

Time-resolved infrared studies of triplet 1,3-cyclopentenediyl

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Received 29 October 1999; revised 7 January 2000; accepted 10 January 2000

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ABSTRACT: Triplet-sensitized photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) in argon- or oxygen- saturated acetonitrile-*d*₃ solutions results in the formation of bicyclo[2.1.0]pentane (**3**), a ring closure product arising from an intermediate 1,3-cyclopentenediyl triplet biradical (**2**). Time-resolved infrared (TRIR) spectroscopy was used to monitor the kinetics of bicyclopentane **3** production. This analysis provides a measurement of the triplet biradical lifetime and an estimate of the bimolecular reaction rate between biradical **2** and oxygen, both in good agreement with previous investigations. Our studies also indicate that certain IR bands due to **3** in the C–H stretching region overlap with corresponding bands in biradical **2**. This interpretation is supported by computational investigations. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: Time-resolved infrared spectroscopy; 1,3-cyclopentenediyl; triplet biradical

INTRODUCTION

Triplet¹ and singlet² hydrocarbon biradicals, molecules possessing two weakly interacting unpaired electrons, are an important class of organic free radicals. Their chemistry has received increasing attention owing to their potential use as building blocks of high-spin organic molecules with unique magnetic properties.³ Recently, they have also been used to analyze substituent effects on zero-field splitting parameters⁴ and on intersystem crossing rate constants.⁵

While direct detection of biradicals in solution is possible for derivatives possessing chromophoric groups,^{2a,5} characterization of prototypical hydrocarbon triplet biradicals such as 1,3-cyclopentenediyl (**2**) and its alkyl-substituted derivatives has been accomplished largely through indirect means. Since the pioneering experiments of Buchwalter and Closs⁶ on direct detection

of **2** by low-temperature matrix EPR and the first report of oxygen trapping of **2**,⁷ the lifetime of this fundamental triplet biradical has been measured by various experimental methods. In solution, these include quantitative oxygen trapping experiments (351 ± 57 ns)^{8,9} and photoacoustic calorimetry (258 ± 14 ns⁹ and 316 ± 80 ns¹⁰), while in the gas phase time-resolved coherent anti-Stokes Raman spectroscopy has been used (195 ns).¹¹ In addition, photoacoustic calorimetry experiments have provided a measurement of the bimolecular rate constant for the reaction of **2** with oxygen ($k_{\text{O}_2} = 5.3 \times 10^9$ l mol⁻¹ s⁻¹).¹⁰ Oxygen also catalyzes intersystem crossing of **2** to the singlet state; however, experiments suggest that this process is negligible relative to chemical trapping.⁹

The lifetimes of triplet biradicals are usually governed by intersystem crossing rates, which depend on numerous factors including the effects of orbital geometry and singlet–triplet energy gaps on spin–orbit coupling.^{12,13} Thus, the relatively long lifetime of **2** is the result of slow intersystem crossing, a direct consequence of limited spin–orbit coupling. The latter is mainly due to the time-averaged planarity of the biradical and the resulting near-parallel orientation of the orbitals bearing the unpaired electrons. Confirmation of this structural characteristic is available from low-temperature matrix EPR experiments⁶ and quantum chemical calculations.¹⁴

In an attempt to provide the first experimental insight into the solution-phase structure of **2**, we undertook a time-resolved infrared (TRIR) spectroscopic study. As described here, we were unable to detect IR bands due to

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Contract/grant sponsor: Camille and Henry Dreyfus New Faculty Awards Program.

Contract/grant sponsor: Petroleum Research Fund.

Contract/grant sponsor: NSF.

Contract/grant sponsor: Research Corporation.

Contract/grant sponsor: Office of Research Services of Towson University.

