Time-Resolved ESR Study of the Quadricyclane Radical Cation

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The photochromic valence isomerization of the system nor-bornadiene (N)–quadricyclane (Q) has attracted much attention in the field of photochemical energy storage[1] and, more recently, has been considered as the basis for an optical memory system.[2] The energy-releasing conversion of Q to N can be achieved with high efficiency via a free-radical-cation chain reaction, initiated by chemical,[3] electrochemical,[4] or photosensitized one-electron oxidations (eq 1).[5] The existence of two distinct radical cations,
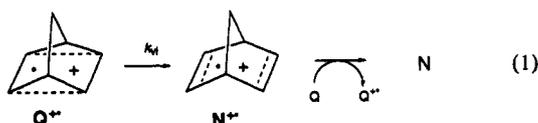
Q[•+] and N[•+], and the qualitative hyperfine coupling pattern for Q[•+] have been established by chemically induced dynamic nuclear polarization (CIDNP) results.[6] However, the direct spectroscopic observation of Q[•+] has not been achieved; hence, only indirect information is available about the reactivity of Q[•+].[7,8] We have applied time-resolved ESR (TR-ESR) to study Q[•+] and wish to report the first direct observation of this elusive species as well as supporting studies by kinetic laser flash photolysis (LFP) and TR-CIDNP. Our results suggest a symmetric electronic structure for this species; a detailed kinetic analysis indicates that its valence isomerization to N[•+] is relatively slow ($k_{vi} \sim 10^6$ s^{-1}).

We chose chloranil (CA) as the sensitizer for this study because it is known to be an effective sensitizer for the conversion of Q to N[5b] and has proved useful in CIDNP studies.[6] In addition, photoinduced electron-transfer reactions involving triplet quinones may be expected to generate spin-polarized radical ions.[9] The TR-ESR spectrum was obtained upon photolysis (Nd:YAG laser, 355 nm, 10 ns) of 20 mM chloranil and 0.1 M quadricyclane in

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Ar-purged acetonitrile at room temperature. The spectrum acquired 300–600 ns after the laser pulse (Figure 1a) is entirely emissive, indicating that the CIDEP signals originated mainly from spin-polarized ^{3}CA* via the triplet mechanism with only a minor contribution due to the radical pair mechanism.[10] The intense signal at 3483.6 G ($g = 2.0058$) was assigned to CA[•−],[11] whereas the emissive ESR spectrum with complex hyperfine structure centered at 3487.7 G ($g = 2.0035$) is assigned to Q[•+]. The signals of Q[•+] disappeared within ~1.5 μs after the laser pulse, whereas that of CA[•−] persisted considerably longer.

The ESR spectrum ascribed to Q[•+] is quite different from the spectra reported for N[•+] [12] or other C$_7$H$_8$[•+] isomers;[13] it can be satisfactorily simulated (Figure 1b) with hyperfine couplings (hfc) of 5.1 (4H; cyclobutane protons, H$_{cb}$), 6.6 (2H; bridgehead protons, H$_{bb}$), and 2.0 G (2H; bridge protons, H$_b$). The splittings of the cyclobutane hydrogens are quite similar to those observed for the homologous tetracyclooctane radical cation ($A_{cb} = 5.7$ G).[14] A comparison of the experimental hfcs of Q[•+] with those calculated by ab initio methods ($A_{cb} = -10.5$ G; $A_{bh} = 7.9$ G; and $A_b = -4.0$ G)[15] shows that the *positive* coupling (due to π,σ delocalization) is predicted adequately, whereas the *negative* hfcs (resulting from π,σ polarization) are overestimated by a factor of ~2. The disagreement between the experimental and calculated values of *negative* hfcs is not unexpected; the calculated Fermi contact terms significantly overestimate *negative* hfcs, often by factors greater than 2. On the other hand, ab initio calculations reproduce *positive* hfcs within ±15%.[16] In the light of these considerations, the hfc pattern observed for Q[•+] is consistent with the symmetric structure predicted by theoretical calculations.[5e,8,15] Also, a comparison of the calculated and experimental hfcs for N[•+] [14] show similar deviations.[12b,15]

