

# Observation of Radical Cations by Swiftmess or by Stealth

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The widespread occurrence of radical cations in chemical processes drives their study under diverse conditions and in every conceivable kind of environment. Radical cations are primary species in ionization events involving high-energy radiation and in photoinduced electron-transfer reactions. They are key intermediates in redox reactions in solution, and they occur on surfaces of strongly oxidizing solid catalysts. To better understand the role played by radical cations in technologically important applications, such as solar energy conversion, catalysis, radiation damage, and the factors that control their reactions, they are studied in neat liquids, concentrated solutions, molecular solids, and heterogeneous solids, on surfaces, and at interfaces. This undertaking requires many different approaches and time scales.

What makes the study of radical cations experimentally challenging is their short lifetimes. In nonpolar liquids, most radical cations created by radiolysis undergo geminate recombination with electrons in picoseconds.<sup>1</sup> Recombination can be slowed by use of electron scavengers, increasing solvent polarity (to increase the escape probability for geminate pairs) or viscosity, or virtually stopped altogether by sequestering the charge pairs in a rigid matrix. Besides recombination, fast chemical reactions shorten radical cation lifetimes. Thus, experimental observation of radical cations is based on fast detection techniques and strategies for controlling radical cation reactions—slowing them down, as well as changing the outcome.

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Alexander D. Trifunac was born in Yugoslavia. He was educated at Columbia University (B.A.) and the University of Chicago (Ph.D.). His thesis work was on CIDNP, radical pair theory and experiments, with Gerhard L. Closs. He joined the Chemistry Division of Argonne National Laboratory in 1972 in a postdoctoral position. He is a senior scientist and is (since 1982) a group leader of the Radiation and Photochemistry Group. His research interests are in the study of chemistry of transient paramagnetic species involved in energy and charge-transfer processes occurring in radiolysis and in photoionization in liquids, glasses, and amorphous solids.

In our laboratory, strong emphasis has been placed on the utilization of novel magnetic resonance methods to augment our fast optical and conductivity studies of condensed-phase photoionization and pulse radiolysis. Although methods based on electron paramagnetic resonance (EPR) cannot equal the time resolution of these faster techniques, the structural information from magnetic resonance greatly enhances chemical identification and provides crucial insights into intermolecular interactions of radical cations. Our utilization of EPR techniques has followed a dual track: (1) With time-resolved fluorescence-detected magnetic resonance (FDMR), we achieve the greatest possible time resolution (for EPR) and gain a dynamic window onto radical cations undergoing fast reactions in liquid solution and in solids. (2) Following the work of others, we have exploited specialized matrixes for stabilization of radical cations.<sup>2–6</sup> By broadening the concept of matrix isolation with the use of microporous zeolite reactors, we obtain new means of controlling radical cation reactions and can study them on the slow time scale by variable-temperature, X-band EPR.

With time-resolved FDMR, we can answer the question, how fast? FDMR can sometimes allow observations of very elusive (reactive) radical cations that cannot be stabilized under matrix-isolation conditions. FDMR is often the only way to compare liquid-phase conditions to solid-state EPR experiments and has afforded new insights into the role of solvation in radical cation structure and reactions.

We shall use the term matrix isolation to include stabilization of radical cations both by dilution in an inert frozen solvent and by sequestration in the micropores of zeolites. The latter technique adds several new dimensions to the matrix-isolation approach. Most significant are the geometrical constraints imposed on molecular motion and chemical reactions. Other advantages include the ability to vary the host–guest interactions and the possibility of adding extrinsic solvents to the zeolite-plus-adsorbate system. Radical cations trapped in zeolites also serve as useful probes of their environment, and their study sheds light on important processes such as charge transfer and energy transfer. Zeolites are useful surrogates for metal oxide, network solids (e.g., glasses) and other heterogeneous solid systems where the understanding of radiation chemistry is of much interest. Because of their well-defined structure and their ability to admit probe molecules, they support a more systematic, graded experimental approach to complex issues.

