

Time-Resolved IR Studies of 2-Naphthyl(carbomethoxy)carbene: Reactivity and Direct Experimental Estimate of the Singlet/Triplet Energy Gap

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Received September 14, 1998

Abstract: To clarify the role of diazocarbonyl excited states in Wolff rearrangement chemistry, time-resolved infrared (TRIR) spectroscopy has been used to study methyl 2-diazo-(2-naphthyl) acetate (**1**) and the subsequently produced 2-naphthyl(carbomethoxy)carbene (**2**). TRIR analysis of the growth rate of the ketene rearrangement product following laser excitation of diazoester **1** demonstrates that in this case ketene is formed almost exclusively from the carbene. The absence of reaction from the diazoester excited state is likely due to the highly preferred anti relationship between the diazo and carbonyl groups in **1**. In addition, the detection of IR bands from *both* the singlet and triplet states of spin-equilibrated carbene **2** has allowed a direct experimental estimate of the singlet/triplet energy gap in solution at ambient temperature. This work represents the first TRIR detection and study of a carbene intermediate and demonstrates the potential value of TRIR spectroscopy in structural and mechanistic aspects of carbene chemistry.

Introduction

Chemists have long appreciated that photolysis of diazirines or diazo compounds often leads to product mixtures different from those observed on thermolysis of the same carbene precursors.³ More recent photochemical studies of these nitrogenous carbene precursors have confirmed that rearrangement products can originate from a short-lived precursor excited state as well as from the carbene.⁴ (Alternatives to the excited state, such as a carbene–olefin complex in the case of an olefin-trapping agent,⁵ unstable diazo isomers in the case of diazirines,⁶ and excited carbenes,⁷ have also been proposed.) With the exception of recent diazirine fluorescence studies, which indicate that diazirines less prone to rearrangement fluoresce more strongly,⁴ evidence for the involvement of a precursor excited

state in rearrangement chemistry has been based mainly on product studies. For example, even in the presence of a large excess of a carbene trap such as an olefin or alcohol, rearrangement products are still observed.^{4,5} Analysis of the ratios of trapping product to rearrangement product can provide the extent to which rearrangement occurs from a precursor excited state.

We have begun to examine this issue by monitoring directly the kinetics of carbene rearrangement processes with nanosecond time-resolved infrared (TRIR) spectroscopy. In those cases where excited-state contributions are important, the rearrangement-product growth rate should be biexponential and consist of two components, viz., a fast, unresolvable component (production from a short-lived excited state) and a slower, resolvable component (production from carbene). Our current time-resolution restricts this approach to the study of carbenes with lifetimes greater than 50 ns. Reported herein is a TRIR study of 2-naphthyl(carbomethoxy)carbene (**2**), produced upon photolysis of diazoester **1**. To our knowledge this report represents the first TRIR detection and study of a carbene intermediate.⁸

The chemistry of carbonyl carbenes is closely associated with the Wolff rearrangement, a versatile reaction that has found wide application in diverse areas of research and technology.⁹ A persistent question concerning the photoinduced Wolff rearrangement is whether the derived ketene can arise directly from an excited state of the diazo precursor as well as from the relaxed carbene intermediate (Scheme 1). In this paper, we demonstrate by TRIR analysis of the growth rate of ketene **3** following laser excitation of diazoester **1** that this rearrangement product arises from the carbene with very little if any contribution from the

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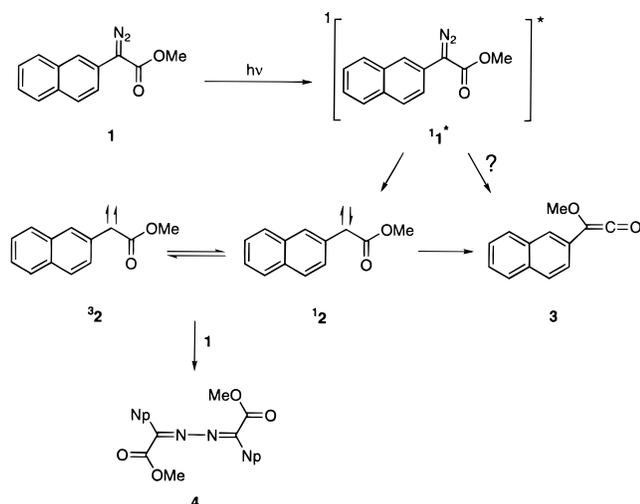
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Scheme 1



diazo excited state. Our findings are consistent with the chemical trapping and transient absorption experiments of Wang, Lithovorok, and Platz (WLP)¹⁰ and also with the low-temperature matrix studies and calculations of Zhu, Bally, Stracener, and McMahon (ZBSM).¹¹ Our work proceeded concurrently with those investigations, which are described in the accompanying papers.

TRIR investigations of carbene reactivity not only allow product-growth kinetics to be monitored but also supply structural information not available from standard transient absorption experiments. In the past, low-temperature matrix IR or ESR studies normally have been relied upon for structural characterizations. Concurrent observation of kinetics and structure by TRIR spectroscopy can enhance our fundamental understanding of carbenes and other reactive intermediates. For example, as reported below, the detection of IR bands from both the singlet and the triplet state of spin-equilibrated carbene **2** allows a direct experimental estimate of the singlet/triplet energy gap in solution at room temperature. With the exception of a small number of studies in the gas phase using photoelectron spectroscopy,¹² previous estimates of carbene singlet/triplet gaps have relied on combinations of product studies and kinetics and required assumptions concerning the spin selectivity of carbene trapping agents (e.g., that alcohols selectively trap singlet carbenes).¹³ Direct observation of both the singlet and triplet carbene by TRIR spectroscopy eliminates the need for assumptions and any ambiguities associated with them. Of course, this

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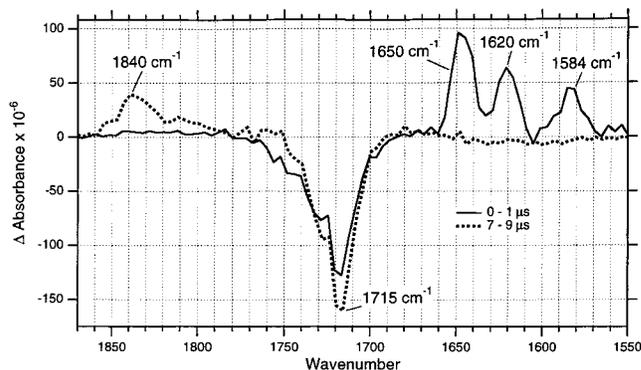


Figure 1. TRIR difference spectra observed from 0 to 1 μs and 7–9 μs following 266-nm laser photolysis of diazoester **1** (1.1 mM) in argon-saturated Freon-113.

approach requires that IR signals from each spin state can be differentiated and that the energy difference between them be small enough to allow significant thermal population of each state.