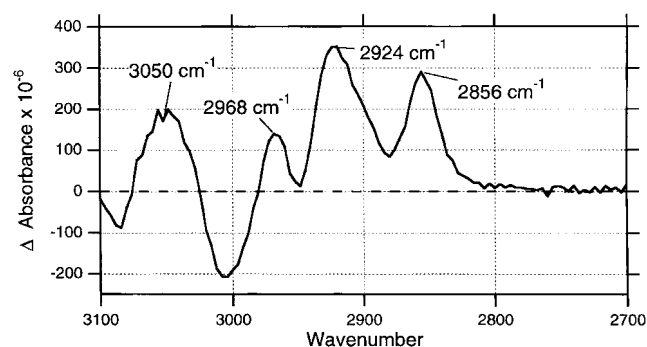


Figure 1. TRIR difference spectrum averaged over 7–9 μs following triplet-sensitized (45 mM anisole) photolysis (266 nm, 10 ns, 0.4 mJ) of diazene **1** (87 mM) in argon-saturated acetonitrile- d_3

2 cleanly. We have, however, analyzed the kinetics of bicyclo[2.1.0]pentane (**3**) formation despite the fact that certain IR bands for **3** in the C–H stretching region overlap with corresponding bands in biradical **2**. This analysis is supported by computational investigations.

RESULTS AND DISCUSSION

Typical TRIR data observed from 3100 to 2700 cm^{-1} following triplet-sensitized photolysis of diazene **1** in argon-saturated acetonitrile- d_3 are shown in Fig. 1. Data are obtained in the form of difference spectra. We observe depletion of the 3004 cm^{-1} band due to diazene **1**

Table 1. Comparison of experimental and calculated IR frequencies in the C–H stretching region for bicyclo[2.1.0]pentane (**3**) and triplet 1,3-cyclopentenediyl (**2**)

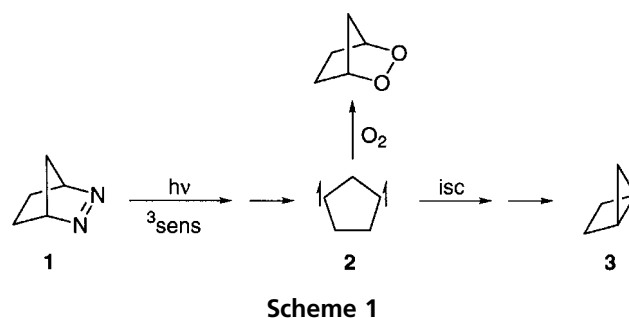
3 TRIR observed (cm^{-1}) ^a	3 Thin film observed (cm^{-1}) ^b	3 Calculated (cm^{-1}) ^c	2 Calculated (cm^{-1}) ^d
3050	3056 [cp CH ₂ (–)] 3045 (bh CH)	3058 (29) 3042 (4)	3064 (3) 3061 (36)
2968	2974 [cp CH ₂ (+)] 2961 [cb CH ₂ (–)]	3036 (25) 2976 (50)	
2924	2939 (bh CH) 2929 [cb CH ₂ (+)]	2964 (25) 2958 (2)	
2900 (sh)	2910 [cb CH ₂ (–)]	2916 (70)	
2856	2861 [cb CH ₂ (+)]	2908 (53)	2898 (32) 2895 (39) 2824 (50) 2816 (20) 2772 (56) 2748 (27)

^aThis work. sh = shoulder.

^bRef. 15. Assignments: bh = bridgehead; cp = cyclopropyl; cb = cyclobutyl; (+) = in-phase; (–) = out-of-phase.

^cB3LYP/6–311 + G(2d,p) scaled by 0.96. Calculated intensities are given in parentheses.