## FDMR: Detection of Transient Radical Cations

Time-resolved FDMR and its antecedents have been reviewed previously.<sup>7–9</sup> FDMR has been applied to pulse radiolysis and photoionization and to both liquid and solid samples. The following discussion includes much that applies to the general case with special attention to pulse radiolysis of liquid solutions.

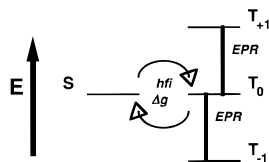
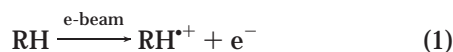


FIGURE 1. Energy level diagram showing the mixing of radical pair spin states in a high magnetic field.

As its name indicates, FDMR is a double-resonance technique. To gain the necessary sensitivity for observing short-lived radical ions, microwave transitions are detected via emission of optical photons. The relationship of FDMR to other optically detected magnetic resonance techniques (e.g., detection of microwave transitions in neutral excited states) has been fully discussed.<sup>8</sup> FDMR is also related to other reaction-yield methods (measurement of magnetic field effects on reaction yields) that depend on the existence of spin coherence in pairwise generated radicals.<sup>10</sup>

Scheme 1 summarizes several of the ionic processes in pulse radiolysis of nonpolar liquids that underlie the FDMR experiment. Energy from the incident beam of 3

#### Scheme 1



MeV electrons is absorbed by the solvent, RH, and results in the creation of radical cation–electron pairs, eq 1. Geminate recombination (the fate of over 90% of pairs in alkanes) of the initial ion pairs would be complete in picoseconds if some of the electrons were not intercepted by a scavenger, eq 2. The electron acceptor, A, is typically an aromatic hydrocarbon (e.g., anthracene), and it serves the 2-fold purpose of converting some of the electrons to slower diffusing radical anions and providing an excited state,  ${}^1\text{A}^*$ , with high fluorescence quantum yield. This state is generated by a variety of charge recombination reactions (not all shown in Scheme 1), the relative importance of which depends on the solution composition, rates of chemical transformations, and time after the ionization pulse.

The relative yield of singlet vs triplet excited states upon recombination is determined by the relative singlet or triplet character of the ion pair population, and for this reason it is useful to describe the ion pair spin states in terms of the basis set of singlet,  $|S\rangle$ , and triplet,  $|T_{-1}\rangle$ ,  $|T_0\rangle$ ,  $|T_{+1}\rangle$ , pair functions, although for the average separation of the ions prior to recombination the electron–electron exchange interaction is very small. Figure 1 shows the ordering of these states when the degeneracy of the triplet states is lifted by an externally applied magnetic field. Radiolysis creates ion pairs that are initially  $|S\rangle$ .<sup>11</sup> Spin evolution on the FDMR time scale ( $10^{-8}$ – $10^{-5}$  s) is caused

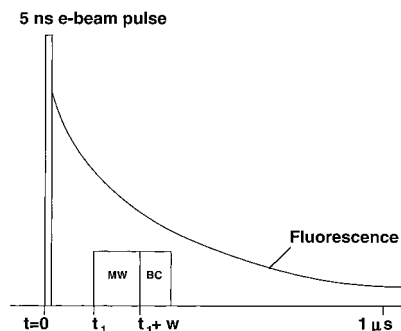


FIGURE 2. Timing diagram for the pulsed FDMR experiment. MW = microwave pulse. BC = boxcar gate.

by spin dephasing via differences in the electron–nuclear hyperfine coupling (hfc) and  $g$  factors (spin–lattice relaxation is considerably slower than charge recombination). When the electronic Zeeman splittings are larger than the hfc, only  $|S\rangle \rightleftharpoons |T_0\rangle$  mixing occurs (Figure 1).

