Oxidation of Terpenes in H-Mordenite

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The behaviour of three terpenes, α-pinene, *trans*-isolimonene, and α-terpinene, in H-mordenite was investigated by EPR. All three species were found to give the same EPR spectrum, which was assigned to the radical cation of α-terpinene. No deuterium was incorporated when α-pinene in D-mordenite was measured, suggesting that rearrangement to α-terpinene is not catalysed by Brønsted acidity but probably by Lewis sites.

Radicals and radical cations generated in zeolites have been investigated by EPR in order to follow and understand the catalytic processes which occur.[1] These catalysts are used mainly in the petrochemical industry, but have also attracted some attention as catalysts in the synthesis of fine chemicals.[2] Although a great deal of research has been carried out on the structures and properties of zeolites, very little is known about the mechanisms of the organic reactions which take place in them. The transformations which occur are usually attributed to Brønsted acid sites which protonate alkanes and alkenes, thus initiating a variety of reactions including polymerisation and dehydrogenation.[2] EPR has proved to be a useful tool in investigating these reactions, as intermediates in the catalytic process can be selectively observed, and although these may not represent a major reaction pathway, they do allow monitoring of the possible transformations induced by zeolites. Deuteriation of the zeolite, by exchanging protons with deuterons, aids in the determination of possible reaction mechanisms.[3] Incorporation of deuterium into the observed radical cation indicates that Brønsted acid sites are involved in the transformations which take place.

Zeolites are also a useful medium in which radical cations can be studied. Appropriate treatment of several zeolites leads to defects in the structure which can accept an electron from an organic molecule with a sufficiently low ionisation potential[4] (below about 11 eV). The observed radical cation is usually persistent and the EPR spectrum can be measured over a wide temperature range. In the case of H-mordenite, a high silica zeolite with elliptical channels with diameters of 700 and 650 pm, this treatment involves heating in air, thus converting Brønsted acid sites to Lewis acid sites.[5] The latter are believed to be responsible for the spontaneous generation of radical cations.

Whereas small alkenes react rapidly in zeolites, the size of the channel hinders intermolecular reactions between larger organic molecules, often without affecting intramolecular processes. Cyclic alkenes were found to take part in dimerisation or transannular reactions[6] depending on the size of the ring and extent of substitution. In order to ascertain the consequence of further steric hindrance on intermolecular reactions, we have investigated the transformations of three terpenes on H-mordenite.

Results and Discussion

Three terpenes, α-pinene (1), *trans*-isolimonene (2), and α-terpinene (3) were adsorbed onto activated H-mordenite (H-MOR). The EPR spectra obtained from the three samples were identical to each other, and could therefore be assigned to the same species. The EPR spectra obtained from the terpenes
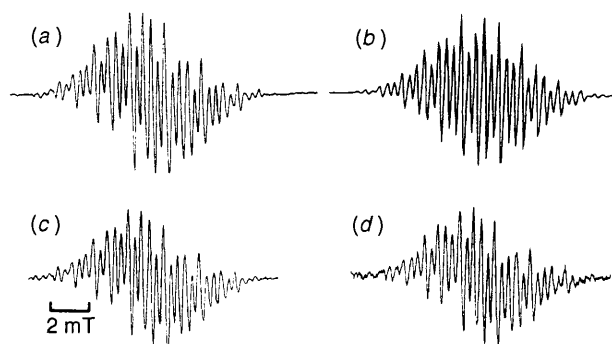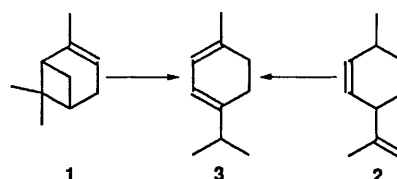

