

**Radical Cations of Quadricyclane and Norbornadiene in Polar ZSM-5
Matrices: Radical Cation Photochemical Transformations Without
Photons***

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ABSTRACT

Radical cations of quadricyclane (Q) and norbornadiene (NBD) are produced by γ -radiolysis in zeolites. In polar ZSM-5, only one radical cation is initially observed below 100K. Increasing the temperature above 200K gives rise to the cyclopentadiene radical cation. Higher temperatures (>260K) give rise to the cyclopenten-4-yl radical. The observation of cyclopentadiene radical cation implies the occurrence of the reverse Diels-Alder reaction. This is a thermally forbidden, photochemically allowed, process, which is made possible by the interaction of the polar zeolite matrix sites with the parent NBD and Q radical cations.

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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 past studies, only one radical cation species was 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 radical cations of Q and NBD comes from elegant CIDNP studies of Roth and coworkers.³ Optical spectroscopy in solution radiolysis also suggests the occurrence of two distinct transient radical cations.⁴

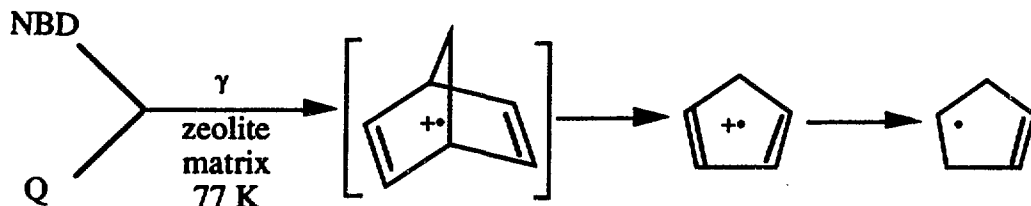
The observation of a single radical cation species in low-temperature matrices by EPR was recently augmented by the work of Williams and coworkers, who observed additional radical cation species by radiolytic oxidation of Q and NBD in freon matrices.⁵ Several photochemical studies of Q and NBD have described various products and suggested possible reaction pathways.⁶

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.⁷ We have also illustrated how one can control the ion-molecule reactions of radical cations.⁸

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.⁷⁻⁹ Zeolite polarity is a function of the SiO_2/Al_2O_3 ratio. High Al content and hence high 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: toluene radical cation, benzyl radical, bicyclo[3.2.0]hepta-2,6-diene radical cation⁵ and its corresponding radical, and cyclopentadienyl radical cation and its H-adduct. We focus here on the last two species in this list. The scheme below outlines the species under consideration:



The EPR spectra of these paramagnetic species are illustrated in Figures 1 & 2. These species are only observable in the more polar zeolite matrix. These species were not observed in less polar zeolites having Si/Al ratios greater than 200.

EPR spectra of $Q^{+\bullet}$ and $NBD^{+\bullet}$ are shown in Figure 1. The hyperfine structure observed at 100K can be simulated with coupling constants of 8.0G(4H) and 3.0G(2H)¹. The spectra recorded at 100K after annealing at 200K exhibit hyperfine coupling constants of 12.7G(2H) and 2.7G(2H). The latter species, i.e., the cyclopentadiene radical cation, has been observed by the radiolysis of cyclopentadiene¹⁰ in a freon matrix. Figure 2 shows the spectra observed for the same samples at 260K and a higher microwave power (10mW). Both spectra exhibit hyperfine couplings of 24G(4H) and 14G(2H), and are attributed to the cyclopenten-4-yl radical that is formed as a hydrogen adduct of the cyclopentadienyl radical cation.¹⁰

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) cyclo-reversion, which is a "forbidden" radical cation pericyclic reaction, as discussed by Bauld¹¹. A reverse Diels-Alder process was observed in pyrolysis and electron-impact studies of norbornadiene¹². The observation of such a process requires the involvement of radical cation excited states. 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 intermediates⁶. Our forthcoming publication will provide further evidence on this point¹³. The variety of isomers and transformations of the C₇H₈ family observed in zeolites is consistent with the wide range of ion transformations suggested and, to some extent, characterized in gas-phase studies².