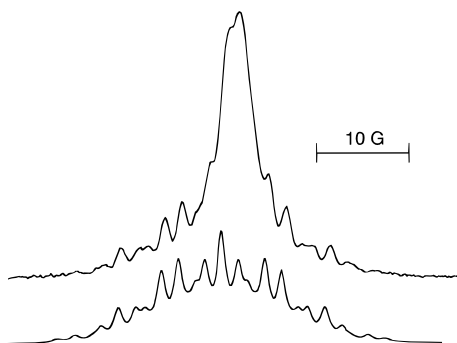
The observation of magnetic resonance is achieved by mixing the states of  $|S\rangle$   $|T_0\rangle$  character with the  $|T_{-1}\rangle$  and  $|T_{+1}\rangle$  states via an alternating magnetic field,  $\mathbf{H}_1$ , applied perpendicular to the static field. This is a resonant process and corresponds to EPR transitions of the constituent ions of the pair. Application of the  $\mathbf{H}_1$  field depletes the singlet population and causes a resonant decrease in the fluorescence yield resulting from geminate recombination.

The FDMR experiment is carried out at X-band (9.5 GHz) with pulsed microwave excitation. The timing diagram is shown in Figure 2. The FDMR spectrum (fluorescence intensity vs magnetic field) is the superposition of EPR spectra of radical cations and radical anions that recombined geminately to give fluorescence and which were present during the microwave pulse. The radical cation may be the solvent radical cation or a secondary radical cation,  $\text{S}^{\bullet+}$ , formed by charge transfer or by chemical transformation, processes that preserve the spin coherence of the ion pairs.

In summary, FDMR observes geminate radical ions; it does not detect randomly paired radical ions, neutral radicals, or diamagnetic ions. The time evolution of processes involving radical ions can be observed only if it occurs on a time scale comparable to the geminate ion recombination time which is the internal clock in the FDMR experiment. The pulsed FDMR experiment described here is practiced nowhere except at Argonne. The group in Novosibirsk has pioneered the successful application of nonpulsed methods based on the same principles.<sup>12,13</sup>

## Speed Is Essential

Speed is not always better, but sometimes it is essential. Unimolecular reactions can preclude matrix stabilization of even well-isolated radical cations. The reaction barrier may be too small to prevent rapid transformation to a lower energy radical cation under equilibrium conditions even at low temperature. Generally speaking, however, radical cations formed by electron transfer to matrix holes



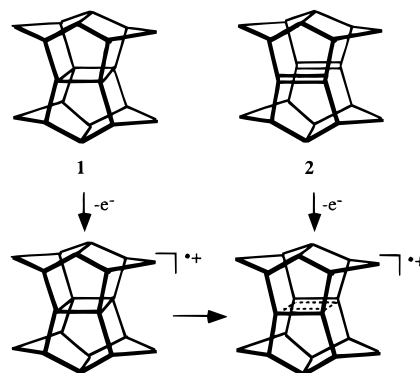
**FIGURE 3.** Upper trace: FDMR spectrum of the quadricyclane radical cation observed in *n*-hexane at 190 K. Lower trace: calculated spectrum,  $a(4H) = 4.8$  G,  $a(2H) = 6.6$  G,  $a(2H) = 1.9$  G. The underlying intense line near the center of the experimental spectrum is due to the anthracene radical anion.

are not initially at equilibrium with their surroundings, but possess excess energy due to the exothermicity of the electron transfer. This energy (2 eV or more) may be channeled into chemical reactions before it can be transferred as heat to the matrix. The competition between chemical reaction and energy transfer is matrix dependent, and the zeolite matrix is a relatively less efficient heat sink compared to halocarbon matrixes. This quality can promote excited-state-like reactivity, as we have shown in a few cases involving double-bond isomerization and fragmentation.<sup>14–17</sup>

A class of saturated hydrocarbon radical cations that have frustrated all attempts at matrix isolation are the cage molecules with strained four-membered rings. The prototype of this class is the cubane radical cation,  $(CH)_8^{+\bullet}$ , which isomerizes under matrix conditions<sup>18</sup> but was observed by FDMR in cyclopentane at 190–240 K.<sup>19</sup> Similarly, the quadricyclane radical cation undergoes valence isomerization, eq 5 (and other reactions), under matrix conditions, and observation of its EPR spectrum was only recently accomplished by time-resolved methods, both by direct microwave detection<sup>20</sup> and by FDMR (Figure 3).