Fig. 1 (*a*) EPR spectrum of α-terpinene in H-MOR at 295 K; (*b*) isotropic simulation of (*a*) using coupling constants in Table 1; (*c*) EPR spectrum obtained at 295 K after adsorption of isolimonene onto H-MOR; (*d*) EPR spectrum measured at 295 K after adsorption of α-pinene onto D-MOR

in D-mordenite (D-MOR) were identical to those obtained in H-MOR, as shown for α-pinene in Fig. 1(*d*). The spectrum obtained at 295 K [Fig. 1(*a*)] had a *g*-factor of 2.0028, and the isotropic simulation [Fig. 1(*b*)] was carried out using the coupling constants: *a*(3 H) 1.17, *a*(2 H) 0.43, *a*(1 H) 0.74 and *a*(4 H) 1.96 mT. The coupling constants were not consistent with those anticipated for the radical cations of α-pinene or isolimonene. It could be predicted that both would have large α-proton couplings which lead to a larger anisotropy, and therefore to broader lines. Also the α-pinene and isolimonene radical cations would not have enough β-protons in the ring to account for the observed couplings. The spectrum was therefore assigned to the radical cation of α-terpinene as shown in Table 1. The EPR spectrum of α-terpinene has been reported[7] as measured after γ-radiolysis of the parent compound at 77 K, with coupling constants given as: *a*(3 H) 1.2, *a*(2 H) 0.3, *a*(2 H) 2.4 and *a*(2 H) 3.6 mT. In H-MOR the coupling constants for the pseudo-equatorial (peq) and pseudo-axial (pax) methylene protons at 110 K [Fig. 2(*a*)] were found to be approximately *a*(2 H) 1.25 and *a*(2 H) 2.67 mT, respectively, and the isopropyl β-hydrogen was 0.46 mT (Table 1). The spectrum at 110 K is not well simulated due to the large anisotropy,[8] which broadens some lines to a greater extent than others, although the main features are reproduced. Thus the spectrum measured after

Table 1 Hyperfine coupling constants (mT) for radical cations derived from substituted cyclohexa-1,3-dienes

| Species	T/K	X	Y	$H_{2,3}$	$H_{5,6}^{peq}$	$H_{5,6}^{pax}$	Ref.
X = CH(CH₃)₂, Y = CH₃	295	0.74 (1 H)	1.17 (3 H)	0.43 (2 H)	1.96 (2 H)	1.96 (2 H)	This work
X = CH(CH₃)₂, Y = CH₃	110	0.46 (1 H)	1.17 (3 H)	0.43 (2 H)	1.25 (2 H)	2.67 (2 H)	This work
X = CH(CH₃)₂, Y = CH₃	77	—	1.2 (3 H)	0.3 (2 H)	2.4 (2 H)	3.6 (2 H)	7
X = CH(CH₃)₂, Y = CH₃	0	0.07 (1 H)	1.29 (3 H)	0.12 (2 H)	1.36 (2 H)	3.09 (2 H)	AM1-UHF this work
X = Y = CH₃	77	0.6 (3 H)	0.6 (3 H)	0.5 (2 H)	1.20 (2 H)	2.95 (2 H)	11
X = Y = H	77	0.84 (1 H)	0.84 (1 H)	0.42 (2 H)	1.34 (2 H)	4.24 (2 H)	12
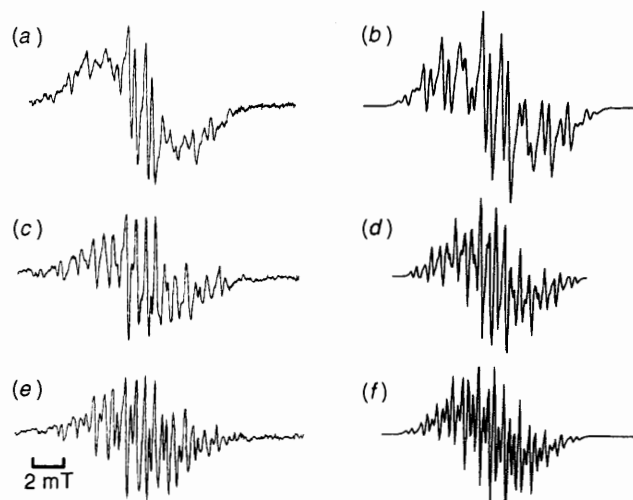
Fig. 2 (a) EPR spectrum of α-terpinene on H-MOR at 110 K; (b) isotropic simulation of (a) using data given in Table 1; (c) EPR spectrum of α-terpinene at 200 K; (d) isotropic simulation with coupling constants given in text, and a rate of ring inversion of 7.6×10^8 s⁻¹; (e) EPR spectrum of α-terpinene at 250 K; (f) isotropic simulation with coupling constants given in text, and a rate of ring inversion of 2×10^9 s⁻¹

