Formation of the Radical Cation of 1,2,3,4,5,6,7,8-Octahydronaphthalene by Adsorption of Cyclopentene onto H-Mordenite

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Following adsorption of cyclopentene onto H-mordenite, the ESR spectrum of the 'dimeric' 1,2,3,4,5,6,7,8-octahydronaphthalene radical cation was observed.

Radical cations of alkenes have been observed by ESR spectroscopy, following their adsorption onto high-silica zeolites, even at low temperatures.[1-8] The possibility exists, therefore, that radical cations may play an intermediary role in the catalytic conversions of alkenes on the surfaces of these materials.

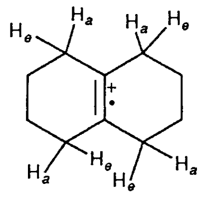
The adsorption of cyclopentene on H-mordenite was studied previously by ESR spectroscopy,[1-3] and the resulting spectrum was assigned to the primary radical cation of cyclopentene **1** with the hyperfine splittings $a(4\text{H}) = 37.0$; $a(2\text{H}) = 14.5$ G (1 G = 10^{-4} T). We have repeated this experiment, and while our ESR spectra agree closely with those previously reported,[1-3] we are inclined strongly to the view that the radical species responsible is not the parent cyclopentene radical cation, but rather the 'dimeric' *octahydronaphthalene radical cation* **2**. There are compelling reasons for this view, as we now show.

Firstly, authentic spectra of the cyclopentene radical cation **1** are available in the literature,[9,10] obtained through the agency of the Freon (CFCl_3) radiolysis method: the couplings reported at 77 K are $a(2\text{H}) = 48.5$, $a(2\text{H}) = 53.0$, $a(2\text{H}) = 8.6$, $a(1\text{H}) = 12.5$, $a(1\text{H}) = 5.5$ G, and are thus entirely different from those reported on H-mordenite. Furthermore, the ESR spectra[1-3] have been assumed to consist of a quintet (37.0 G) of triplets (14.5 G) pattern, and this is probably the only way that the spectral features could reasonably be reconciled with a radical structure based on a single 5-membered ring. However, the pattern (Fig. 1) is actually a quintet or quintets, and so 8 not 6 protons are coupled with the unpaired electron.

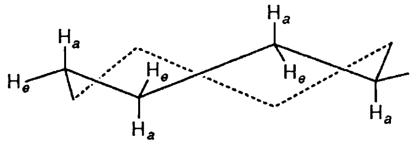
Convincing evidence for the true identity of the radical is provided by the ESR spectrum measured for the authentic octahydronaphthalene radical cation **2**, obtained by radiolysis of the parent compound in CFCl_3 at 77 K (Fig. 2). Our parameters [$a(4\text{H}_a) = 37.0$; $a(4\text{H}_e) = 14.5$ G; **2**] are in

1 **3**

Scheme 1



2



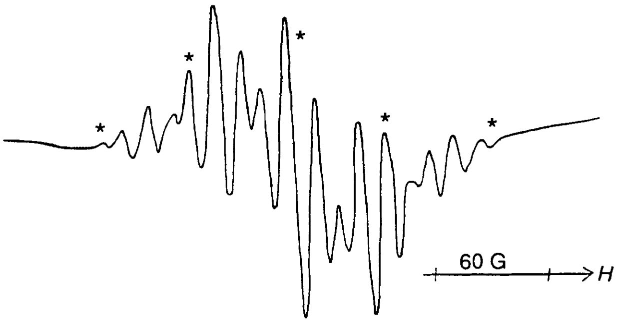


Fig. 1 ESR spectrum recorded at 77 K, following adsorption of cyclopentene onto H-mordenite. (*) Marks lines that remain invariant to linewidth alternation (see Fig. 3).

complete agreement with those previously reported[11] for this cation in $CFCl_3$ at 77 K, and most significantly in the present context, are identical with those measured from cyclopentene on H-mordenite.

On warming the impregnated zeolite sample to 295 K, the appearance of the spectrum changes in a dramatic way (Fig. 3), and thus led Shih[2] to assign a similar spectrum recorded at a higher temperature to a secondary radical species, *viz*. the allylic radical **3** assumed to be formed by the ion–molecule reaction in Scheme 1. However, there is no doubt that both spectra are from the *same* radical, since the original form of the 77 K spectrum (Fig. 1) is essentially restored on subsequently recooling to 77 K. Thus no further chemical change has occurred; it is simply that **2** undergoes pronounced linewidth alternation, as discussed in detail by Shida and his coworkers.[11] In the spectrum in Fig. 3, the invariant lines (marked *) are dominant, and give the false impression[2] that a new set of couplings is present.

One very important observation is that **2** is still far from its 'fast-exchange' limit in the zeolite at 295 K; this is in marked contrast with its behaviour in liquid solution, as observed by ODMR (optically detected magnetic resonance),[11] since in this medium the limiting set of 9 lines, with some residual broadening, was apparent even at 190 K. Thus there is some interaction between the radical cation and the zeolite that markedly reduces the ring inversion frequency. This may relate to surface adsorption, or to physical constraints imposed upon a channel-occupied radical, both of which might be expected to inhibit dynamic behaviour.

We must of course consider how **2** might originate. One possibility is that it may be formed by an ion–molecule reaction between cyclopentene radical cations and neutral cyclopentene molecules. In this context, we can again appeal to results for authentic cyclopentene radical cations in Freon matrices. In $CFCl_3$,[9] on prolonged annealing at 155 K, the *genuine* radical **3** was observed, with couplings $a(4H) = 22.5$, $a(2H) = 14.1$, $a(1H) = 2.3$ G.

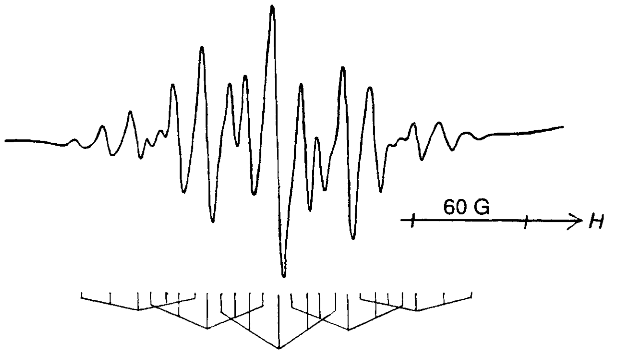


Fig. 2 ESR spectrum of **2**, recorded at 77 K following γ-radiolysis of octahydronaphthalene in solid $CFCl_3$ at 77 K

Fig. 3 ESR spectrum recorded following warming of the sample from Fig. 1 to 295 K. (*) Marks invariant lines.

The evidence is, then, that Scheme 1 is the chosen ion–molecule pathway for cyclopentene at least in the solid $CFCl_3$ medium, and it therefore seems unlikely that the octahydronaphthalene structure is formed directly from **1**. It is more probable that cyclopentene is converted to octahydronaphthalene prior to radical cation formation; indeed, previous work[12] has shown that cyclopentene is partially converted to octahydronaphthalene-type structures on treatment with Lewis acids, so this is a definite possibility. An octahydronaphthalene molecule may be subsequently converted to its radical cation on encountering an appropriate solid state defect.[8]

In terms of the potential role of acid and defect sites in zeolite catalysis, these observations are rather significant, since they establish that the acidic properties of the zeolite can certainly promote molecular transformations that are not available *via* a radical (cation) mediated route. However, the possibility of alternative or subsequent radical formation suggests further potential conversion pathways.

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