The success of fast detection to observe the thermodynamically less stable partner of a pair of valence isomers was of interest to other experimentalists and theorists alike. Horst Prinzbach engaged our attention on the valence isomer pairs in the novel family of cage molecules called pagodanes that he and co-workers developed in order to synthesize dodecahedranes. The parent molecule of this family, [1.1.1.1]pagodane, upon one-electron oxidation gives rise to the “tight” cyclobutanoid, four-center three-electron radical cation,  $1^{+\bullet}$ , which is predicted by ab initio theory to be higher in energy than the “extended”  $\pi$ -complex-like radical cation,  $2^{+\bullet}$ .<sup>21</sup> Accordingly, ionization of **1** under matrix-isolation conditions had not resulted in the trapping of  $1^{+\bullet}$ , giving rise instead to the EPR spectrum of  $2^{+\bullet}$ .<sup>22</sup>



The FDMR study of **1** in liquid *n*-hexane not only led to the first observation of  $1^{+\bullet}$ , but also allowed the first direct measurement of the interconversion rate of two valence isomeric radical cations.<sup>21</sup> Figure 4a shows the FDMR spectrum of  $1^{+\bullet}$  observed at early time and low temperature ( $a(8H_\beta) = 10.2$  G). At later delay times the FDMR spectrum was a composite of  $1^{+\bullet}$  and  $2^{+\bullet}$ . Figure 4b shows the spectrum obtained near room temperature after a time delay of 300 ns, where the dominant species was  $2^{+\bullet}$  ( $a(8H_\beta) = 15.5$  G). The half-life for the conversion  $1^{+\bullet} \rightarrow 2^{+\bullet}$  varied from approximately 1.1  $\mu$ s at 193 K to approximately 0.15  $\mu$ s at room temperature. From the Arrhenius plot, an activation energy of  $2.3 \pm 0.3$  kcal mol<sup>-1</sup> was determined.

## Solvent Stabilization of Radical Cations

While fast detection can be indispensable for observation of unstable radical cations, it also affords the only means of observing transient radical cations in the liquid phase where radical cation reactivity and dynamical processes involving radical cations are strongly solvent dependent. The example presented here, involving thioether radical cations, is used to illustrate a case with a profound solvent effect, the nature of which was solved via spin resonance information from the FDMR experiment together with EPR results in low-temperature matrixes.

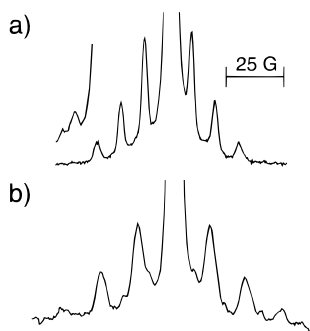
In studies of the oxidation of thioethers, it is common to observe complex radical cations in which a monomer thioether radical cation is stabilized by coordination of the unpaired p-electron of the oxidized sulfur atom with the free p-electron pair on another sulfur atom to form a three-electron  $\sigma$ -bond, eq 6.<sup>23</sup> The dimer radical cations are quite stable compared to the monomer radical cations which in aqueous solutions undergo fast deprotonation reactions.<sup>24</sup>



Similarly, in alkane solvents dimerization and deprotonation reactions make thioether radical cations very short-lived. On the FDMR time scale (the minimum radical cation lifetime for detection is tens of nanoseconds) only the dimer radical cations were detected at temperatures between 190 and 295 K.<sup>25</sup>

When toluene or *m*-xylene was used in place of the alkane solvent, the monomer thioether radical cation





**FIGURE 4.** FDMR spectra observed in *n*-hexane containing 5 mM [1.1.1.1]pagodane and 0.3 mM anthracene- $d_{10}$ : (a)  $T = 190$  K, microwave pulse applied from  $t = 0$  to  $t = 150$  ns; (b)  $T = 290$  K, microwave pulse applied from  $t = 300$  ns to  $t = 450$  ns. The intense central line (off scale) in each spectrum is due to the anthracene radical anion.

lifetimes were significantly increased (at least an order of magnitude).<sup>25</sup> This is a dramatic solvent stabilization of the thioether radical cations, but what is the cause? The answer is very apparent from examination of the spin resonance parameters for the monomer radical cations.

