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Ultrafast UV−Visible and Infrared Spectroscopic Observation of a Singlet Vinylcarbene and the Intramolecular Cyclopropenation Reaction

Yunlong Zhang,[†] Jacek Kubicki,[‡] and Matthew S. Platz*,[†]

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210, and Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland

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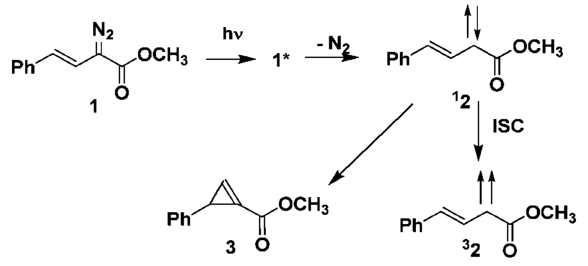
Singlet carbenes are reactive intermediates that undergo unique inter- and intramolecular reactions.[1] Intermolecular reactions of arylcarbenes have been studied extensively.[1] Vinylcarbenes undergo intramolecular cyclization to form cyclopropenes.[2] Triplet vinylcarbene has two geometric isomers which have been detected by matrix isolation spectroscopy.[3] Calculations indicate that singlet vinylcarbene resides 12−13 kcal/mol above the triplet ground state.[4,5] Vinylchlorocarbene has a singlet ground state as demonstrated by Sheridan and Zuev.[6] The Moss and Sheridan groups[7] directly detected two singlet vinylchlorocarbenes in solution and reported that they have ns lifetimes and cyclize over barriers of 5.7−6.6 kcal/mol. Singlet vinylcarbenes have not been directly observed when the triplet is the ground state because rapid intersystem crossing (ISC) and intramolecular cyclopropenation prevent their detection using either matrix isolation or nanosecond laser flash photolysis. Thus, the detection of a singlet vinylcarbene remains a challenging application of ultrafast time-resolved techniques.

Methyl styryldiazoacetate[8] ($PhCH{=}CHCN_2CO_2CH_3$, **1**, Scheme 1) was chosen for this inaugural fs/ps time-resolved study. The phenyl group provides a UV−vis chromophore and the ester moiety does the same for IR techniques. The anticipated carbene $PhCH{=}CHCCO_2CH_3$ (**2**) is predicted to have triplet ground state by B3LYP/6-31G(d) calculations[9] and it was previously shown by Schmitz that ^{1}**2** can be trapped with neat methanol at a rate that is competitive with cyclization.[10]

Scheme 1. Photochemical Reactions of $PhCH{=}CHCN_2CO_2CH_3$



Ultrafast UV−vis ($\lambda_{ex} = 310$ nm) of (**1**) in acetonitrile produced the spectra shown in Figure 1. A broadly absorbing transient with absorption maximum near 470 nm is formed within the laser pulse (300 fs). As it decays, a new transient is observed with $\lambda_{max} = 385$ nm. The former band is attributed to an excited state of the diazo precursor (**1***) based on previous studies[11] and the latter to singlet vinylcarbene (^{1}**2**). The latter assignment is based in part on a TD B3LYP calculation which predicts that ^{1}**2** absorbs at 378 nm ($f = 0.1220$, Table S1), in excellent agreement with the experimental results. The absorption band of ^{1}**2** decays exponentially with a time constant of 25.7 ± 1.6 ps (Figure S1a). This result is consistent with calculations that predict a singlet carbene lifetime of 30 ps in the gas phase (SI, Figure S2), further supporting the assignment of the transient to ^{1}**2**.

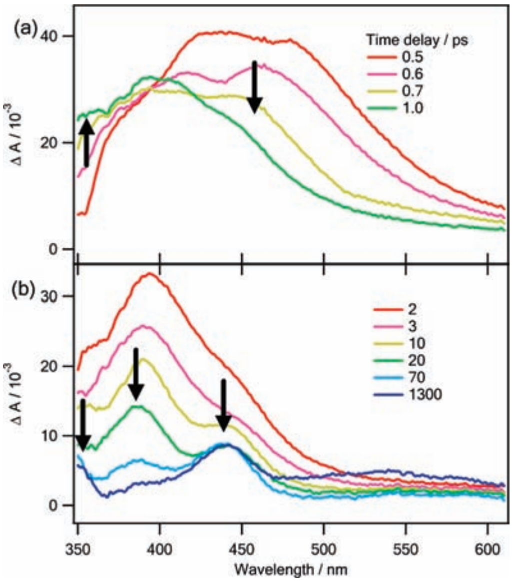


Figure 1. Transient UV−vis spectra produced upon 310 nm photolysis of $PhCH{=}CHCN_2CO_2CH_3$ in acetonitrile.

As the singlet carbene (^{1}**2**) decays, two very weak bands at 440 and 350 nm are revealed that have constant intensity for 3 ns.[14] The long lifetimes are consistent with triplet vinylcarbene ^{3}**2**; however, TD B3LYP calculation predicts triplet carbene absorption at 392 nm ($f = 0.0028$) and 342 nm ($f = 0.5761$, Table S1), in only fair agreement with the experimental data.

In methanol, the relaxed singlet carbene (^{1}**2**) decays with a lifetime of 38.4 ± 2.4 ps (Figure S1b, Table S2). The observation that the relaxed singlet carbene (^{1}**2**) decays faster in acetonitrile than in methanol runs counter to most studies of singlet carbenes.[12−15] We speculate that the singlet carbene lifetime in acetonitrile is unusually short because of cyclopropene (**3**) formation, rather than control by intersystem crossing and intermolecular reaction, as is usually the case for the more thoroughly studied aryl carbenes in this solvent.[11,15,16] The rate of cyclization in methanol is slower than in acetonitrile, probably because of more intimate solvation of the carbene.[17] Indeed, in a noncoordinating solvent (cyclohexane) the lifetime of the singlet carbene is only 6.5 ± 1.1 ps (Figure S1c, Table S2). Similar solvent effects on the rate of Wolff rearrangement have been reported.[18]

[†] The Ohio State University.
[‡] Adam Mickiewicz University.