Results and Discussion

Observation of 2-Naphthyl(carbomethoxy)carbene (2**) by TRIR Spectroscopy.** Typical TRIR data observed following 266-nm laser excitation of **1** in argon-saturated Freon-113 (1,1,2-trichlorotrifluoroethane) are shown in Figure 1 for the spectral region 1870–1550 cm^{-1} . Data are obtained in the form of difference spectra. We attribute the positive bands at 1650, 1620, and 1584 cm^{-1} (observed over the first 1.0 μs after photolysis) to 2-naphthyl(carbomethoxy)carbene (**2**) on the basis of a comparison with the low-temperature matrix IR data of ZBSM (carbene bands detected at 1660, 1640, 1625, and 1590 cm^{-1});¹¹ the negative band at 1715 cm^{-1} in Figure 1 is due to the depletion of diazoester **1**.

The reported 1640- cm^{-1} signal is not resolved in our TRIR data as a result of its low intensity and the relative broadness of solution IR bands. Matrix experiments indicate that the 1640- cm^{-1} band is approximately one-half as intense as the 1590- cm^{-1} peak.¹¹ Our data shown in Figure 1 were acquired at 16- cm^{-1} resolution; however, increasing the spectral resolution to 8 cm^{-1} did not result in the observation of sharper IR bands. ZBSM have demonstrated that the matrix IR band they observed at 1660 cm^{-1} is due to the triplet carbene ($^3\mathbf{2}$) and those observed at 1640, 1625, and 1590 cm^{-1} arise from the singlet carbene ($^1\mathbf{2}$).¹¹ Analogously, we have assigned our TRIR band detected at 1650 cm^{-1} to $^3\mathbf{2}$ and those detected at 1620 and 1584 cm^{-1} to $^1\mathbf{2}$.

We further confirmed the identities of the 1650-, 1620-, and 1584- cm^{-1} bands of Figure 1 by kinetic studies. In their accompanying paper, WLP have shown that singlet/triplet spin equilibration of carbene **2** is much faster than reaction from either spin state.¹⁰ Consistent with that observation, we find that signals at 1650, 1620, and 1584 cm^{-1} decay at equal rates. A kinetic trace at 1650 cm^{-1} (Figure 2) indicates that the lifetime of the spin-equilibrated carbene in argon-saturated Freon-113 ($[\mathbf{1}] = 1.1 \text{ mM}$) is 830 ns.

This TRIR-determined lifetime is significantly shorter than that reported by WLP (2.2 μs) in their laser flash photolysis (LFP) study of $^3\mathbf{2}$.¹⁰ However, since typical path lengths for our TRIR experiments (0.2–0.5 mm) are 50–25 times shorter than that for LFP experiments (10 mm), we required significantly higher concentrations of diazoester **1** to achieve comparable optical densities at the photolysis wavelength. We have

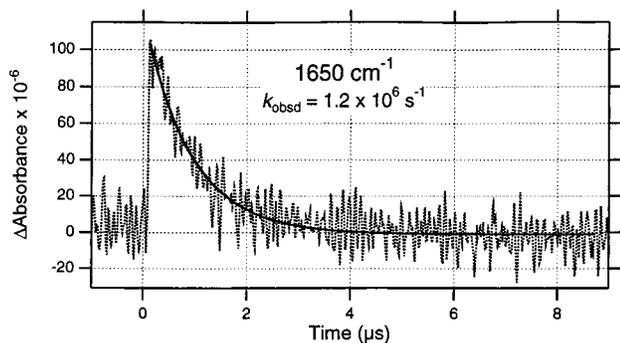


Figure 2. Kinetic trace observed at 1650 cm^{-1} following 266-nm laser photolysis of diazoester **1** (1.1 mM) in argon-saturated Freon-113. The dotted curve is experimental data; the solid curve is the calculated best fit to a single exponential.

found that the lifetime of carbene **2** depends on the initial concentration of diazoester **1**. Rate constants for carbene decay at 1650 cm^{-1} were measured in Freon-113 as a function of the concentration of **1** and analyzed according to pseudo-first-order equation 1

$$k_{\text{obsd}} = k_0 + k_{\text{diazo}}[\mathbf{1}] \quad (1)$$

where k_{diazo} is the second-order rate constant for reaction of diazoester **1** with carbene **2** to form azine **4** and k_0 is the rate of carbene decay at infinitely dilute concentrations of **1**. This analysis leads to the values $k_0 = 3.8 \times 10^5\text{ s}^{-1}$ and $k_{\text{diazo}} = 6.8 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$. The latter value is consistent with previous studies of singlet and triplet diphenylcarbene reaction with diphenyldiazomethane (singlet, $k_{\text{diazo}} = 2.3 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$, triplet, $k_{\text{diazo}} = 3.4 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$).¹⁴ In addition, at high concentrations of **1** ($>5\text{ mM}$) a new stable IR band appears at 1746 cm^{-1} . This signal, which grows at the same rate as carbene IR bands decay, is assigned to azine **4** on the basis of these kinetics and comparison with the reported IR spectrum of its phenyl analogue.¹⁵