Comparison of the isotropic  $g$  factors and proton hfc constants of monomer thioether radical cations in arene solvents (FDMR) to those values obtained in halocarbon matrixes (EPR) shows that these parameters are systematically lower in the arene case. Reduction of the hfc constants by 30% or more indicates considerable spin transfer from the radical cation to the arene solvent (the only available donor). What were actually observed in the FDMR experiments were not free thioether radical cations, but solvent-complexed radical cations.

If the thioether radical cations are stabilized by complexation with solvent molecules, then the extent of charge transfer, as reflected in the spin resonance parameters, should depend on the donor/acceptor ability of the partners. This expectation is borne out.<sup>25</sup> The ratio of the hfc constant in toluene to that in the halocarbon matrix (that is, for the uncomplexed radical cation) is seen to decrease (less charge transfer) with increasing thioether ionization potential (IP). Likewise, the hfc constants and  $g$  factors of thioether radical cations are smaller in *m*-xylene than in toluene, which is consistent with the relative ionization potentials of toluene (8.8 eV) and *m*-xylene (8.4 eV).

The solvent-stabilized thioether radical cations in arene solvents are examples of heterocomplex radical cations involving, something rarer still, donor/acceptor interactions between lone pair and  $\pi$ -orbitals. A key to proving the nature of the solvent stabilization of thioether radical cations in arene solvents was reference to the halocarbon matrix EPR data, since matrix isolation was the only way to obtain the spin resonance parameters for the noninteracting monomer radical cations.

## Matrix Isolation and Zeolite Microreactors

The counterpart to speed is stealth, and in the study of reactive intermediates, stealth means stabilization. Stealth

can be combined with fast detection methods; a trivial example is to lower the temperature to decrease reaction rates. As in the example above, solvation effects can decrease the reactivity of radical cations and extend their lifetimes by orders of magnitude. The ultimate stabilization is achieved by trapping reactive intermediates in an inert rigid matrix. Chemical inertness is one desirable attribute of an isolation matrix; for the stabilization of metastable species, the ability of the matrix to remove excess energy from the guest and convert it to heat is another important matrix attribute.

Key to matrix stabilization of radical cations is isolation of the radical cations from neutral molecules, and naturally the matrix molecules must be more difficult to oxidize than the guest. Successful matrixes for stabilization of radical cations have included rare gas matrixes and halocarbon matrixes (including Freons). The rare gas method involves matrix deposition on a cold surface with a very high matrix-to-guest molecule ratio.<sup>2</sup> Most commonly used halocarbon matrixes are liquids at room temperature, and solutions can be prepared in the usual way. This convenience and their higher melting points compared to rare gas matrixes have made halocarbons the matrix of choice of many experimenters.<sup>3–6</sup>

EPR detection of radical cations adsorbed on silica gel, silica–alumina, and Vycor glass and in zeolites has demonstrated the possibility of studying radical cations adsorbed on surfaces as an alternative to frozen solutions.<sup>26–31</sup> The use of solid adsorbents offers a much wider temperature range for spectroscopic studies. The most promising adsorbents for stabilizing radical cations are zeolites. Zeolites are more than adsorbents; they are microreactors with tunable porosity, polarity, and acidity. Zeolites are crystalline materials made up of  $(\text{SiO}_4)^{4-}$  and  $(\text{AlO}_4)^{5-}$  tetrahedra connected in different ring structures to form varied channel-type and cage-type lattice architectures with pore sizes of molecular dimensions. Several important zeolite types are listed in Table 1. Exchangeable cations are present in stoichiometric amounts to balance the negatively charged lattice. Although zeolites are known, because of their important industrial applications, as strong solid acids, the  $\text{Na}^+$  forms are quite inert.