γ-radiolysis is clearly very different from that measured in H-MOR, and they, therefore, must belong to two different species. In both cases, after γ-radiolysis, and oxidation in zeolite, a reaction of the α-terpinene cannot be ruled out. Hydrogen loss can occur in the zeolite and after γ-radiolysis,[9] whereas further dehydrogenation is more likely in the zeolite due to the highly acidic conditions,[10] this would, however, lead to the *p*-cymene radical cation which is not consistent with the observed spectra. A Diels–Alder reaction is also in both cases possible but unlikely in the zeolite due to the large steric requirements of such a reaction.

The coupling constants found for the α-terpinene radical cation in H-MOR are similar to those reported for 1,4-dimethylcyclohexa-1,3-diene[11] (Table 1), with the exception of the methyl protons [a(3 H) 0.6 mT]. The value for α-terpinene [a(3 H) 1.17 mT] is, however, compatible with the values measured for the methyl groups in 2,5-dimethylhexa-2,4-diene of 1.072 and 1.328 mT.[8] The EPR spectrum of cyclohexa-1,3-diene at 77 K, has couplings of a(2 H) 1.34 and a(2 H) 4.24 mT for the pseudo-equatorial and pseudo-axial protons, respectively.[12] It can be envisaged that a withdrawal of spin density from the ring by the alkyl substituents in the terpinene radical cation leads to a reduction in the methylene coupling constants. For example, the average coupling constant for the β-methylene groups in the cyclohexene radical cation is 3.825 mT,[12] and is reduced to 2.73 mT in the 1,2-dimethylcyclohexene radical cation.[13]

As further confirmation for the assignment given in Table 1, an AM1-UHF calculation[14] was carried out to optimise the geometry of the radical cation of α-terpinene. The spin densities were calculated with quartet annihilation,[15] reducing $\langle S^2 \rangle$ from 0.8074 to 0.7505. This method has been shown to give

remarkably accurate results for a number of radicals.[16] The geometry of cyclohexa-1,3-diene has been studied by a number of techniques[17] and was found to have a C_2 symmetry with a torsion angle between the two ethylene groups of between 17 and 18°. In general, AM1 calculations tend to result in rings which are too flat. For example, in the optimised geometry of α-terpinene the torsion angle was only 11°. However, when this was fixed as 18°, the other angles and bond lengths in the ring agreed with the measured values[17] to within 1° and 5 pm, respectively. In the AM1-UHF optimised geometry of the terpinene radical cation this angle, the dihedral angle between carbons 1–2–3–4, was 5°. This was increased gradually, and the best agreement between measured and calculated coupling constants was found when the torsion angle was 10°. The coupling constants thus obtained were: a(2 H) 1.36 and a(2 H) 3.09 mT for the pseudo-equatorial and pseudo-axial β-protons, respectively, a(3 H) 1.29 mT for the methyl group, a(1 H) 0.07 mT for the isopropyl β-proton, and a(2 H) 0.12 mT for the two inner α-protons. Increasing, or decreasing, the torsion angle had no significant effect on the α-proton coupling constants, but led to β-proton couplings which are further from the measured values. A large decrease in the dihedral angle between carbons 1–2–3–4 is to be expected, as a result of the shortening of the single bond between C-2 and -3, and an increase in the length of the double bonds between C-1 and -2, and between C-3 and -4 in the radical cation. The three bonds between C-1 and -4 became equal, 140 pm, in the optimisation, and the spin and charge were delocalised along the bonds, therefore a conformation nearer to planarity is preferred.