^dUB3LYP/6–311 + G(2d,p) scaled by 0.96 ($s^2 = 2.01$). Calculated intensities are given in parentheses.



and the production of a series of signals that agree very well with the known IR spectrum¹⁵ of bicyclo[2.1.0]pentane **3** (Table 1). We also examined the spectral region 1550–1150 cm^{-1} , but only depletion bands due to **1** are observed at 1494, 1446, 1282, 1254, and 1194 cm^{-1} . Comparable results were obtained with 4,4'-dimethoxybenzophenone ($E_T = 70 \text{ kcal mol}^{-1}$),¹⁶ 4-methoxyacetophenone ($E_T = 72 \text{ kcal mol}^{-1}$)¹⁶ and anisole ($E_T = 81 \text{ kcal mol}^{-1}$)¹⁶ as the triplet sensitizer consistent with efficient quenching by **1** ($E_T = 62 \text{ kcal mol}^{-1}$)¹⁷. The rate constant for diazene **1** quenching of a 4-methoxyacetophenone triplet excited-state IR band¹⁸ was determined to be approximately $1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

Given the known photochemistry of **1** (Scheme 1), we initially expected that each positive IR band due to **3** in Fig. 1 would display the same, single-exponential kinetics defined by the lifetime of biradical **2** under the conditions of our TRIR experiments. As shown in Fig. 2, this initial expectation was not realized. The growth kinetics for peaks at 3050, 2924, and 2856 cm^{-1} are not identical. We have analyzed the kinetic data in Fig. 2 by considering the possibility that the observed kinetics may be complicated by overlapping bands due to biradical **2** and product **3**.

Idealized kinetic traces for the growth and decay of biradical **2** and for the growth of bicyclo[2.1.0]pentane **3** are shown in Fig. 3. Here, the rate of production of biradical **2** is given as $2 \times 10^7 \text{ s}^{-1}$, the present time response of our spectrometer, since previous studies^{9–11} have indicated that **2** is formed within 25 ns of the laser pulse. Its rate of decay is, of course, required to equal the rate of growth of **3**. For an overlapping band, different relative contributions of the two kinetic traces in Fig. 3 will result in different observed kinetics. A greater intensity contribution from biradical **2** will result in what appears (given the limited signal-to-noise ratio of our data) to be a faster initial growth rate. Substantial signal averaging was required to obtain the kinetic traces in Fig. 2. Each trace is the result of averaging approximately 6500 laser shots.

Thus, we have assumed that the IR band observed at 2924 cm^{-1} is due exclusively to bicyclo[2.1.0]pentane **3**. Its rate of growth can be fit [Fig. 2(b)] to a single exponential function [$k_{\text{obsd}} = (3.6 \pm 0.4) \times 10^6 \text{ s}^{-1}$] that corresponds to a biradical lifetime of $278 \pm 30 \text{ ns}$, in very good agreement with previous work.^{9–11} Kinetics observed at