Figure Legends:

1. EPR spectra of the sample with 0.15%w/w Q in ZSM-5 after γ -radiolysis at 77K and observed at (a) 100K, (b) 100K after annealing at 200K. (d) and (e) are the same for NBD. (c) is the simulated spectrum for the cyclopentadiene radical cation using the literature values of 12.7G(2H) and 2.7G(2H).
2. EPR spectra of the sample with 0.15%w/w (a) Q and (b) NBD in ZSM-5 after γ -radiolysis at 77K and observed at 260K, microwave power 10mW. (c) is the simulated spectrum for the cyclopenten-4-yl radical, 24G(4H), 14G(2H), very similar to the published values of 22 G and 14 G (experimental)^{10b} and 30.5 G and 14.7 G (INDO-calculation)^{10a}.

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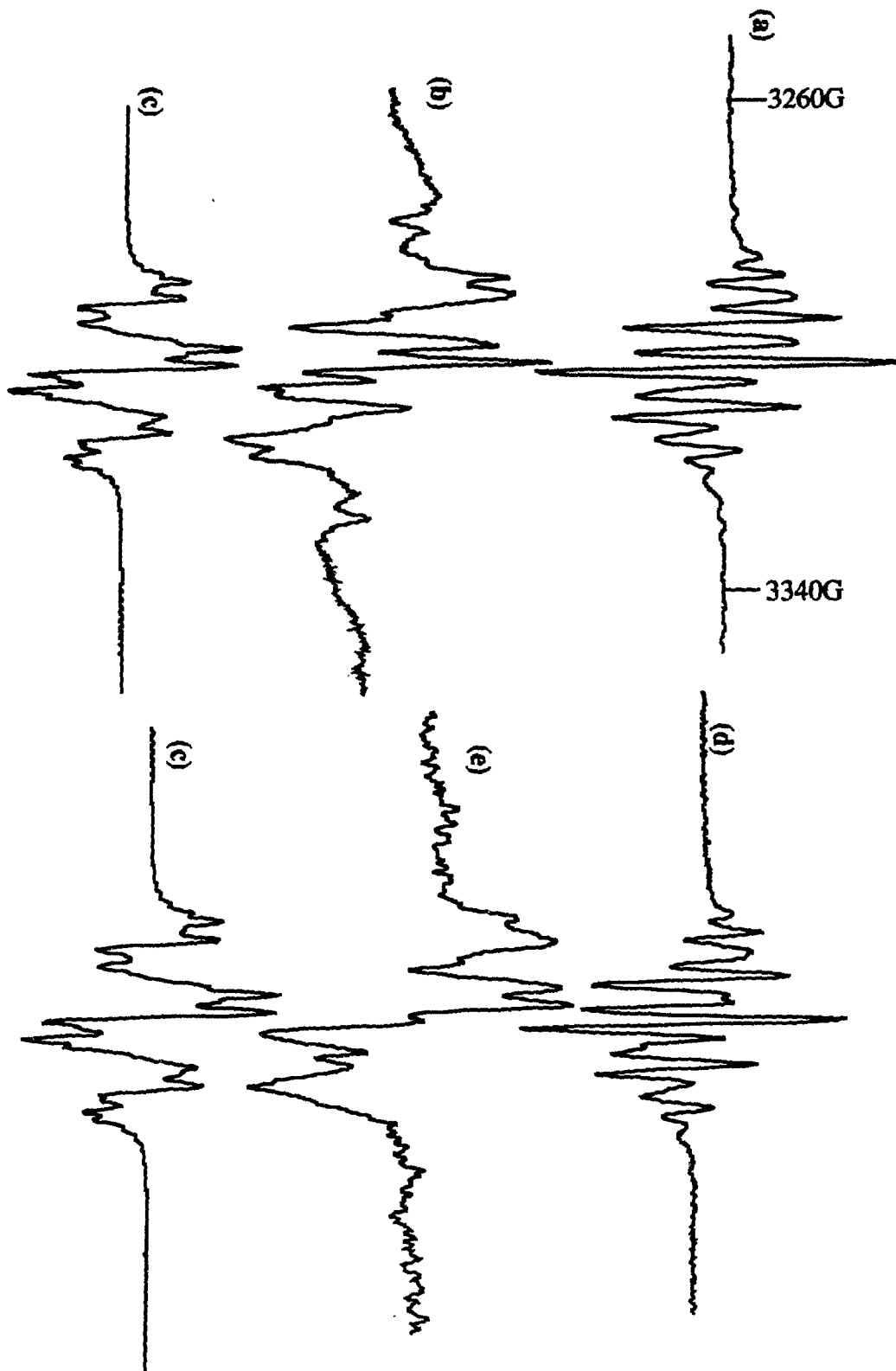