We have also examined the reaction of carbene **2** in Freon-113 with the representative quenchers, 2,3-dimethyl-2-butene (DMB) and methanol, at a fixed diazoester concentration. The rate of carbene decay at both a triplet signal (1650 cm^{-1}) and a singlet signal (1584 cm^{-1}) was monitored as a function of quencher concentration and analyzed according to pseudo-first-order equation 2

$$k_{\text{obsd}} = k_0' + k_q[\text{quencher}] \quad (2)$$

where k_q is the second-order rate constant for reaction of carbene **2** with quencher and k_0' is the rate of carbene decay in the absence of quencher and at fixed diazoester concentration (typically 1.1 mM). Plots of k_{obsd} vs quencher concentration are linear (e.g., Figure 3) and give the quenching rate constants shown in Table 1. These derived values agree well with Itoh, Tomioka, and co-workers' previous study of the reaction of phenylcarbomethoxycarbene with 2-methyl-2-butene (MB) and methanol ($k_{\text{MB}} = 7.0 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$ and $k_{\text{MeOH}} = 2.7 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$).¹⁶ Carbene **2** is also quenched by oxygen. Its lifetime (monitored at either 1650 or 1584 cm^{-1}) is reduced to 120 ns in oxygen-saturated Freon-113 solutions (vs 830 ns in argon-

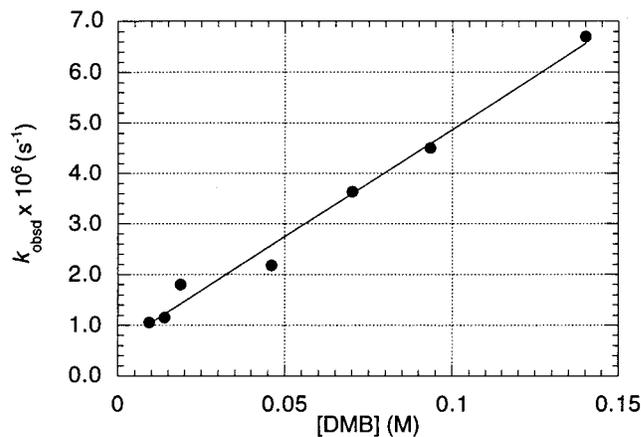


Figure 3. Plot of the observed rate of decay (k_{obsd}) at 1650 cm^{-1} vs concentration of 2,3-dimethyl-2-butene (DMB) in argon-saturated Freon-113. The concentration of diazoester **1** was kept constant at 1.1 mM.

Table 1. Second-Order Rate Constants Observed in Freon-113 for the Reaction of **32/2** with Representative Quenchers

quencher	$k_q\text{ (M}^{-1}\text{ s}^{-1}\text{)}$	
	1650 cm^{-1} (32)	1584 cm^{-1} (12)
2,3-dimethyl-2-butene	$(4.2 \pm 0.4) \times 10^7$	$(4.9 \pm 0.5) \times 10^7$
MeOH	$(1.0 \pm 0.1) \times 10^8$	$(9.2 \pm 0.9) \times 10^7$

saturated solutions), again in good agreement with the previous work of Itoh and Tomioka¹⁶ and the present accompanying study of WLP.¹⁰ Note that quenching rate constants observed at 1650 cm^{-1} (**32**) and 1584 cm^{-1} (**12**) for reagents that could potentially react in a multiplicity-dependent fashion (e.g., methanol and oxygen) are the same within experimental error, again consistent with fast singlet/triplet spin equilibration of carbene **2**.

We find that the lifetime of carbene **2** is shortened in more reactive solvents such as hexane and acetonitrile. In hexane ($[\mathbf{1}] = 1.1\text{ mM}$), its lifetime decreases to 130 ns; in acetonitrile ($[\mathbf{1}] = 1.1\text{ mM}$) it is reduced to 420 ns. TRIR experiments also reveal additional positive signals in each case. For example, in hexane a new stable IR band (not observed in Freon-113) appears at 1742 cm^{-1} . This band, which grows at the same rate ($k_{\text{obsd}} = 7.5 \times 10^6\text{ s}^{-1}$) as carbene IR bands decay, is attributed to ester(s) **5** formed by carbene C–H insertions into the hexane solvent (Scheme 2) on the basis of these kinetics and comparison with the reported IR spectra of analogous methyl α -alkylaryl acetates.¹⁷ Since the available spectral window in hexane includes the C–O region $1300\text{--}1100\text{ cm}^{-1}$ (unlike Freon-113), we are also able to detect carbene **2** bands at 1210 and 1170 cm^{-1} and an ester-insertion-product(s) **5** band at 1160 cm^{-1} (Figure 4). The observed rates of decay at 1210 cm^{-1} ($k_{\text{obsd}} = 8.0 \times 10^6\text{ s}^{-1}$) and 1170 cm^{-1} ($k_{\text{obsd}} = 9.0 \times 10^6\text{ s}^{-1}$) are the same within experimental error ($\pm 10\%$) and are also equivalent to the observed rates of decay for the higher frequency carbene bands. As displayed in Figure 5, the 1160-cm^{-1} ester(s) band develops at the same rate as the 1210-cm^{-1} carbene band decays.

The low-temperature matrix IR experiments of ZBSM reveal strong carbene bands in the region $1300\text{--}1100\text{ cm}^{-1}$.¹¹ Although overlapping **32** and **12** bands in this spectral region make assignments less straightforward than those for carbene signals observed at higher frequencies, we tentatively assign the 1210-cm^{-1} band to **32** and the 1170-cm^{-1} band to **12** on the basis of a comparison with the matrix data.