The assignments of the hfcs are fully supported by a TR-ESR study of Q-7-d_1, prepared from 7-Cl-N[17] by reduction with Na/*tert*-butyl alcohol-OD in tetrahydrofuran[16] followed by acetophenone photosensitized cyclization.[18] The TR-ESR spectrum of Q-7-d_1[•+] (Figure 1c) showed characteristic changes relative to that of Q[•+], viz., hfcs of 4.86 (4H; cyclobutane protons, H$_{cb}$), 6.9 (2H; bridgehead protons, H$_{bb}$), and 1.59 G (1H; bridge protons, H$_b$). The splitting due to the 7-D nucleus is not resolved; however, the line width of the spectrum is increased to 0.61 from 0.33 G for Q[•+], an observation compatible with a D splitting of ~0.3 G (1.59:6.5 = 0.25; cf. Figure 1d). The variations in ^{1}H hfcs (A_{cb} −4%; A_{bh} +4%; and A_b −19%) as a result of D-substitution are not unexpected in the light of similar observations for small paramagnetic ions; for example, the ^{1}H hfcs of benzene-d_1 and the 1,3-d_2 radical anion are changed by as much as +17% and +23%, respectively, relative to C$_6$H$_6$[•−].[19]

The direct observation of Q[•+] makes it possible to probe its reactivity, for example, its nucleophilic capture by alcohols. The TR-ESR signal of Q[•+] was suppressed, when the experiment was carried out in varying concentrations of *t*-BuOH. The changes in the intensities of Q[•+] relative to CA[•−] as a function of [*t*-BuOH] clearly establish that Q[•+] is intercepted by *t*-BuOH; the rate constant for *t*-BuOH addition is $k_{nu} = 2.0 \times 10^6$ M^{-1} s^{-1}. This

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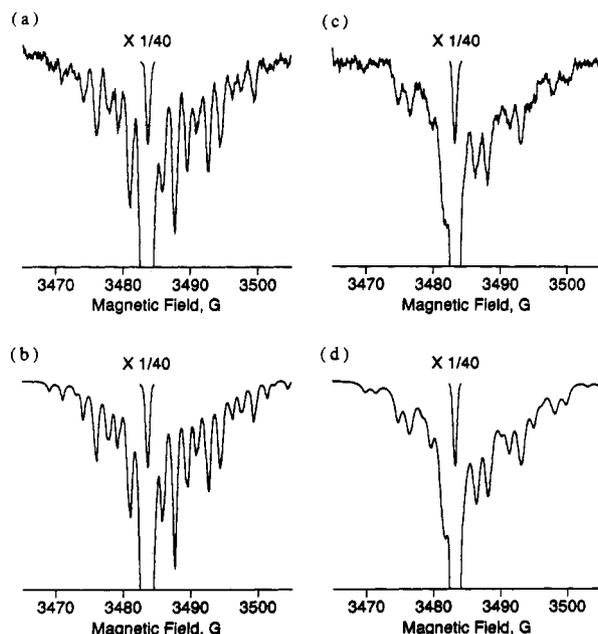(15) Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110.
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Figure 1. TR-ESR spectra collected 300–600 ns after excitation of an acetonitrile solution containing 20 mM chloranil and either 0.1 M quadricyclane (a) or 0.1 M quadricyclane-7-d_1 (c) with the frequency-tripled output of a Nd/YAG laser. The spectra can be simulated (b and d) with hyperfine coupling parameters and line widths as described in the text.

is in keeping with the reported reactivity of several phenylcyclopropane radical cations,[20] although in contrast to at least one report concerning the reactivity of $Q^{\bullet+}$.[21]