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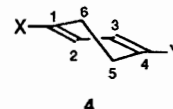
The optimised geometry corresponds to the preferred conformation of the radical cation in a frozen state, thus the low value for the isopropyl β-hydrogen coupling of 0.07 mT, which is calculated for a dihedral angle (θ) of 86.6° between the 2pz orbital at C-1 in the ring and the isopropyl carbon–β-proton bond. Assuming that this value corresponds within error to the given dihedral angle, and that the free rotation coupling is that of the methyl protons of 1.17 mT, values for A and B of 0.2 and 6.9 mT respectively were obtained for the expression:[18] $a(H\beta) = \langle A + B \cos^2 \theta \rangle \rho_{C_\alpha}$, where the spin density at C-4 was taken as 0.32, the value calculated from the optimised geometry of the radical cation. This corresponds to values for $\cos^2 \theta$ of 0.306 at 295 K and 0.179 at 110 K and leads to average dihedral angles for the isopropyl hydrogen of 56° at 295 K and 65° at 110 K. This preference for a conformation in which the angle (θ) between the 2pz orbital and the β-hydrogen (5) is the same as that observed[19] for ˙CMe₂CHMe₂, as opposed to conformation (6).

The anisotropy in the EPR spectra of radical cations in H-MOR,[8] which increases with decreasing temperature, makes an analysis of the rate of ring inversion difficult, and less

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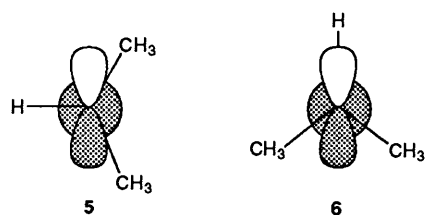
accurate than measurements in solution. However, spectra were measured at two other temperatures [Fig. 2(c) and (e)], and the simulations were carried out with the same coupling constants as at 110 K (Table 1), with the exception of the isopropyl hydrogen. At 200 K, [Fig. 2(d)] the isopropyl hydrogen coupling was 0.62 mT, and the rate of exchange between the pseudo-axial and -equatorial hydrogens, used in the simulation,[20] was 7.6×10^8 s^{-1}, and at 250 K [Fig. 2(f)] these were 0.68 mT and 2×10^9 s^{-1}.

Liquid acids react with α-pinene to form a complex mixture of products, the composition of which is dependent on the type of acid and the polarity of the solvent.[21] In highly polar protic acids, the formation of monocyclic terpenes is favoured, and bicyclic terpenes are favoured in less polar solvents. On the surface of solid acid catalysts[22] such as silica alumina, nickel sulfate, zinc sulfide and aluminium phosphate, the primary products from α-pinene are camphene, 1,7,7-trimethyltricyclo-[2.2.1.0^{2,6}]heptane, and limonene (7). The product distribution is dependent on the acidity of the catalyst, and on silica alumina the formation of limonene is favoured.[23] The product formation has been rationalised in terms of two reaction pathways following protonation of the double bond (Scheme 1).
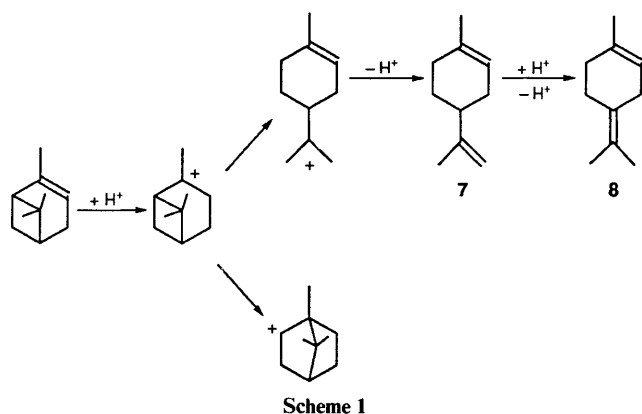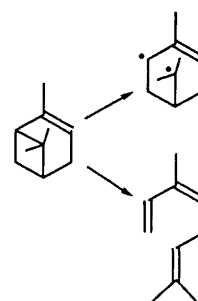