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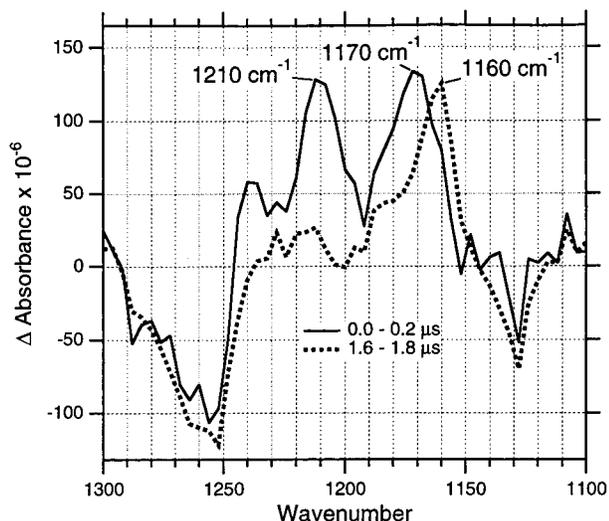
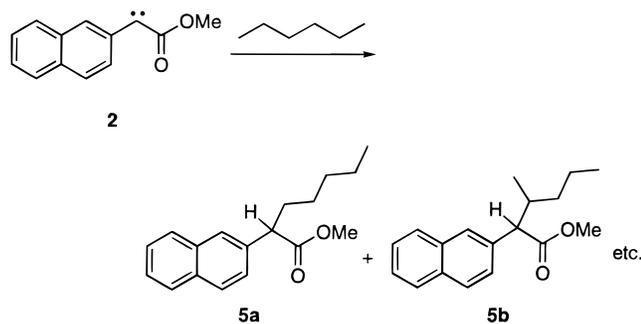


Figure 4. TRIR difference spectra observed from 0 to 0.2 μs and 1.6–1.8 μs following 266-nm laser photolysis of diazoester **1** (1.1 mM) in argon-saturated hexane. The negative bands at 1254 and 1130 cm^{-1} are due to depletion of diazoester **1**.

Scheme 2



In acetonitrile, a new long-lived ($\tau = 18 \mu\text{s}$) IR band (not observed in either Freon-113 or hexane) appears at 1656 cm^{-1} . Again, the rate of growth of this band ($k_{\text{obsd}} = 3.6 \times 10^6 \text{ s}^{-1}$ for $[\mathbf{1}] = 3.1 \text{ mM}$, monitored at 1662 cm^{-1} to avoid complication from the carbene 1650- cm^{-1} band) is nearly equal to the rate of carbene decay ($k_{\text{obsd}} = 3.8 \times 10^6 \text{ s}^{-1}$) observed at 1170 cm^{-1} (Figure 6). The carbene decay rate is the same within experimental error ($\pm 10\%$) in acetonitrile- d_3 ($k_{\text{obsd}} = 3.5 \times 10^6 \text{ s}^{-1}$ for $[\mathbf{1}] = 3.1 \text{ mM}$), indicating that C–H(D) insertions are unimportant in this solvent. Thus, on the basis of this lack of an isotope effect and the observed spectral position, we have assigned the 1656- cm^{-1} band to acetonitrile ylide **6** (Scheme 3).

Singlet/Triplet Energy Gap of 2-Naphthyl(carbomethoxy)-carbene (2). One of the most fundamental properties that determines a carbene's reactivity is its spin state. However, even in those cases where the triplet is of lower energy, chemistry often arises from the higher lying, but more reactive, singlet carbene. Two mechanistic schemes have emerged to explain such observations. The classical mechanism, first advanced by Bethell and co-workers,¹⁸ predicts that the observed barrier (E_a) for a singlet carbene reaction is given by the actual activation barrier of the reaction (ΔH^\ddagger) plus the energy required to populate the singlet from the lower energy triplet carbene (ΔH_{ST}).

$$E_a = \Delta H^\ddagger + \Delta H_{\text{ST}} \quad (3)$$

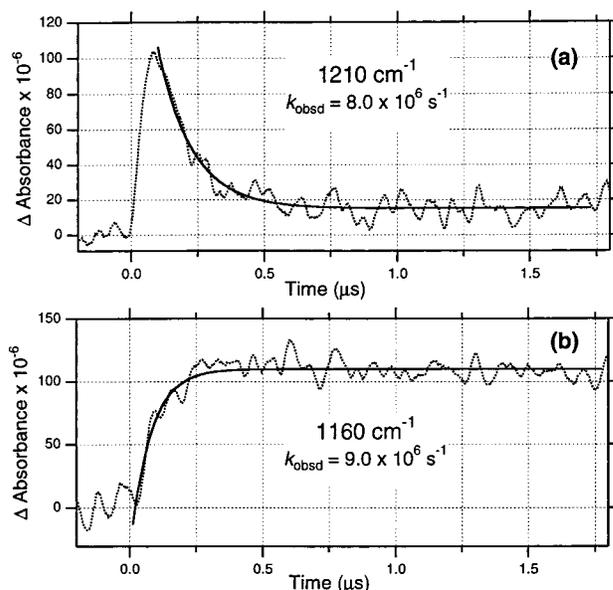


Figure 5. Kinetic traces observed at (a) 1210 cm^{-1} and (b) 1160 cm^{-1} following 266-nm laser photolysis of diazoester **1** (1.1 mM) in argon-saturated hexane. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential.

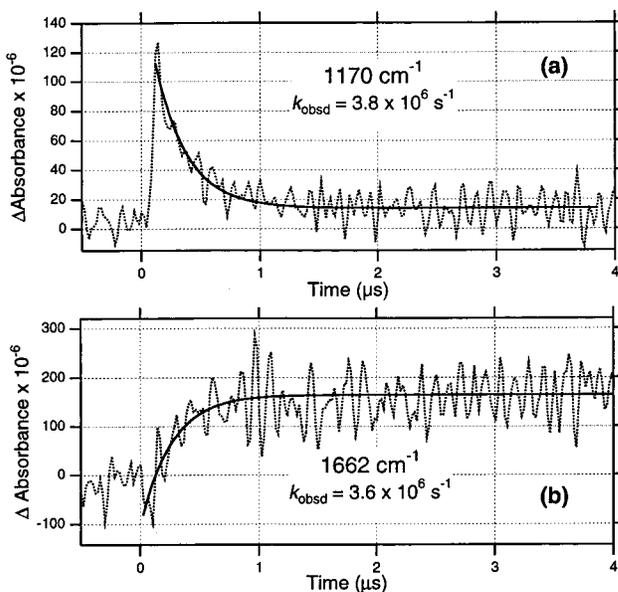
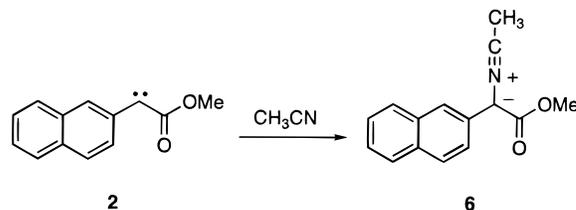


Figure 6. Kinetic traces observed at (a) 1170 cm^{-1} and (b) 1662 cm^{-1} following 266-nm laser photolysis of diazoester **1** (3.1 mM) in argon-saturated acetonitrile. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential.

