Radical Cations of Quadricyclane and Norbornadiene in Polar ZSM-5 Matrices: Thermal Retro Diels–Alder Reaction†

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The radical cation of norbornadiene or quadricyclane (Q) and of norbornadiene (NBD) produced by γ-radiolysis in polar ZSM-5 undergo a reverse Diels–Alder reaction, which is a thermally forbidden, photochemically allowed process, to cyclopentadiene radical cation.

The radical cation chemistry of quadricyclane (Q) and norbornadiene (NBD) continues to provide new insights into transformations of the C_7H_8 molecular framework. In previous studies, only one radical cation species has been observed from both NBD and Q in low-temperature matrices.[1] In gas-phase studies, ions of NBD and Q could not be distinguished.[2] The evidence for distinct racidal cations of Q and NBD comes from CIDNP (chemically induced dynamic nuclear polarisation) studies.[3] Optical spectroscopy in solution radiolysis also suggests the occurrence of two distinct transient radical cations.[4]

The observation of a single radical cation species in low-temperature matrices by EPR (electron paramagnetic resonance) was augmented recently by the work of Williams and coworkers, who observed additional radical cation species by radiolytic oxidation of Q and NBD in Freon matrices.[5] Several photochemical studies of Q and NBD have described various products and suggested possible reaction pathways.[6] A recent report discusses the occurrence of metal-promoted valence isomerizations and cycloreversions in the gas phase for adducts of NBD and Q with either Fe^I or Cu^I.[7]

We have recently examined many radical cation species in zeolite matrices. Our studies have shown that one can stabilize higher electronic states of radical cations.[8] We have also illustrated how one can control the ion–molecular reactions of radical cations.[9] The study of Q and NBD in zeolite matrices reveals a multitude of radical cation and radical species, many more species than observed in other matrix studies. Here, we focus on one aspect of this newly revealed C_7H_8 radical cation chemistry.

The NBD and Q radical cations were produced in a polar ZSM-5 by γ-irradiation after appropriate zeolite activation and substrate adsorption.[8–10] Zeolite polarity is a function of the SiO_2/Al_2O_3 ratio. High Al content and hence counter-ion content increase the polarity. The SiO_2/Al_2O_3 ratio for the ZSM-5 used in our study was 170.
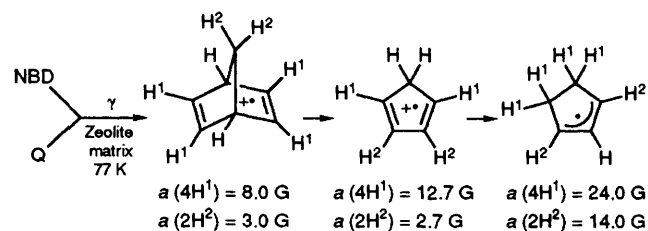
Both Q and NBD give rise to a single dominant radical cation species. At certain substrate concentrations and at different temperatures, additional radical cations and neutral radicals are observed: bicyclo[3.2.0]hepta-2,6-diene radical

cation[5] and its corresponding radical, and cyclopentadiene radical cation and its hydrogen adduct. We focus here on the last two species in this list. Scheme 1 outlines the species under consideration. The EPR spectra of the parent radical cation and the cyclopentadiene radical cation are illustrated in Fig. 1. The latter species was not observed in less polar zeolites having Si/Al ratios greater than 200.