Scheme 1

Direct protonation of the cyclobutane moiety has been ruled out. Cymene and p-mentha-1,4(8)-diene (8) were also formed when the amount of adsorbed α-pinene was small, however α-terpinene was not reported as one of the reaction products.

Pyrolysis of pinene derivatives also produces a large number of products, which have been attributed[24] to a [σ^2 + σ^2] cycloreversion reaction and a 1,4-biradical produced by σ-bond cleavage in the cyclobutane moiety (Scheme 2). Cycloreversion leads to ocimene, which undergoes ring closure to give monocyclic terpene.[24] Among the products formed are limonene, α-phellandrene and α-terpinene.

On H-MOR, the observation of α-terpinene from α-pinene indicates that this is the product with the lowest ionisation potential, and the formation of isomeric terpenes cannot be ruled out. Unlike surface catalysis, in zeolites the molecule is held inside the channel and, therefore, does not need to compete with starting material for active sites. Thus, for example, in Brønsted acid catalysis of α-pinene (Scheme 1), limonene would be converted to p-mentha-1,4(8)-diene (8). From the AM1-UHF optimised geometry the heat of formation of the menthadiene radical cation was calculated to be 749 kJ mol^{-1},

Scheme 2

and that of the α-terpinene radical cation was 707 kJ mol^{-1}. Therefore oxidation of the menthadiene (8) would provide the driving force for isomerisation, formally via a [1,3]-H-shift, to the α-terpinene radical cation. Likewise, the heat of formation of the isolimonene radical cation was calculated to be 845 kJ mol^{-1}, thus oxidation of the limonene can also induce successive hydrogen or proton shifts to form the α-terpinene radical cation.

If the ring opening in α-pinene in H-MOR is induced by Brønsted acid catalysis, a proton from the zeolite must be incorporated into the observed radical cation. However, in deuteriated mordenite the EPR spectrum obtained was identical to that measured for α-pinene in H-MOR, with no indication of the presence of a second radical cation. Although at the end of an acid catalysed rearrangement, a proton, or deuterium must be eliminated from the cationic intermediate, it is highly unlikely that in every molecule a deuterium would be lost. Contrary to expectation, Brønsted acidity does not seem to be responsible for the rearrangement. That deuterium was not incorporated into isolimonene could not be determined as the coupling constants for the hydrogens in the isopropyl methyl groups were too small to be detected.

An alternative mechanism for the rearrangement of α-pinene to α-terpinene, involves, initially, the formation of the radical cation of α-pinene, the optimised geometry of this was calculated to have a heat of formation of 870 kJ mol^{-1}. α-Pinene has an ionisation potential of 8.07 eV,[25] and can, therefore, be easily oxidised in the zeolite. The reactions which follow would then be comparable to those which occur on pyrolysis (Scheme 2) of α-pinene.[24] Opening of the cyclobutane ring could occur either by σ-bond cleavage or by [σ^2 + σ^2] cycloreversion. In both cases the resulting monocyclic terpene radical cation would rearrange to the most stable isomer, the α-terpinene radical cation.

Experimental

Deuteriated mordenite (D-MOR) was prepared by heating a solution of H-MOR in DCl (38% in D$_2$O, >99.5 atom% D) to 343 K for 5 h and then filtering the zeolite. This process was repeated 3 times, and the zeolite finally washed several times with D$_2$O. Both H-MOR and D-MOR were dried at 523 K and 1 Pa for 4–5 h. They were activated by heating in air to 973 K at a rate of 100 K h^{-1}, and then left at this temperature for 12–15 h. The zeolite was evacuated in the EPR tube to about 0.5 Pa, at room temperature, for 3 h. The terpenes were degassed by freeze–pump–thaw cycles, distilled onto the zeolite at 77 K under reduced pressure, and the tubes sealed. The loading was 5–10%wt. of the mordenite and all experiments were repeated at least twice to ensure reproducibil-

ity. Measurements were obtained with a Bruker ESP 300 spectrometer fitted with a variable temperature unit.