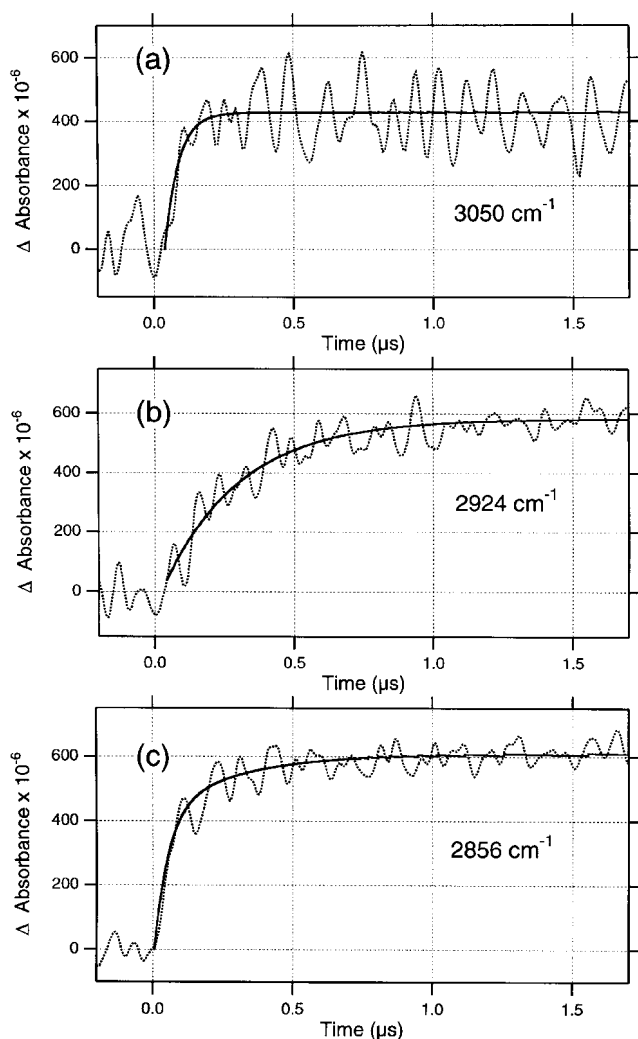


Figure 2. Kinetic traces observed at (a) 3050, (b) 2924 and (c) 2856 cm^{-1} following triplet-sensitized (50 mM 4,4'-dimethoxybenzophenone) photolysis (355 nm, 5 ns, 3 mJ) of diazene **1** (110 mM) in argon- or oxygen-saturated acetonitrile- d_3 . The dotted curves are experimental data; the solid curves are calculated best fits as described in the text

3050 and 2856 cm^{-1} were fitted manually [Fig. 2(a) and (c)] using the traces in Fig. 3 with the decay of **2** and production of **3** fixed at $3.6 \times 10^6 \text{ s}^{-1}$ (from the 2924 cm^{-1} band analysis). The 3050 cm^{-1} fit corresponds to a biradical:bicyclopentane intensity ratio of 1:1; the 2856 cm^{-1} fit corresponds to a ratio of 2:3.

Additional support for overlapping biradical **2** and bicyclopentane **3** IR bands comes from computational studies. As shown in Table 1, experimental IR frequencies of **3** in the C–H stretching region are reasonably reproduced by B3LYP/6–311 + G(2d,p) vibrational frequency calculations (scaled by 0.96).¹⁹ (A table of all calculated frequencies for both **2** and **3** at the HF, MP2, and B3LYP levels of theory is included as Supporting Information; calculated vibrational frequencies at each level are consistent with each other.) Analogous

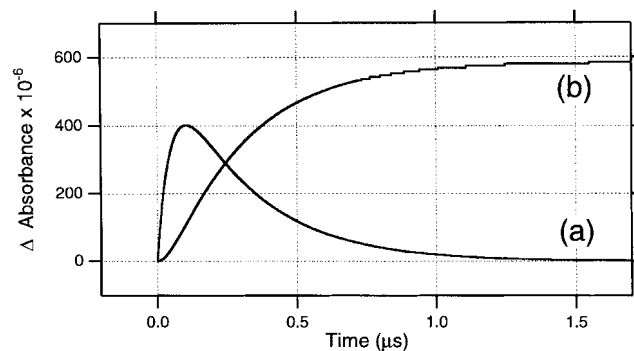


Figure 3. Idealized kinetic traces for (a) the growth and decay of biradical **2** and (b) the growth of bicyclopentane **3**

UB3LYP/6–311 + G(2d,p) calculations on triplet biradical **2** indicate that overlap with **3** is likely for our experimentally observed 3050 and 2856 cm^{-1} bands, but not for bands observed at 2968 and 2924 cm^{-1} . (We were not able to collect adequate kinetic data at 2968 cm^{-1} owing to the low signal intensity.) These calculations also suggest that an unperturbed biradical band should be detectable in the region 2850–2750 cm^{-1} . We did not, however, detect any IR bands in this region (Fig. 1).