Scheme 3



The alternative, proposed by Griller, Nazran, and Scaiano,¹⁹ is an avoided surface-crossing mechanism in which the triplet-carbene surface crosses the singlet carbene \rightarrow product surface

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at a point below the energy of the singlet carbene leading to an observed E_a that is lower than the sum of ΔH^\ddagger and ΔH_{ST} . In this case, if the activation energy for the singlet-carbene reaction is very small, one might experimentally observe an activation barrier less than the singlet/triplet energy gap. Indeed, the avoided surface-crossing mechanism was originally formulated to explain such an observation.¹⁹

Thus, accurate measurements of carbene singlet/triplet energy gaps are both fundamentally and mechanistically very important. However, to our knowledge, a carbene singlet/triplet gap has never been *directly* measured in solution.²⁰ Previous experimental estimates of these splittings usually employ a combination of product studies and kinetic measurements and have been forced to rely on assumptions concerning the spin-selectivity of carbene trapping reagents.¹³ For example, alcohols are thought to be selective traps of singlet carbene; oxygen and isoprene are believed to be selective-triplet-carbene traps. Of course, any inaccuracy in these suppositions could lead to critical errors in the estimated energy difference between the two carbene spin states.

Our observation of IR signals of both singlet and triplet 2-naphthyl(carbomethoxy)carbene (**2**) allows a direct experimental estimate of a carbene singlet/triplet energy gap in solution. Since the relative intensities of these signals are directly related to the concentrations of the singlet and triplet carbene, an equilibrium constant and, subsequently, a standard-free-energy difference can be easily derived. To determine the relative concentrations, however, we need the ratio of extinction coefficients for a singlet and a triplet IR band. Fortunately, an estimate of this ratio is available from the matrix study of ZBSM, who have observed that at 12K overnight **12** thermally relaxes only to **32**.¹¹ Thus, the intensity ratio of final **32** band to initial **12** band reflects the ratio of their extinction coefficients. We chose the well-separated signals observed at 1650 cm^{-1} (**32**) and 1584 cm^{-1} (**12**) for this analysis. The low-temperature matrix-determined ratio (**32**/**12**) for these signals is approximately 1.5; the Freon-113 solution TRIR determined ratio at 21 °C is 2.1. These values lead to an equilibrium constant of 1.4 ± 0.2 at 21 °C and a free energy difference of 0.2 ± 0.1 kcal/mol, with the triplet carbene lower in energy.

Carbene **2** was assigned a triplet ground state by ZBSM on the basis of low-temperature ESR spectroscopy and theoretical calculations as well of their observation that **12** relaxes thermally to **32** at 12 K.¹¹ Thus, our determination that **32** has lower energy than **12** agrees well with their work; however, our experimental value of the singlet/triplet splitting is significantly lower than that calculated by density functional theory ($\Delta H_{ST} = 4.52$ kcal/mol).¹¹ Matrix site effects on observed IR band intensities could certainly lead to errors in our estimated extinction-coefficient ratio, but even a fairly considerable error in equilibrium constant translates to a relatively small absolute error in free-energy difference. Moreover, the fact that we could observe singlet carbene signals at ambient temperature indicates that the singlet/triplet energy separation must be on the order of 1 kcal/mol or less.

Previous work by Eisenthal and co-workers²¹ has shown that singlet diphenylcarbene is stabilized relative to triplet diphenylcarbene in polar solvent, presumably as a result of the

(20) In the gas phase, however, the Lineberger group has directly measured the singlet/triplet splitting of several carbenes by photoelectron spectroscopy.¹²

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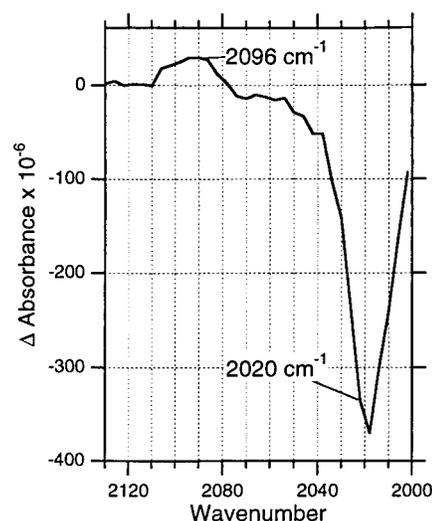


Figure 7. TRIR difference spectrum observed from 7 to 9 μs following 266-nm laser photolysis of doubly ^{15}N -labeled diazoester **1** (3.1 mM) in argon-saturated Freon-113.

zwitterionic nature of singlet carbenes.²² In addition, the groups of Goodman²³ and of Moss²⁴ have recently provided evidence for the stabilization of singlet carbenes through the formation of energetically favorable carbene-benzene complexes. Thus, a possible explanation for the difference between the calculated (gas phase) and experimental (Freon-113 solution) value of the singlet/triplet splitting for carbene **2** is that the singlet is preferentially stabilized in solution. We are currently pursuing this hypothesis by attempting to measure the singlet/triplet gap for **2** as a function of solvent.

Mechanism of Ketene Formation. The original impetus for our TRIR investigation of diazoester **1** was to monitor directly the kinetics of rearrangement to ketene **3**. Specifically, we were interested in determining the portion of ketene **3** produced directly from the singlet excited state of **1** and that formed from spin-equilibrated carbene **2** (Scheme 1). Since the lifetime of **11*** is likely much less than 1 ns and certainly well below the present time resolution (50 ns) of our TRIR spectrometer, ketene production only from **11*** would be indicated by a fast, unresolvable increase in ketene IR absorbance following laser photolysis. Production from carbene **2** only would be revealed by a rate of ketene growth equal to that of carbene decay.