Figure 1

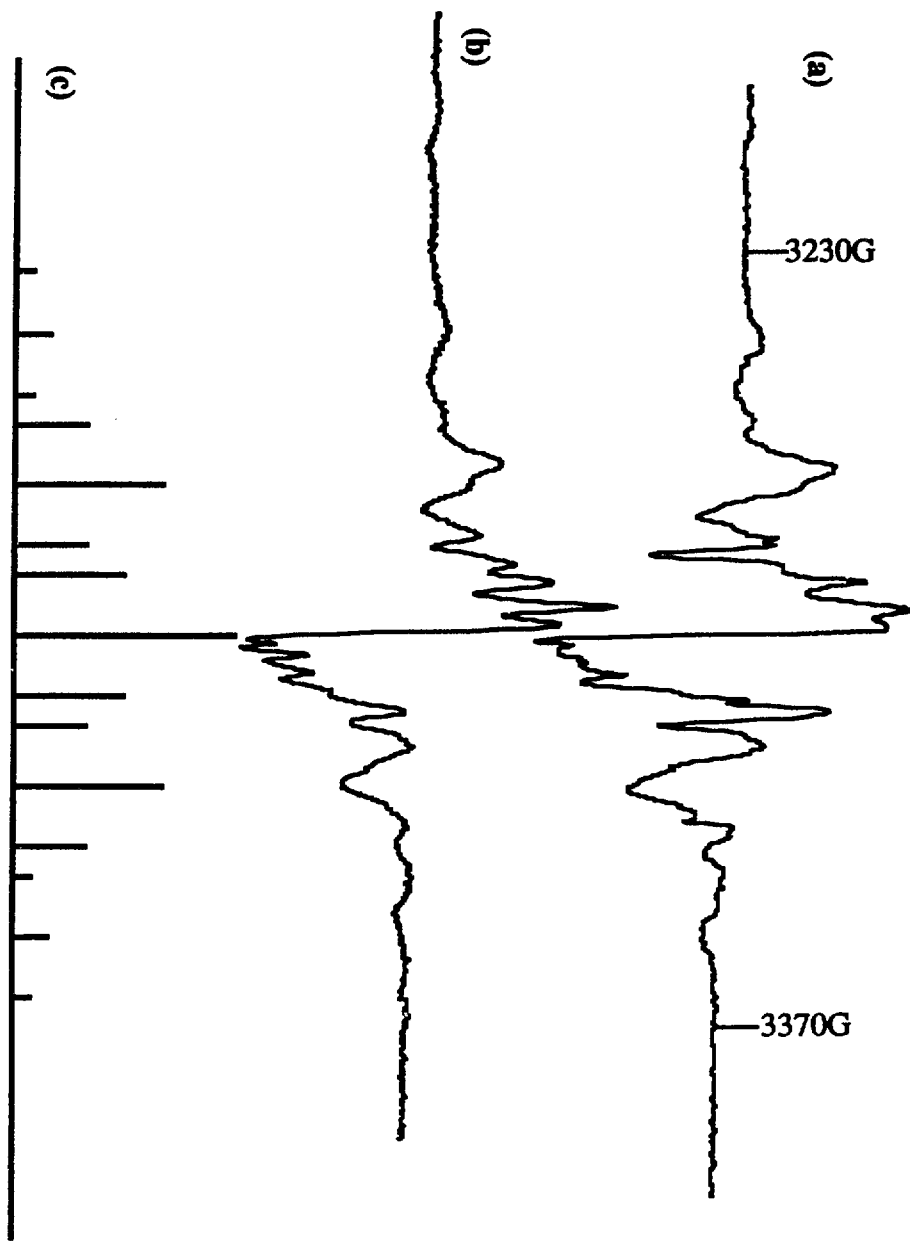


Figure 2