As expected (Scheme 1), we find that the rate of growth of the 2924 cm^{-1} band is affected by oxygen with $k_{\text{obsd}} \geq 2 \times 10^7 \text{ s}^{-1}$ in oxygen-saturated acetonitrile- d_3 . This observed rate constant (which is now limited by the time response of our spectrometer) can be analyzed according to the pseudo-first-order equation $k_{\text{obsd}} = k_0 + k_{\text{O}_2}[\text{O}_2]$, where k_{O_2} is the second-order rate constant for the reaction of biradical **2** with oxygen and k_0 is the rate of biradical decay (and bicyclopentane **3** growth) in the absence of oxygen. (The concentration of oxygen in saturated acetonitrile solutions is 9.1 mM.²⁰) This analysis leads to a lower limit for the oxygen quenching rate constant $k_{\text{O}_2} \geq 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, again in good agreement with previous work.¹⁰

CONCLUSIONS

Kinetic analysis of the rate of growth of bicyclopentane **3** IR bands observed following triplet-sensitized photolysis of diazene **1** has provided a direct measurement of the lifetime of biradical **2**, $278 \pm 30 \text{ ns}$, in good agreement with previous studies. In addition, this analysis, with the support of computational investigations, has indicated that biradical **2** likely possesses observable IR bands near 3050 and 2856 cm^{-1} .

EXPERIMENTAL

Materials. Unless noted otherwise, materials were obtained from Aldrich Chemical and used without further

purification. Acetonitrile- d_3 was used as received from Cambridge Isotope Laboratories. 2,3-Diazabicyclo[2.2.1]hept-2-ene (**1**) was prepared according to the literature procedure.²¹

Time-resolved IR methods. We conducted TRIR experiments following the method of Hamaguchi and co-workers²² as described previously.²³ Briefly, the broadband output of an MoSi₂ IR source (JASCO) is crossed with excitation pulses from an Nd:YAG laser. Changes in IR intensity are monitored by an MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1), amplified, and digitized with a Tektronix TDS520A oscilloscope. The experiment is conducted in the dispersive mode with a JASCO TRIR-1000 spectrometer. TRIR difference spectra were collected at 16 cm⁻¹ resolution using either a Continuum HPO-300 diode-pumped Nd:YAG laser (266 nm, 10 ns, 0.4 mJ; 355 nm, 12 ns, 0.6 mJ) or a Quantronix Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ; 355 nm, 90 ns, 1.5 mJ) operating at 200 Hz. Kinetic traces were collected using a Continuum Minilite II Nd:YAG laser (266 nm, 5 ns, 1–4 mJ; 355 nm, 5 ns, 2–8 mJ) operating at 20 Hz.

Computational methods. All geometry optimizations and frequency calculations were performed with Gaussian 98.²⁴ HF, MP2 and B3LYP calculations²⁵ were performed with the restricted (for **3**) and unrestricted (for **2**) methods with a number of standard basis sets, as implemented in Gaussian 98. The calculated vibrational frequencies were scaled by 0.89 (HF),²⁶ 0.94 (MP2)²⁶ and 0.96 (B3LYP).¹⁹ Structure **3** was minimized in C_s symmetry and **2** was a minimum under C₂ symmetry as a ³B state. All basis sets were used with six cartesian *d* functions.

Supporting information available. Tables of all calculated frequencies for bicyclo[2.1.0]pentane (**3**) and triplet 1,3-cyclopentadienyl (**2**) at the HF, MP2 and B3LYP levels of theory (2 pages) are available from the epc website.

Acknowledgements

J.P.T. gratefully acknowledges the Camille and Henry Dreyfus New Faculty Awards Program, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and an NSF Faculty Early Career Development Award for generous support of this research. J.P.T. and L.R.R. thank the donors of the Petroleum Research Fund, administered by the American Chemical Society for an ACS-PRF Summer Faculty Research Fellowship and the NSF for a Research Opportunity Award. L.R.R. acknowledges the Research Corporation and the Office of Research Services of

Towson University for financial support of this research. C.M.H. thanks the NSF for financial support and the Ohio Supercomputer Center for the use of their computing facilities.

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