is related to Brønsted acidity.[30] However it is unlikely that a highly reactive cycloalkyl carbene would be formed on H-mordenite in the absence of such a catalyst. Carbenes have been proposed as intermediates in organic reactions in zeolites,[31] including H-MOR, but this proposition is based on the observation that a carbene route is energetically more favourable than a cation mechanism in certain reactions. A more probable explanation is that the rings are held in close proximity in the zeolite channel and take part in an acid (Lewis or Brønsted) catalysed cycloaddition reaction, followed by ring opening of the cyclobutane intermediate. The restriction of motion imposed on molecules in the zeolite excludes a direct comparison between the bimolecular reactions of radical cations or cations in this medium and in solution. The transannular reactions of cyclooctene and cyclodecene were the same as those observed in solution. That the reaction of cyclododecene was different from that observed in solution is indicative of conformational restrictions imposed on larger molecules, and agrees with the expectation of a shape selective catalytic effect in the mordenite channel. The different chemical behaviour of the octalin radical cation when the adsorbed cycloalkene was exchanged but other conditions were identical shows that this species is not a common intermediate in the sense of a bottle neck which has to be passed by all molecules undergoing catalytic transformations. It is not unlikely that the presence of the Lewis sites changes the product distribution, but this may be to a minor extent only. It appears that the EPR technique monitors the catalytic process, which takes place also in the absence of Lewis sites, *via* oxidation of a small fraction of intermediates with low ionisation potential. Although this represents a 'selective perception', it is a very sensitive indicator of certain intermediates and of the progress of the reaction.

Experimental

The cycloalkenes were obtained from Fluka and Aldrich in the highest possible purity and where available with stabiliser, with the exception of 3-cyclopentylidenecyclopentene which was prepared by a reported method.[32] H-Mordenite ($SiO_2 : Al_2O_3$, 8.9) was obtained from CU Chemie Uetikon AG, Switzerland. It was dried at 523 K and 1×10^{-5} mbar (1 bar = 10^5 Pa) for 4–5 h. It was activated by heating in air to 973 K at a rate of approximately 100 K h^{-1}, and then left at this temperature for 12–15 h. The zeolite was evacuated in the EPR tube to *ca.* 5×10^{-6} mbar, at room temp., for 3 h. There was no detectable EPR signal prior to adsorption of the alkene. The alkene was degassed by freeze–pump–thaw cycles, distilled onto the zeolite under reduced pressure, and the tube sealed. The loading was 5–10%wt of the H-mordenite and all measurements were repeated at least twice to insure reproducibility. Unless otherwise stated, the alkenes were adsorbed onto the zeolite at 77 K. Measurements were obtained with a Bruker ESP 300 spectrometer fitted with a variable temperature unit.

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