References

1 A. V. Kucherov and A. A. Slinkin, *Kinet. Katal.*, 1982, **23**, 1172; 1983, **24**, 947; 1983, **24**, 955; S. Shih, *J. Catal.*, 1975, **36**, 238.

2 M. S. Rigutto, *Stud. Surf. Sci. Catal.*, 1991, **58**, 727; W. F. Hölderich and H. van Bekkum, *Stud. Surf. Sci. Catal.*, 1991, **58**, 631.

3 C. J. Rhodes and M. Standing, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1455.

4 S. Shih, *J. Catal.*, 1975, **36**, 238.

5 J. C. Védrine, A. Auroux, V. Bolis, P. Dejaifve, C. Nacchache, P. Wierzchowski, E. G. Derouane, J. B. Nagy, J.-P. Gilson, J. H. C. van Hooff, J. P. van den Berg and J. Wolthuizen, *J. Catal.*, 1979, **59**, 248; E. G. Derouane, *Stud. Surf. Sci. Catal.*, 1980, **4**, 5; 1984, **19**, 1; M. S. Rigutto, *Stud. Surf. Sci. Catal.*, 1991, **58**, 727.

6 R. Crockett and E. Roduner, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1503.

7 A. G. Davies and R. Hay-Motherwell, *J. Chem. Soc., Perkin Trans. 2*, 1988, 2099.

8 E. Roduner, R. Crockett and L.-M. Wu, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2101.

9 W. G. Burns, R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, 1967, **70**, 910.

10 C. M. Williams and D. Whittaker, *J. Chem. Soc. B*, 1971, 668.

11 A. G. Davies, R. S. Hay-Motherwell, J. C. Evans and C. R. Rowlands, *J. Chem. Soc., Chem. Commun.*, 1986, 1513.

12 T. Shida, Y. Egawa, H. Kubodera and T. Kato, *J. Chem. Phys.*, 1980, **73**, 5963.

13 R. M. Dessau, *J. Am. Chem. Soc.*, 1970, **92**, 6357.

14 MOPAC Version 6.0, Quantum Chemistry Program Exchange, No. 455.

15 T. Amos and L. C. Snyder, *J. Chem. Phys.*, 1964, **41**, 1773.

16 S. F. Nelson, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1005.

17 S. S. Butcher, *J. Chem. Phys.*, 1965, **42**, 1830; M. Traetteberg, *Acta Chem. Scand.*, 1968, **22**, 2305; G. Luss and M. D. Harmony, *J. Chem. Phys.*, 1965, **43**, 3768.

18 J. L. Courtneidge and A. G. Davies, *Acc. Chem. Res.*, 1987, **20**, 90.

19 P. J. Barker, A. G. Davies and M.-W. Tse, *J. Chem. Soc., Perkin Trans. 2*, 1980, 946.

20 J. Heinzer, Quantum Chemistry Program Exchange, Indiana University, Program 209.

21 F. A. L. Anet, in *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*, VCH, New York, 1987, p. 1; P. W. Rabideau and A. Sygula, *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*, VCH, New York, 1987, p. 1, 65.

22 D. Whittaker, in *Chemistry of Terpenes and Terpenoids*, Academic Press, London, 1972, p. 11.

23 R. Ohnishi, K. Tanabe, S. Morikawa and T. Nishizaki, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 571.

24 J. M. Coxon and P. J. Steel, in *Terpene Chemistry*, McGraw-Hill, New Delhi, 1982, p. 119.

25 M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 1964, 4434.