We were initially disappointed to find that the rate of ketene production was impossible to monitor for diazoester **1** as a result of overlap between the positive ketene IR band (at 2096 cm^{-1}) and the strong negative depletion signal of the diazoester at 2090 cm^{-1} . Thus, we prepared and studied doubly ^{15}N -labeled **1** in order to shift the diazo IR band away from the ketene signal of interest. Typical TRIR data following 266-nm-laser excitation of doubly ^{15}N -labeled **1** in argon-saturated Freon-113 are displayed in Figure 7 for the spectral region 2130–2000 cm^{-1} . Here, the diazo-depletion band is shifted to 2020 cm^{-1} ; the positive ketene band remains at 2096 cm^{-1} . The relative intensities of these bands are consistent with the work of ZBSM, who were able to resolve the ketene and diazo signals even for unlabeled **1** because of the higher spectral resolution of their matrix IR experiment.¹¹ Figure 8 shows that in both Freon-113 (trace b) and in acetonitrile (trace c) the rates of ketene growth ($k_{\text{obsd}} = 2.5 \times 10^6 \text{ s}^{-1}$ in Freon-113; $k_{\text{obsd}} = 3.8 \times 10^6 \text{ s}^{-1}$ in

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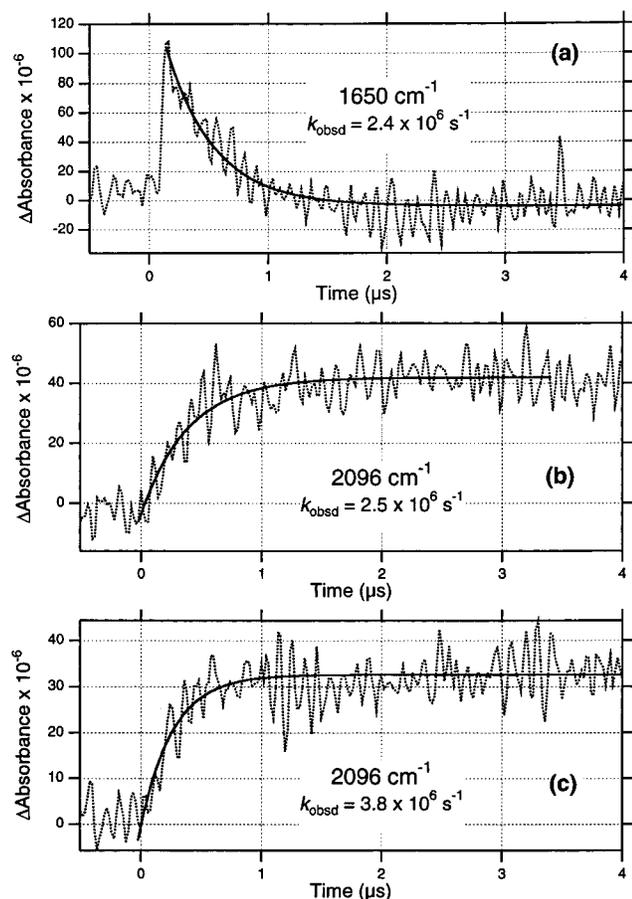


Figure 8. Kinetic traces observed at (a) 1650 cm^{-1} and (b) 2096 cm^{-1} in argon-saturated Freon-113 and at (c) 2096 cm^{-1} in argon-saturated acetonitrile following 266-nm laser photolysis of $^{15}\text{N}_2$ -labeled diazoester **1** (3.1 mM). The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential. The ketene **3** kinetic trace in acetonitrile (c) can be compared to the carbene **2** kinetic trace of Figure 6a.

acetonitrile) equal the rates of carbene decay ($k_{\text{obsd}} = 2.4 \times 10^6\text{ s}^{-1}$ in Freon-113; $k_{\text{obsd}} = 3.8 \times 10^6\text{ s}^{-1}$ in acetonitrile, Figure 6, trace a). These data clearly demonstrate that ketene **3** arises entirely from carbene **2**.

This result is in excellent agreement with the alcohol-trapping experiments of WLP (who isolated essentially only carbene-derived adducts)¹⁰ and the calculations of ZBSM.¹¹ Those calculations indicate that diazoester **1** is planar and exists almost entirely (99%) in conformations in which the diazo and carbonyl groups are anti. Previously, Kaplan and co-workers²⁵ demonstrated that diazocarbonyl compounds can exist as equilibrium mixtures of syn and anti forms (e.g., **1_{syn}** and **1_{anti}**). Kaplan's group, as well as Tomioka's²⁶ and Platz's,²⁷ have shown that concerted rearrangement to ketene from an excited state is facile from the syn conformation, but carbene production occurs from the anti form (Scheme 4).²⁸ Thus, the preferred conformation of **1** leads to efficient carbene production upon photolysis, with very little if any direct rearrangement to ketene **3**.

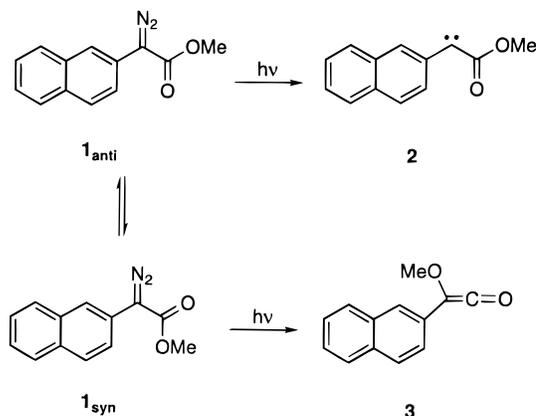
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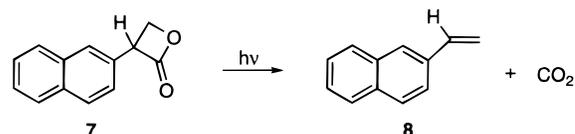
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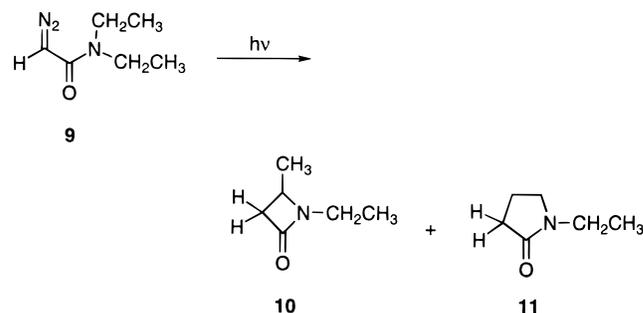
Scheme 4



