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Picosecond Optical Grating Calorimetry of Diradicals: Singlet-Triplet Separation in *m*-Naphthoquinomethane

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A current problem in diradical chemistry is the accurate determination of the energy separation between the lowest singlet and triplet states of a diradical, ΔE_{ST}.[1] Although both *ab initio* and semiempirical methods have been used to obtain molecular geometries and predict the spin state ordering and relative magnitude of ΔE_{ST} for diradicals and related species,[2] experimental confirmation has generally been absent. In fact, although several experimental techniques have been used to determine the ground state of diradicals and estimate the magnitude of ΔE_{ST},[3] no direct calorimetric determinations of ΔE_{ST} in diradicals have been made. The reactivities and short lifetimes of these states necessitate the use of a fast, time-resolved calorimetric technique to resolve their interconversion. In this regard, we wish to report the use of picosecond optical grating calorimetry[4] to measure the singlet-triplet separation in m-naphthoquinomethane (*m*-NQM), a diradical member of the *m*-quinoid series of non-Kekulé molecules. This technique measures the thermal expansion of a system by monitoring its refractive index fluctuations. Analysis of the temporal profile of the diffracted intensity of a nonresonant probe pulse yields kinetic and energetic information about chemical reactions involving transient species.

Picosecond excitation (355 nm, 25 ps) of **1** in either C_6H_6 or CH_3CN yields a transient, Figure 1, which has been previously assigned to singlet *m*-NQM (^{1}*m*-NQM).[5] ^{1}*m*-NQM decays to a second transient, Figure 1, assigned to triplet *m*-NQM (^{3}*m*-NQM).

Both calculations[2a,f] and ESR[3a] spectra indicate that ^{3}*m*-NQM is indeed the ground electronic state. Although the absorption spectrum of ^{3}*m*-NQM is independent of solvent, the absorption maximum of ^{1}*m*-NQM shifts to shorter wavelengths with increasing solvent polarity. This is consistent with the calculated dipolar character of ^{1}*m*-NQM.[2a] The rate constant for intersystem crossing, k_{isc}, decreases with increasing solvent polarity, 1×10^9 in C_6H_6 and $\leq 2.5 \times 10^8$ in CH_3CN. In the presence of CH_3OH, the decay of ^{1}*m*-NQM increases, presumably due to the formation of the phenolic ether **2**, which is formed in high chemical yield.[3a]

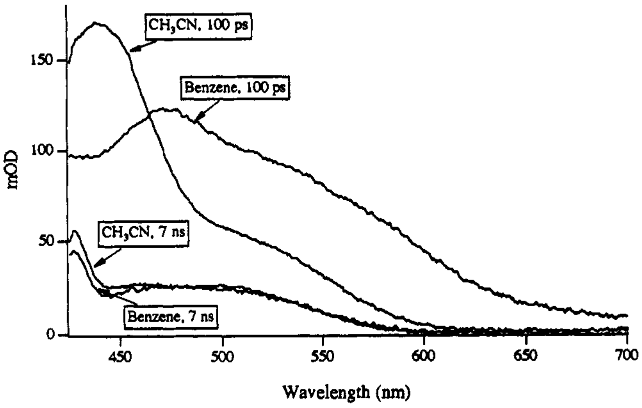
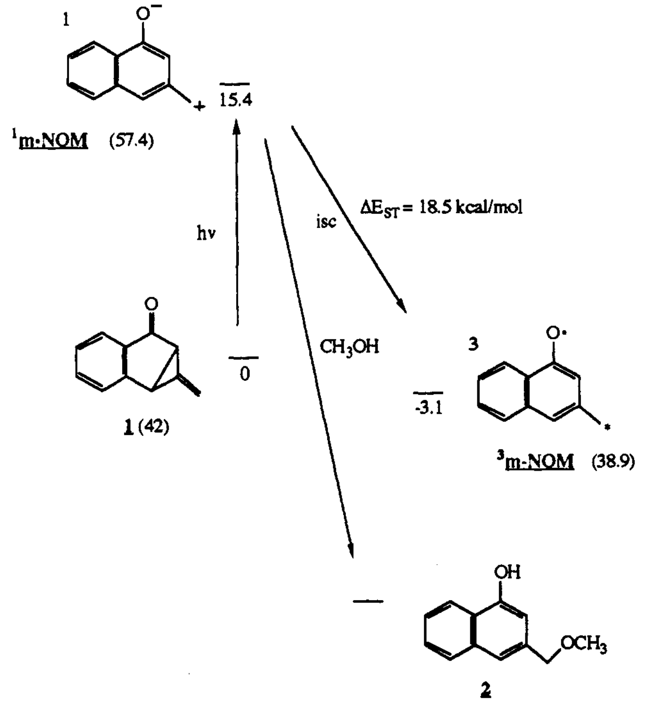