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The decay of singlet carbene (^{1}**2**) is not accompanied by the growth of transient UV−vis absorption of cyclopropene **3**, prompting the use of IR detection.

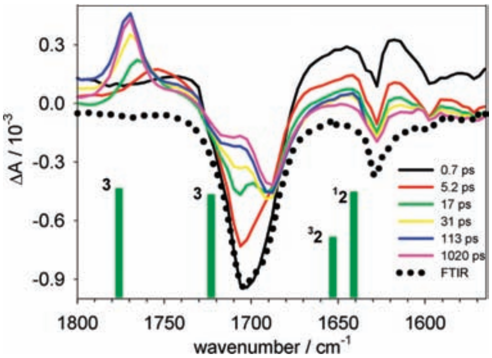

Figure 2. Transient IR spectra produced upon 270 nm photolysis of PhCH═CHCN$_2$CO$_2$CH$_3$ in chloroform. The dotted curve is the FTIR spectrum of PhCH═CHCN$_2$CO$_2$CH$_3$ in chloroform. Bars represent the calculated frequencies for singlet carbene (^{1}**2**), triplet carbene (^{3}**2**), and cyclopropene (**3**).

Ultrafast photolysis (270 nm) of **1** in chloroform produces the transient IR spectra shown in Figure 2. The negative band observed in the 1750−1640 cm^{-1} region is due to the bleaching of the carbonyl (C═O) stretch in the diazo precursor (**1**). However, the carbonyl bleaching band reshapes over 100 ps, clearly indicating that a new species absorbing around 1705 cm^{-1} is formed rapidly. A positive band at 1770 cm^{-1} was also observed. This band narrows and shifts to the blue within 80 ps of the laser pulse and retains the same intensity over 3 ns. Identical kinetic behavior was observed monitoring at 1770 and 1705 cm^{-1} which suggests that both bands are associated with the same intermediate. After subtracting the FTIR spectrum of the diazo precursor, two positive bands at 1770 and 1705 cm^{-1} are clearly observed and persist for at least 3 ns (Figure S4). Both bands are assigned to the cyclopropene (**3**) formed by the intramolecular cyclopropenation reaction (Scheme 1). B3LYP/6-31G(d) calculations predict cyclopropene (**3**) has coupled stretching modes of C═O and C═C at 1776 and 1723 cm^{-1} (Table S3). The direct observation of both vibrational bands and the excellent agreement with calculations indicate that the carrier of the observed transient absorptions is indeed the cyclopropene product (**3**).

Integration of the intensity of both bands indicates that cyclopropene (**3**) is formed with a time constant of 32 ps in chloroform (Table S2, Figure S5), in good agreement with the singlet carbene (^{1}**2**) decay observed in this solvent by ultrafast UV−vis spectroscopy (Figure S1d). This result confirms that singlet carbene (^{1}**2**) is the immediate precursor of cyclopropene (**3**).

B3LYP/6-31G(d) calculations predict singlet carbene (^{1}**2**) vibrations at 1641 cm^{-1} (Table S4) and triplet (^{3}**2**) at 1653 cm^{-1} (Table S5). Indeed, in the 1680−1580 cm^{-1} spectral range (Figure 2) a broad positive band is observed. Its decay correlates with cyclopropene (**3**) growth, and an isosbestic point at 1684 cm^{-1} is observed, clearly suggesting that the singlet carbene is detected. At ~1650 cm^{-1}, absorption is still present 3 ns post laser pulse, consistent with the formation of triplet carbene (^{3}**2**). However, the precise kinetics of either the singlet carbene (^{1}**2**) or triplet carbene (^{3}**2**) cannot be obtained by time-resolved IR methods as they are greatly affected by the overlapping hot ground state **1**$^\#$. The long lifetime of the triplet, relative to the singlet carbene, indicates that the two spin isomers are not in rapid equilibrium, as predicted by the large calculated energy separation (SI, $\Delta E_{\mathrm{ST}} = 7.9$ kcal/mol).

In the diazo stretching region (Figure S6) the negative band observed at 2085 cm^{-1} is due to the bleaching of the ground-state precursor. As usual, the hot ground state is observed on its red edge as a broad positive band, which then undergoes blue-shifting and narrowing within 40 ps, a result typical of vibrational cooling.[19] About 31% of the diazo bleaching band was recovered within 3 ns. The growth time constant of 18.4 ps (Figure S7), as probed at 2085 cm^{-1}, is assigned to the vibrational cooling of diazo precursor. The exact correspondence of the FTIR spectrum with the transient spectrum at 2.5 ns, post flash, convinces us that a ketene is not detected.

In summary, we have observed a singlet vinylcarbene (^{1}**2**) produced directly from the excited state of a diazo precursor (**1**). The singlet carbene undergoes intramolecular cyclopropenation reaction to produce the cyclopropene product (**3**) in acetonitrile, chloroform and cyclohexane, and undergoes intersystem crossing to ground triplet carbene (^{3}**2**) to a small extent. The triplet carbene is not in rapid equilibrium with the singlet due to a relatively large singlet triplet separation.

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Supporting Information Available: A brief description of the spectrometers, complete ref 9, Figures S1−S6, and Tables S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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