Scheme 5



Scheme 6



Mechanism of β -Lactone Formation. As shown in Figure 1, several microseconds after laser photolysis of **1** we observed a relatively weak IR band at 1840 cm^{-1} , in good agreement with that detected at 1846 cm^{-1} by low-temperature matrix IR.¹¹ On the basis of those matrix experiments and the product studies of WLP, this band is assigned to β -lactone **7**. ZBSM have observed that in an argon matrix **7** can be converted photochemically to 2-vinylnaphthalene (**8**) plus carbon dioxide (Scheme 5).¹¹ Consequently, after steady-state photolysis of diazoester **1**, WLP isolated 2-vinylnaphthalene rather than β -lactone **7**.¹⁰

Tomioka and co-workers have previously observed similar chemistry in their study of diazoamide **9** (Scheme 6).²⁹ In this case, however, β -lactam **10** is stable and can be isolated. Interestingly, the formation of **10** was unaffected by the addition of carbene quenchers such as methanol. Conversely, methanol completely suppressed the formation of γ -lactam **11**. On the basis of these results, Tomioka proposed that γ -lactam **11** is formed from a carbene intermediate, but β -lactam **10** arises directly from the excited state of diazoamide **9**.

Thus, we were interested in determining the precursor to β -lactone **7** by monitoring, with TRIR spectroscopy, its rate of production. As with ketene **3**, β -lactone production from **1^{1*}** would be indicated by a fast, unresolvable growth; whereas production from carbene **2** would be revealed by a rate of β -lactone

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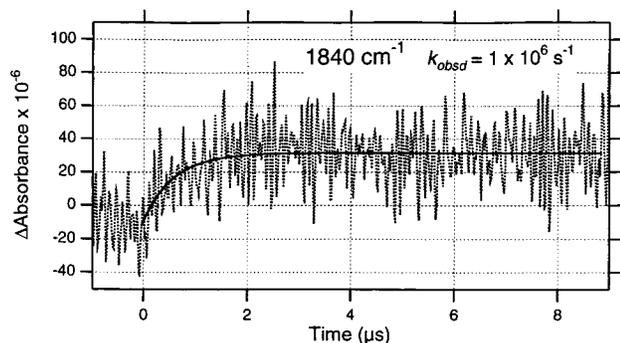
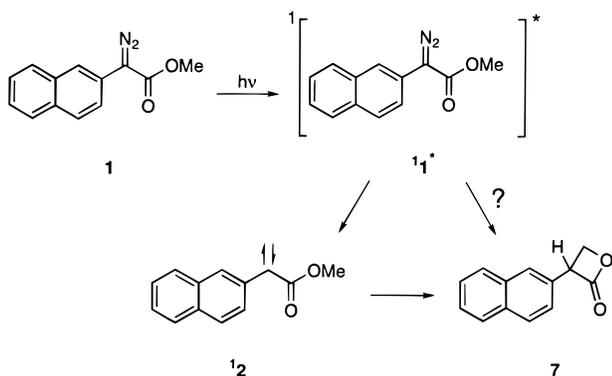


Figure 9. Kinetic trace observed at 1840 cm^{-1} following 266-nm laser photolysis of diazoester **1** (1.1 mM) in argon-saturated Freon-113. The dotted curve is experimental data; the solid curve is the calculated best fit to a single exponential.

Scheme 7



growth equal to that of carbene decay (Scheme 7). Although the observed TRIR signal at 1840 cm^{-1} is quite weak, the kinetic trace of Figure 9 indicates that the rate of β -lactone growth ($k_{\text{obsd}} = \text{ca. } 1 \times 10^6\text{ s}^{-1}$) is approximately the same as the rate of carbene decay ($k_{\text{obsd}} = 1.2 \times 10^6\text{ s}^{-1}$, Figure 2). This finding suggests that β -lactone **7**, like ketene **3**, is formed entirely from carbene **2** with very little if any contribution from 1^1 .

Conclusions

This work demonstrates the potential value of TRIR spectroscopy in structural and mechanistic aspects of carbene chemistry. Through application of this method we provide the first direct experimental estimate of a carbene singlet/triplet gap in solution. Furthermore, by monitoring directly the kinetics of ketene and β -lactone formation following photolysis of diazoester **1**, we reveal that these products arise almost exclusively from a carbene intermediate. The absence of reactions from the diazoester excited state is likely due to the highly preferred anti relationship between the diazo and carbonyl groups in **1**. This lack of excited-state involvement for **1** is in contrast to behavior in systems that have substantial equilibrium concentrations of the syn conformer.^{25–27,29} Such systems are presently under investigation by TRIR methods in our laboratory.

Experimental Section

General Methods. Unless otherwise noted, materials were obtained from Aldrich Chemical Co. and used without further purification. Acetonitrile and methylenechloride were distilled from CaH_2 before use. Tetrahydrofuran was distilled from sodium/benzophenone before use. Freon-113 was dried by passage through a neutral-alumina column and stored under argon. Acetonitrile- d_3 (Cambridge Isotope Laboratories) and methanol (Burdick and Jackson) were used as received. 2,3-

Dimethyl-2-butene was passed through a small neutral-alumina column immediately before use.

^1H NMR spectra were recorded on a Bruker AMX 300 (300 MHz) Fourier transform NMR spectrometer. Resonances are reported in δ units downfield from tetramethylsilane. IR spectra were recorded on a Bruker IFS-55 Fourier transform IR spectrometer at 4-cm^{-1} resolution. Melting points were measured with a MEL-TEMP metal-block apparatus and are uncorrected.