Figure 1. Absorption spectra 25 ps and 7 ns after excitation of **1** (355 nm, 25 ps, <1 mJ) in C_6H_6 and CH_3CN.

Scheme 1



The diffracted grating signals obtained following picosecond excitation (355 nm, 25 ps) of **1** in C_6H_6 and 12.5% CH_3OH/CH_3CN are shown in Figures 2 and 3. The waveforms from excitation of the calibration compound copper(II) tetramethylheptanedionate are also shown. Fast radiationless decay of the calibration compound yields a single heat deposition. In contrast, excitation of **1** results in two heat depositions, corresponding to a fast, α_1, and a slow chemical process, α_2. Analysis of the experimental waveforms yields the ratio of the fast to slow heat depositions, $R = \alpha_1/\alpha_2$, and the rate constant for the slow process, k_2. The details of the analysis have been previously described.[4b,c] The R values are 3.5 and 1.4 in C_6H_6 and CH_3OH/CH_3CN, respectively. The rate constants k_2 in these solvents are $(1.0 \pm 0.2) \times 10^9$ and $(1.5 \pm 0.1) \times 10^9$ s^{-1}, which are equal to those obtained from absorption spectroscopy kinetic experiments. This correlation and previous chemical studies[3a] strongly suggest that the second heat deposition is due to intersystem crossing of ^{1}*m*-

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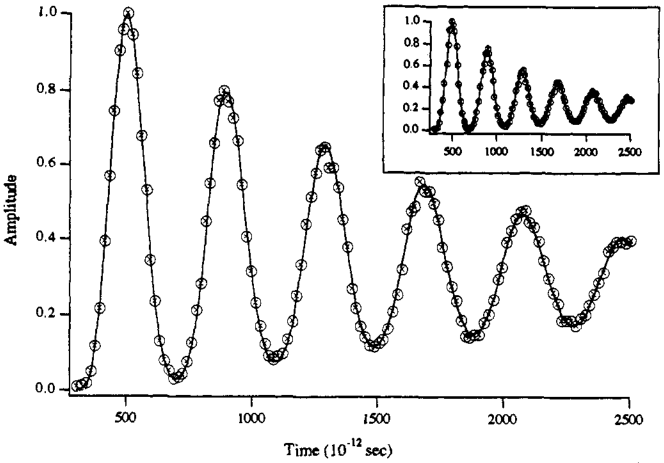

Figure 2. Transient grating signal amplitude vs time after excitation of **1** (355 nm, 25 ps, <1 mJ) in C_6H_6. The solid line is the best fit to the experimental data, ⊗. Inset: signal amplitude vs time after excitation of copper(II) tetramethylheptanedionate. The solid line is the best fit to the experimental data, ⊗.

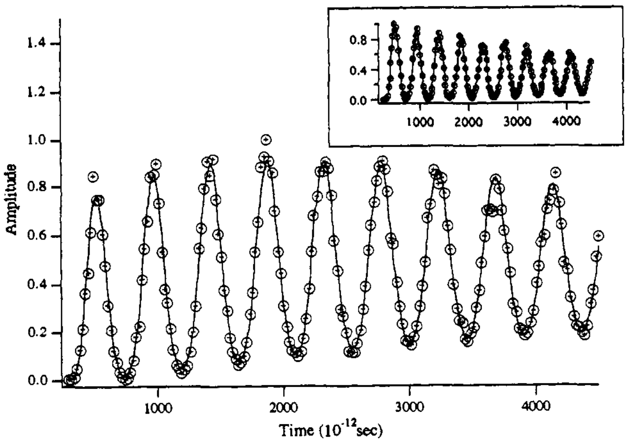

Figure 3. Transient grating signal amplitude vs time after excitation of **1** in 12.5% CH_3OH/CH_3CN. The solid line is the best fit to the experimental data, ⊕. Inset: signal amplitude vs time after excitation of copper(II) tetramethylheptanedionate. The solid line is the best fit to the experimental data, ⊕.