Radiolytic generation ( $\gamma$ -rays, X-rays, fast electrons) of radical cations in a dilute matrix is a two-step process. Energy is absorbed by the matrix, which is ionized, and then matrix holes are transferred to electron donors, D, eqs 7 and 8. Electrons are trapped by the matrix itself (halocarbons, zeolites) or by extrinsic acceptors (rare gas matrix) to preserve the charge separation.



At sufficiently low temperatures, depending on the matrix, this technique produces isolated radical cations for spectroscopic characterization. Of equal interest is the study of radical cation reactions, including bimolecular reactions requiring diffusive motion. The impossibility of

**Table 1. Zeolite Structure Types<sup>a</sup>**

zeolite type	channel/cage system
MFI (ZSM5)	3-D, straight 10-ring $5.3 \times 5.6$ Å channels connected by sinusoidal $5.1 \times 5.5$ Å channels
MOR (Mordenite)	2-D, straight 12-ring $7.0 \times 6.5$ Å channels connected by short alternating 8-ring $2.6 \times 5.7$ Å channels
BEA (Beta)	3-D, 12-ring $7.6 \times 6.4$ Å channels connected by 12-ring $5.5 \times 5.5$ Å channels
FAU (X, Y)	3-D, circular 12-ring $7.4$ Å windows connecting spherical $11.8$ Å cavities
LTL (Linde type L)	1-D, circular 12-ring $7.1$ Å channels

<sup>a</sup> Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Zeolites* **1996**, *17*, 1.

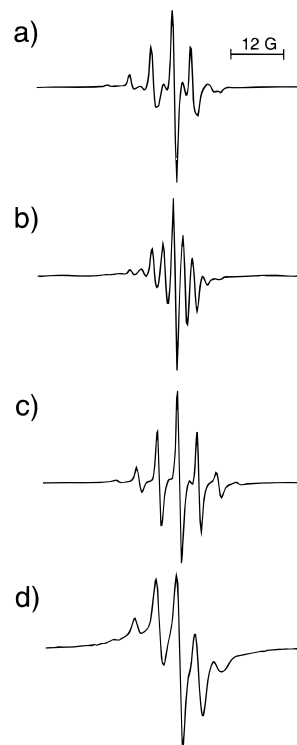
diffusion is a drawback of rare gas matrixes. Several of the haloethane matrixes undergo a phase transition slightly above 100 K to a relatively mobile phase in which limited molecular diffusion can take place. This useful property has been exploited to carry out carefully controlled annealing experiments in which cation–molecule reactions can be studied.<sup>4–6</sup> Thus, the counterpart to time resolution in the matrix-isolation arena is temperature control of diffusion.

The ability to study ion–molecule chemistry in zeolites greatly surpasses that in frozen matrixes. The zeolite allows greater temperature variation. Adsorbate mobility and distribution depend on size and the specific details of the zeolite–adsorbate interactions. The geometry constraints in zeolites also give rise to steric effects on ion–molecule encounter complexes and product formation.

Some of the basic effects of size constraints can be illustrated by our early studies of hydrocarbon radical cations in zeolites with ZSM5 as our principal example.<sup>21–17,32–35</sup> The first, most obvious constraint is on the maximum size of the adsorbate. For ZSM5 there is a more-or-less sharp cutoff for adsorption (from the gas phase) of cyclic or branched hydrocarbons at roughly eight carbons. The correlation between adsorbate size and our ability to generate the radical cation demonstrates that we do not stabilize radical cations on the external surfaces of the zeolite crystals.

Another proof that the radical cations are inside the zeolite pores and not outside are the geometry constraints on reactions.<sup>34,35</sup> A good example is the benzene radical cation. The benzene radical cation can be stabilized on amorphous silica gel<sup>31</sup> and on the surface of a mesoporous MCM-41 molecular sieve (silica form, pore diameter 33 Å), where in the absence of significant geometry constraints, it readily reacts (upon annealing) with a neutral benzene molecule to form a dimer radical cation (Figure 5). In contrast, dimer formation is not observed in ZSM5, the pore volume apparently being too small.<sup>34</sup> If benzene radical cations were formed on the external surface of ZSM5, then dimer formation should also occur there. This is not observed. The benzene dimer radical cation can be formed inside a zeolite by relaxing the geometry constraints, for example, by using Beta<sup>34</sup> or Y zeolite.<sup>31</sup>