Methyl 2-Diazo-2-(2-naphthyl)Acetate (1). A solution of methyl-2-naphthyl acetate (2.0 g, 10 mmol) and *p*-toluenesulfonyl azide (2.17 g, 11 mmol) in 25 mL of freshly distilled methylenechloride was cooled with an ice bath. Diazo transfer³⁰ was initiated upon the dropwise addition of 1.6 g (10 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) freshly distilled from KOH. The ice bath was removed after complete addition of the DBU, and the mixture was stirred at room temperature until thin-layer chromatography (hexane/ether, 5/1) indicated that the reaction was complete. Methylenechloride (25 mL) was then added, and the mixture was extracted with $2 \times 25\text{ mL}$ of 0.3 M KOH solution. The organic layer was washed with $5 \times 10\text{ mL}$ of water and dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was recrystallized from methylenechloride/ether (4/1) to provide 1.47 g (65%) of diazoester **1**: mp $79\text{--}80\text{ }^\circ\text{C}$; IR (CH_2Cl_2 , cm^{-1}) 3055, 2980, 2090, 1710, 1435, 1242, 1121; ^1H NMR (300 MHz, CDCl_3) δ 3.91 (s, 3H), 7.43–8.02 (m, 7H).

***p*-Toluenesulfonyl Azide- $^{15}\text{N}_3$.**^{31,32} A 25-mL flask was charged with 0.5 g (3.8 mmol) of $^{15}\text{N}_2$ -labeled hydrazine sulfate (Cambridge Isotope Laboratories), and a 40% NaOH solution was added dropwise until the pH was 9. The flask was cooled with an ice bath, and 0.8 g (4.2 mmol) of *p*-toluenesulfonyl chloride dissolved in 2 mL of tetrahydrofuran was slowly added, with the temperature kept below $10\text{ }^\circ\text{C}$. After 1 h, 1 mL (17.5 mmol) of 100% acetic acid was added, followed by the dropwise addition of 0.3 g (4.3 mmol) of ^{15}N -labeled sodium nitrite (Cambridge Isotope Laboratories) dissolved in 2 mL of water, again keeping the temperature below $10\text{ }^\circ\text{C}$. After being stirred for 3 h, the reaction mixture was washed with a saturated sodium bicarbonate solution and extracted with ether. The ether was removed under vacuum to provide 0.6 g (80%) of *p*-toluenesulfonyl azide- $^{15}\text{N}_3$: IR (CH_2Cl_2 , cm^{-1}) 2058 (vs 2130 for unlabeled *p*-toluenesulfonyl azide).

Methyl 2-Diazo-2-(2-naphthyl) Acetate- $^{15}\text{N}_2$ (1- $^{15}\text{N}_2$). We followed the procedure described above for methyl 2-diazo-2-(2-naphthyl) acetate using *p*-toluenesulfonyl azide- $^{15}\text{N}_3$: IR (CH_2Cl_2 , cm^{-1}) 3050, 2950, 2026, 1705, 1435, 1242, 1121; ^1H NMR (300 MHz, CDCl_3) δ 3.92 (s, 3H), 7.43–8.02 (m, 7H).

Time-Resolved IR Methods. We conducted TRIR experiments following the method of Hamaguchi and co-workers³³ as described briefly previously.³⁴ This method allows access to the entire mid IR spectrum ($4000\text{--}800\text{ cm}^{-1}$) with high sensitivity and sufficient time (ca. 50 ns) and frequency ($4\text{--}16\text{ cm}^{-1}$) resolution to probe a wide range of transient intermediates in solution. The broad-band output of a newly developed MoSi_2 infrared source (Jasco) is crossed with excitation pulses (266 nm, 10 ns, 0.4 mJ) from a Continuum HPO-300 diode-pumped 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. Data are collected at a repetition rate of 200 Hz, the maximum data handling speed of our digital oscilloscope.

Time-resolved IR measurements are obtained from three different recordings of the emission spectrum of the IR light source. These include a spectrum of the IR source without the sample in the beam

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path (I_0), a spectrum of the IR source with the sample in the beam path (I), and the IR intensity changes induced by photoexcitation (ΔI). The absorbance spectrum of the unexcited sample is derived from I_0 and I , $A = \log(I_0/I)$. The time-resolved IR absorbance spectrum is obtained in the form of a difference spectrum, $\Delta A = -\log(1 + \Delta I/I)$. Thus, depletion of the reactant ground state gives rise to negative signals, and formation of transient intermediates or products leads to positive bands. In ideal cases, the depletion of reactants, the growth and decay of intermediates, and the growth of products of a photoinitiated reaction can be monitored.

To obtain spectra with sufficient sensitivity, we typically signal average several thousand laser shots at each IR frequency of interest. Thus, a flowing cell is necessary to prevent excessive sample decomposition. A reservoir of 10–15 mL of solution is continually circulated between two CaF₂ salt plates. A fresh reservoir of solution was used for each 50-cm⁻¹ spectral segment. Since the detection of transient species is more problematic in regions with strong solvent bands as a result of the low transmission of IR light,³³ available spectral windows are limited by solvent absorbance and path length. Major

spectral windows available for the solvents employed in this study (0.5-mm path length) are as follows: Freon-113, 2200–1420 cm⁻¹; hexane, 2550–1500 cm⁻¹ and 1300–900 cm⁻¹; acetonitrile, 2200–1500 cm⁻¹ and 1300–1100 cm⁻¹; and acetonitrile-*d*₃, 2200–1200 cm⁻¹.

For carbene-quenching experiments, we prepared a series of solutions in volumetric flasks using one stock solution of diazoester **1** in Freon-113 and another stock solution of a carbene quencher in Freon-113. A constant volume of the diazoester stock solution was added to varying volumes of the carbene-quencher solution. Freon-113 was then added so that for each kinetic measurement the total volume, and thus the concentration of **1**, was constant.

Acknowledgment. J.P.T gratefully acknowledges the Camille and Henry Dreyfus New Faculty Awards Program and an NSF Faculty Early Career Development Award for generous support of this research. We also thank Professors Platz, Bally, and McMahon for sharing their results prior to publication.

JA983278O