NQM to ^3m-NQM in C_6H_6 and to the reaction of ^1m-NQM with CH_3OH in CH_3OH/CH_3CN.

The relative enthalpies determined by picosecond optical grating calorimetry experiments can be quantified if the total enthalpy changes for the overall reactions are known. These values can be obtained by photoacoustic calorimetry.[6] Excitation of **1** in C_6H_6, $C_2H_4Cl_2$, or CH_3CN results in only a single heat deposition, <10 ns, reflecting the formation of ^3m-NQM. The enthalpy of this reaction, ΔH_r, is -3.1 ± 1.0 kcal/mol. Excitation of **1** in 12.5% CH_3OH/CH_3CN also results in a single heat deposition, reflecting the formation of the phenolic ether **2**. The enthalpy of this reaction, ΔH_r, is -35.0 ± 1.5 kcal/mol and is constant when CH_3OH is varied from 10% to 100%. The reaction enthalpy of −35 kcal/mol in CH_3OH/CH_3CN is in reasonable agreement with the MMX calculated heat of reaction of −40 kcal/mol for $\mathbf{1} \Rightarrow \mathbf{2}$.[8]

The fast and the slow heat depositions can be calculated using the equations $\alpha_1 = R(E_{h\nu} - \Delta H_r)/(1 + R)$ and $\alpha_2 = (E_{h\nu} - \Delta H_r)/(1 + R)$, where $E_{h\nu}$ is the photon energy, 80.2 kcal/mol. In C_6H_6, α_1 and α_2 are 64.8 and 18.5 kcal/mol, respectively. The α_2 reflects intersystem crossing from ^1m-NQM $\Rightarrow$ ^3m-NQM, and $(E_{h\nu} - \alpha_1)$, 15.4 kcal/mol, corresponds to $1 \Rightarrow {}^1m$-NQM (Scheme 1).[8] This experimental value of 18.5 kcal/mol for ΔE_{ST} is in excellent agreement with a recent semiempirical molecular orbital calculation, which found $\Delta E_{ST} = 18.6$ kcal/mol.[2a] The calculated ΔH_f values of ^1m-NQM and ^3m-NQM in benzene are 57.4 and 38.9 kcal/mol, respectively, using the MMX value of 42 kcal/mol for $\Delta H_f(\mathbf{1})$, Scheme 1, in parentheses. The $\Delta H_f(\mathbf{1})$ is greater than that of the isomeric ^3m-NQM species, which implies that **1** has a "negative" bond dissociation energy.

In CH_3OH/CH_3CN, α_1 and α_2 are 67.2 and 48.0 kcal/mol. The $(E_{h\nu} - \alpha_1)$ value, 13.0 kcal/mol, again corresponds to $1 \Rightarrow {}^1m$-NQM, but the α_2 now reflects ^1m-NQM $\Rightarrow$ **2**. Although the difference in $(E_{h\nu} - \alpha_1)$ values between the two solvents is small, it may be due to the stabilization of the ^1m-NQM state relative to ^3m-NQM in the more polar CH_3OH/CH_3CN solvent.

In conclusion, picosecond optical grating calorimetry has been used to determine ΔE_{ST} for m-NQM in benzene. We believe this to be the first calorimetric measurement of a singlet–triplet splitting in a diradical. In addition, the heats of formation of the singlet and triplet states of m-NQM are obtained. We hope to apply this general picosecond calorimetric technique to other diradicals and transient species to measure both their energetics and kinetics in solution.

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(7) These calculated values neglect any contribution to the photoacoustic signal or diffracted signal due to reaction volume changes. This contribution is considered to be negligible in these studies.

(8) The obtained heats of reaction and formation assume unit quantum efficiency for the formation of ^1m-NQM and hence ^3m-NQM and **2**. Although the chemical yield of **2** in CH_3OH is quantitative,[3a] the quantum yield has not been determined. However, the agreement between the calculated heat of reaction of **1** to **2** with the photoacoustic value suggests that the quantum yield is close to unity. Picosecond absorption data indicate that some ^3m-NQM may be formed in benzene within 25 ps, presumably from intersystem crossing of excited **1**, but spectral analysis indicates that it is <10%.