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2-Naphthyl(carbomethoxy)carbene Revisited: Combination of Ultrafast UV−vis and Infrared Spectroscopic Study

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Ultrafast laser flash photolysis (310 nm) of methyl 2-napthyldiazoacetate (2-$NpCN_2CO_2CH_3$) in acetonitrile or cyclohexane produces a diazo excited state which absorbs broadly in the visible region ($\tau = 300$ fs). The decay of the excited diazo compound is accompanied by growth of the vibrationally excited singlet 2-naphthyl(carbomethoxy)carbene ($^1NpCCO_2CH_3$). The singlet carbene absorbs at 360 and 470 nm. In acetonitrile these bands do not decay over 3 ns, but they do decay by ~50% of their original intensity in cyclohexane in 3 ns. It is concluded that $^1NpCCO_2CH_3$ has a singlet ground state in acetonitrile but a triplet ground state in cyclohexane. Related experiments reveal a singlet ground state in Freon-113 and chloroform. This interpretation is supported by ultrafast IR spectroscopy, which confirms that only $^1NpCCO_2CH_3$ is formed within 50 ps of the laser pulse rather than a singlet−triplet equilibrium mixture of carbene. The planar singlet relaxes to the preferred perpendicular singlet over a few tens of picoseconds, as evidenced by a red shift of the carbonyl stretching vibration. Although our data agrees with previous studies, its interpretation is somewhat altered.

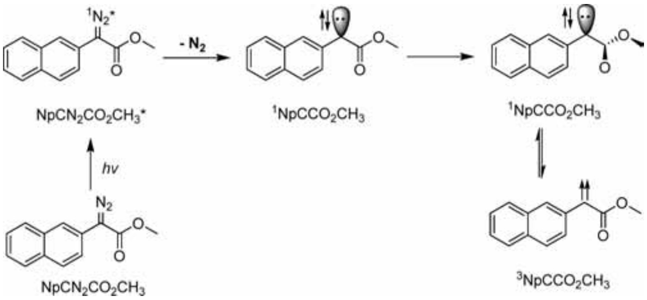
I. Introduction

The spin state of carbene is a fundamental value that determines its reactivity.[1,2] The energy gap between carbene singlet−triplet states (ΔE_{ST}) and the rate of intersystem crossing (ISC) from singlet to triplet (k_{ST}) carbenes ultimately determines the nature of the stable products these intermediates eventually produce.

The "pyridine-yield" method has been extensively applied to the study of singlet carbenes.[3] However, this is an indirect kinetic measurement, and its analysis can be always based on various assumptions, such as bimolecular reaction rates between singlet carbene and pyridine in the case of carbenes with *ps* lifetimes and the spin selectivity of carbene-trapping reagents, etc.[3] Interpretations based on these assumptions may introduce up to an order of magnitude error in the lifetime of singlet carbenes. Conceptually, the best way to determine the singlet−triplet gap of a carbene is to directly observe both species and measure their equilibrium populations.

Eisenthal et al. studied the relationship between ΔE_{ST} and k_{ST} in different solvents and found that ISC is fastest in nonpolar solvents where ΔE_{ST} is presumably largest.[4,5] This trend was supported by subsequent studies of diphenylcarbene (DPC),[4,6−9] fluorenylidene (Fl),[10,11] and *p*-biphenylylcarbene (BpCH)[12,13] and by calculations,[14] although exceptions to the rule were later found in halogenated solvents.[15] The halogen effect was attributed to formation of singlet carbene−solvent complexes between the empty *p* orbital of the carbene and lone pairs of electrons on the halogen atom. Complexation with solvent clearly influences both the singlet−triplet separation and the rate of ISC.

SCHEME 1: Reaction Pathways of Methyl 2-Napthyldiazoacetate ($NpCN_2CO_2CH_3$) upon Photolysis



Hess, Kohler, Likhotvorik, Peon, and Platz (HKLPP) reported an ultrafast study of 2-naphthyl(carbomethoxy)carbene ($NpCCO_2CH_3$) using femtosecond time-resolved UV−vis techniques (Scheme 1).[16] The authors reported that the equilibrium mixture of singlet and triplet $NpCCO_2CH_3$ was observed within 50 ps of the laser pulse in acetonitrile (where the singlet is the ground state) and Freon-113 (where the triplet is the ground state).