One of the key questions in the system Q–N concerns the rate of conversion of $Q^{\bullet+}$ to $N^{\bullet+}$. The TR-ESR signal of $Q^{\bullet+}$ decays within microseconds, but the process underlying the decay has not been identified; possible explanations include (a) electron spin relaxation (the T_1^e of $Q^{\bullet+}$ is not known, nor do we know any radical cation with a T_1^e of this magnitude); (b) valence isomerization to $N^{\bullet+}$; or (c) an (unspecified) reaction with the solvent. We have ruled out conversion to bicyclo[3.2.0]hepta-2,6-diene radical cation, $H^{\bullet+}$. Although the spectrum of $H^{\bullet+}$ has been observed upon radiolysis of Q at cryogenic temperatures,[13] we have been unable to find any evidence for the corresponding conversion in solution.

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To measure the rate of conversion of $Q^{\bullet+}$ to $N^{\bullet+}$ unambiguously, one would ideally follow the decay of $Q^{\bullet+}$ as well as the rise of $N^{\bullet+}$ and observe matching kinetics. However, under our reaction conditions, any $N^{\bullet+}$ generated from $Q^{\bullet+}$ is quickly depleted by exothermic electron-transfer from Q to $N^{\bullet+}$ which, at the same time, regenerates $Q^{\bullet+}$ rapidly.[22] For [N] = 0.02 M and k_{et} = 3 × 10⁹ M^{-1} s^{-1} (k_{et}[N] = 6 × 10⁷ s^{-1}), the lifetime of $N^{\bullet+}$ with respect to depletion by reaction with Q is τ_{et} = 2 × 10⁻⁸ s. Under these reaction conditions, the decay of $N^{\bullet+}$ is faster than its buildup; hence, the conversion of $Q^{\bullet+}$ to $N^{\bullet+}$ cannot be followed by TR-ESR or by conventional spectroscopic techniques.

Transient absorption spectroscopy following LFP failed to reveal evidence for either $Q^{\bullet+}$ or $N^{\bullet+}$. The pulsed laser excitation of acetonitrile solutions containing 2.0 mM CA with 0.4–4.0 mM of Q under Ar resulted in the rapid decay of triplet CA* (λ_{max} = 510 nm) and the buildup of $CA^{\bullet-}$ (λ_{max} = 450 nm) with a quenching rate constant, k_q^Q = 1.1 × 10¹⁰ M^{-1} s^{-1}. However, no absorption band was observed that could be assigned to either $Q^{\bullet+}$ or $N^{\bullet+}$.[5b] The absence of $N^{\bullet+}$ had to be expected, whereas the failure to detect $Q^{\bullet+}$ suggests that its spectrum lies outside the range covered in these experiments (380–700 nm).

On the other hand, the valence isomerization of $Q^{\bullet+}$ to $N^{\bullet+}$ can be confirmed indirectly by TR-CIDNP. Any N generated by electron-transfer from Q to $N^{\bullet+}$ is expected to show CIDNP effects if the lifetime of $N^{\bullet+}$ with respect to electron transfer is shorter than its nuclear spin lattice relaxation time, $\tau_{et} < T_1^n$. A TR-CIDNP experiment with CA and Q showed that spin-polarized N was generated within <10 μs of the laser pulse; its polarization pattern is characteristic for the intermediacy of $Q^{\bullet+}$ and is compatible with the generation of N after diffusive separation of the ion pair, $Q^{\bullet+}$-$CA^{\bullet-}$, as previously concluded from steady-state CIDNP studies.[6]

In conclusion, the TR-ESR technique has been applied for the observation of the elusive quadricyclane radical cation, elucidating its hyperfine structure and clarifying its reactivity toward nucleophiles. The conversion of $Q^{\bullet+}$ to $N^{\bullet+}$ has been confirmed by TR-CIDNP. In the light of these findings, the design of any photochromic system utilizing the radical cation isomerization requires careful exclusion of nucleophiles.

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