EPR spectra of radical cations from Q and NBD are shown in Fig. 1. The hyperfine structure observed at 100 K can be simulated with coupling constants of 8.0 G(4H) and 3.0 G(2H) $(1\ G = 10^{-4}\ T)$.[1] The spectra recorded at 100 K after annealing at 200 K exhibit hyperfine coupling constants of 12.7 G(2H) and 2.7 G(2H). The latter species, *i.e.* the cyclopentadiene radical cation, has been observed by the radiolysis of cyclopentadiene[11] in a Freon matrix. The spectra observed at 260 K exhibit hyperfine couplings of 24 G(4H) and 14 G(2H), very similar to the published values of 22 G and 14 G (experimental)[11b] and 30.5 G and 14.7 G (INDO-calculation)[11a] for the cyclopentene-3-yl radical (a hydrogen adduct of the cyclopentadiene radical cation), which has been reported in the study of cyclopentadiene radical cation.[11]
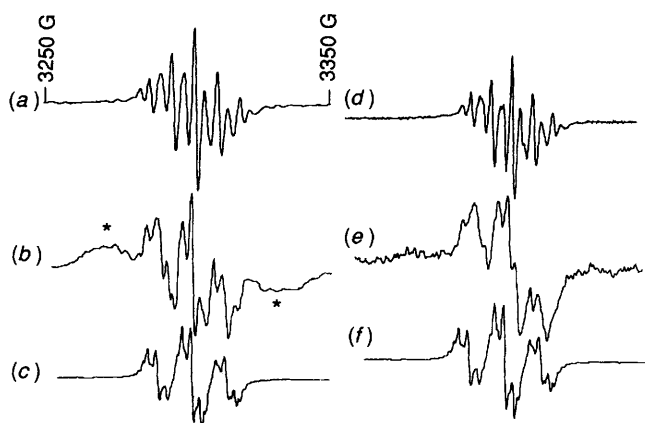
The radical cations in zeolites or in Freon matrices are generated *via* charge transfer from the matrix radical cation. Thus, the substrate radical cation is created with little excess energy, *i.e.* less than or equal to the difference between the ionization potentials of the matrix and the substrate. This initial excess energy is not important, since we observe that the loss of the C_2 fragment to give cyclopentadiene radical cation occurs only when the temperature of the matrix is raised, and not at the instant of the parent radical cation creation.

The observation of the cyclopentadiene radical cation requires that a reverse Diels–Alder reaction takes place. Such a process is a [3 + 2] cycloreversion, which is a 'forbidden'

$a\,(4H^1) = 8.0\ G$ $a\,(4H^1) = 12.7\ G$ $a\,(4H^1) = 24.0\ G$
$a\,(2H^2) = 3.0\ G$ $a\,(2H^2) = 2.7\ G$ $a\,(2H^2) = 14.0\ G$

Scheme 1

Fig. 1 EPR spectra of the sample with 0.4% w/w Q in ZSM-5 after γ-radiolysis at 77 K and observed at (a) 100 K, (b) 100 K (and at 5 mW) after annealing at 200 K. The asterisk in (b) represents an overlapping signal from other species; (d) and (e) are the same for 0.15% w/w NBD. (c) and (f) The simulated spectrum for the cyclopentadiene radical cation using the literature values of 12.7 G(2H) and 2.7 G(2H).

radical cation pericyclic reaction, as discussed by Bauld.[12] A reverse Diels–Alder process was observed in pyrolysis and electron-impact studies of norbornadiene.[13] The observation of such a process requires the involvement of radical cation excited states assuming a concerted reaction. The cyclopentadiene radical cation is produced in the zeolite matrix from the parent NBD or Q radical cations by a thermal process. The parent radical cations must be adsorbed at certain polar zeolite sites that stabilize higher electronic states of the radical cation and allow the transformation that is forbidden in the ground state.

Several conclusions and conjectures are possible from the insights provided by this study. We may be justified in suggesting that many, if not all, condensed-phase transformations in the NBD and Q systems, which were observed in photochemical and other studies, can be accounted for by considering the transformations and reactions of radical cations alone; there is no need to invoke diradical or other transient neutral intermediates.[6] Our forthcoming publication will provide further evidence on this point.[14] The variety of isomers and transformations of the C_7H_8 family observed in zeolites is consistent with the wide range of ion transformations suggested and, to some extent, characterized in gas-phase studies.[2]

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