Isolation of radical cations from neutral molecules inside the zeolite is not always achieved, as evidenced by the occurrence of ion–molecule reactions, such as dimerization and proton transfer, despite very dilute loading (30–120  $\mu\text{mol/g}$  of adsorbate—approximately 0.2–0.7 molecule per ZSM5 unit cell) and very low temperatures.<sup>32,34,35</sup> This is generally the case for hydrocarbons

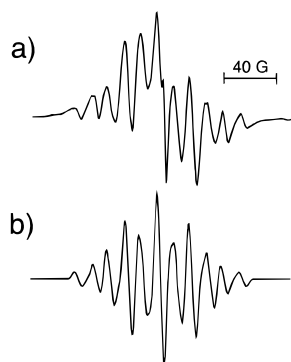


**FIGURE 5.** (a) Ionization of benzene (60  $\mu\text{mol/g}$ ) on the surface of MCM-41 at 77 K gave almost exclusively the monomer radical cation ( $a = 4.5$  G). EPR spectrum recorded at 100 K. (b) Annealing of the same sample to 120 K converted most of the monomer radical cations to dimer radical cations ( $a = 2.2$  G). (c) Because of volume constraints, only monomer benzene radical cations were observed in ZSM5 over the temperature range studied (<200 K). Shown:  $T = 170$  K; benzene loading 120  $\mu\text{mol/g}$ . (d) EPR spectrum obtained at 140 K for 60  $\mu\text{mol/g}$  of benzene on MCM-41. Following adsorption of benzene, the sample was saturated with perfluoromethylcyclohexane.

smaller than  $\text{C}_6$  in ZSM5. Although diffusion at 77 K cannot be ruled out for very small molecules, diffusion probably cannot account for the failure to stabilize the radical cation of a molecule as large as cyclopentene. As a further test, we have irradiated cyclopentene in ZSM5 at 4 K and obtained the same result: the cyclopentenyl radical (formed by proton transfer from the radical cation to cyclopentene<sup>36</sup>) was the only species observed (Figure 6). A probable explanation is that adsorption is heterogeneous and that molecules are not isolated to begin with. This is an open question that we are pursuing, but it suggests the importance of the adsorbate distribution.

## Control of Radical Cation Reactions in Solids

A future goal of our research is to reach a deeper understanding of environmental factors that control the



**FIGURE 6.** The cyclopentene radical cation was not trapped upon ionization of cyclopentene at 4 K in ZSM5. The only species observed was the cyclopentenyl radical: (a) experimental EPR spectrum, cyclopentene loading  $60 \mu\text{mol/g}$ ; (b) calculated EPR spectrum,  $a(4\text{H}) = 24.5 \text{ G}$ ,  $a(2\text{H}) = 14.3 \text{ G}$ ,  $a(\text{H}) = 3 \text{ G}$ .

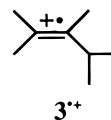
chemical reactions of reactive intermediates in complex, heterogeneous systems. Zeolites offer a versatile framework in which to systematically vary microenvironmental factors, such as geometric constraints, polarity, and acidity. The well-defined, ordered structures of zeolites and related mesoporous molecular sieves are useful for designing simulants of heterogeneous, multiphase systems which retain a desirable level of experimental simplicity and control. In addition to the variables intrinsic to zeolites (pore size, network connectivity, Si/Al ratio, extraframework cations), inert molecules can be added to the zeolite-plus-adsorbate as diluents, electron traps, energy acceptors, site blockers, etc.

Since rational control of radical cation reactivity is a goal and not a present capability, our initial approach is to develop rich chemical probes and determine their reactions under different environmental conditions. In this section, we present two brief examples in which some measure of control over radical cation reactions is gained by combining an extrinsic solvent/diluent with the silica adsorbent. The examples are taken from preliminary work, and thus they are presented for the purpose of illustration with a minimum of interpretation.

The first example simply shows the use of a diluent to hinder ion–molecule encounters on the surface of an adsorbent. It involves the dimerization of benzene radical cations in MCM-41, as mentioned above. At a loading of  $60 \mu\text{mol/g}$ , the benzene molecules are isolated from one another and the monomer radical cation is stable below approximately 100 K (Figure 5a). Upon annealing the sample to 120 K, monomer radical cation is irreversibly converted to benzene dimer radical cations, signaling the onset of molecular diffusion (Figure 5b). This ion–molecule reaction can be delayed or prevented altogether by depositing an overlayer of coadsorbed molecules. Figure 5d shows the result when adsorption of benzene was followed by adsorption of perfluoromethylcyclohexane (to saturation). The EPR line width of the benzene radical cation was affected by the coadsorbate, but the dimer radical cation was not observed when the sample was annealed as high as 150 K where the EPR signal decayed.

While trivial, this example illustrates the control of ion–molecule interactions by concentration, temperature and use of a diluent. The mobility of benzene on the MCM-41 surface is also controlled by the density of silanol groups.<sup>37</sup> These measures can be applied in other cases where the ion–molecule nature of the reaction mechanism is in question or exclusion of an ion–molecule reaction channel is desirable.

In NaZSM5, the isobutene ion–molecule chemistry can be completely switched from proton transfer (the only product is 2-methylallyl) to radical cation dimerization by coadsorption of carbon monoxide into the isobutene-loaded zeolite prior to radiolysis.<sup>33,35</sup> This remarkable result has a precedent in the study of isobutene radical cation reactions in Freons. It has been found that the ratio of proton transfer to dimerization can be controlled by subtle variation of the Freon matrix.<sup>38</sup> In NaZSM5, however, the stable dimer product is the radical cation  $3^{+\bullet}$ , whereas in Freon matrixes the product is an unspecified alkyl-type propagating radical.



Is the role of coadsorbed CO to stabilize the dimer radical cation or is it again acting merely as a diluent and blocking other interactions that lead to the 2-methylallyl product? The answer in this case is complex and will require further study. In general, the extrinsic molecules can perform a variety of roles, including deactivation of excited species, solvation, and dilution. The effects on chemistry can include control of reactant encounters, quenching of hot processes, and changing branching ratios between different reaction channels. The design and variation of zeolite-plus-additive systems can provide means of controlling reactions and elucidating reaction mechanisms as well as simulate realistic conditions (phase boundaries, volume constraints, etc.) in heterogeneous environments.

Radical cations are excellent probes of environmental effects on chemistry—first because they are highly reactive, and second because they are paramagnetic, which facilitates their detection. EPR, while providing excellent chemical identification, enjoys many advantages over other spectroscopic techniques in applications involving opaque and heterogeneous samples. Radiolytic generation of radical cations can be universally applied to produce homogeneous ionization, and the zeolite backbone provides the glue that holds it all together and also serves the crucial roles of energy absorber, electron trap, and hole-transfer agent.

## Summary

To meet the challenge of studying radical cation structure and reactivity in the condensed phase, both time-resolved methods and stabilization methods have an important role. In certain cases, fast detection is the only means of



observation, whereas matrix isolation at times is the only way to observe the radical cation under conditions where solvent interactions are minimized. The combination of FDMR and matrix-isolation/EPR provides a fuller understanding of the role of intermolecular interactions in the structure and dynamics of radical cations.

Radical cation chemistry is very sensitive to the environment, making radical cations versatile probes of the factors which control chemical reactivity. We have touched on some of the many factors (excess energy, energy transfer, distribution/orientation of reactants, steric effects/space constraints, solvation) whose combined effects we need to understand better to rationalize chemistry under complex heterogeneous conditions, such as solid-state catalysis and radiation effects in multiphase systems. A promising approach is the development of microreactors, such as zeolites, which allow more systematic variation of environmental factors in a controlled fashion. The dividends from such studies are expected to be rational models of reaction control in the condensed phase.

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