The sensitivity of the ground-state multiplicity of this carbene to solvent was later discovered by nanosecond time-resolved IR spectroscopy by the preferred conceptual method of direct observation of both spin states at equilibrium. Wang, Yuzawa, Hamaguchi, and Toscano (WYHT) and later Wang, Hadad, and Toscano (WHT) studied the same carbene using nanosecond time-resolved infrared spectroscopy and the predictions of theory and estimated that ΔE_{ST} of $NpCCO_2CH_3$ is 0.2 ± 0.1 kcal/mol in Freon-113[14,17] with a triplet ground state in this solvent. According to the Eisenthal et al. studies, one would predict that the time constant of ISC in $NpCCO_2CH_3$ should be relatively slow (200−1000 ps) in a polar solvent such as acetonitrile, and according to our recent studies a slow ISC rate should also be observed in a halogenated solvent. Thus, there is an apparent contradiction between HKLPP's conclusion of ultrafast ISC in

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the case of $NpCCO_2CH_3$[16] and Eisenthal's work on diphenylcarbene[5,7−9,18,19] and later studies of fluorenylidene[10,11,20−22] and biphenylcarbene[12] and our observation that halogenated solvents can retard ISC by complex formation.[18]

Finally, our laboratory recently studied a closely related carbene *p*-biphenylyl(carbomethoxy)carbene ($BpCCO_2CH_3$) and found that the ISC time constant of this carbene can be quite large, >2 ns,[23] as expected from Eisenthal's rule, which draws more scrutiny to the conclusions of HKLPP.[9,19] This study also led us to reinvestigate the 2-$NpCCO_2CH_3$ system.

The UV spectra of singlet and triplet 2-$NpCCO_2CH_3$ overlap severely as first reported by Zhu, Bally, Stracener, and McMahon (ZBSM) in an argon matrix study.[24] Argon matrix infrared spectroscopy provides more distinct spectroscopic signatures of the singlet and triplet carbenes relative to solution-phase flash photolysis studies in addition to providing greater structural information. It was, in fact, the argon matrix IR work which allowed Toscano and co-workers to analyze the solution-phase, nanosecond time-resolved infrared spectroscopic data in terms of equilibrium populations of singlet and triplet 2-$NpCCO_2CH_3$.[17] Thus, in this work we will apply both ultrafast UV−vis and infrared spectroscopies to measure the ISC rate of 2-$NpCCO_2CH_3$ as we revisit the conclusions of HKLPP.

II. Experimental Section and Computational Details

Methyl 2-naphthyldiazoacetate (2-$NpCN_2CO_2CH_3$) was prepared by the diazo transfer method as described by WYHT[17] and purified by repeated recrystallization to give orange crystals.

Ultrafast UV−vis [25]and infrared absorption[26] measurements were performed using the home-built spectrometer described previously. Samples were prepared in 50 mL of solvent with absorption 1.0 at the excitation wavelength with 1.0 mm optical length. All measurements were performed at room temperature.

DFT and TD-DFT calculations were performed using the Gaussian 03 suite of programs at The Ohio Supercomputer Center.[27] All calculations were performed in the gas phase, and geometries were optimized at the B3LYP/6-31+G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31+G(d) level were utilized to verify that stationary points obtained corresponded to energy minima.[23] The frequencies were scaled by 0.98. TD-DFT calculations were performed using B3LYP/6-31+G(d) on the optimized geometry.

III. Ultrafast UV−vis Spectroscopic Results

III.1. Acetonitrile. Ultrafast photolysis (λ_{ex} = 310 nm) of diazo ester 2-$NpCN_2CO_2CH_3$ in acetonitrile (ACN) produces the transient UV−vis spectra of Figure 1.[28] A broad band is formed and decays within our instrument response function. Following our previous studies,[11−13,15,25,29−31] this band is assigned to a singlet excited state of the diazo ester. As it decays (τ_1 < 300 fs), two new bands centered at 360 and 470 nm are simultaneously formed in excellent agreement with HKLPP.[19] The fast decay (less than 300 fs) is assigned to the decay of the initially formed diazo excited state, which decomposes to form vibrationally hot singlet carbene $^1NpCCO_2CH_3$. This hot singlet carbene decays with a time constant of 14 ps due to vibrational cooling.[32] Both the 360 and 470 nm bands maintain the same intensity from 50 ps to 3 ns. According to HKLPP[19] the carrier of the 470 nm band was assigned to the singlet carbene. HKLPP obtained similar results in Freon-113 but observed sharper bands relative to acetonitrile.[19] In Freon-113, where WYHT[17,20] had by then reported that the triplet is the ground state of the carbene in this solvent, the carriers of the 360 nm band were reasonably attributed to a mixture of both spin states.[16] Our recent ultrafast studies on a related diazo ester, *p*-$BpCN_2CO_2CH_3$, revealed that the triplet carbene derived from this diazo compound was not formed within 2 ns of the laser pulse in acetonitrile,[23] which is inconsistent with HKLPP's report of ultrafast ISC for 2-$NpCN_2CO_2CH_3$. As the change from biphenyl to naphthyl is not expected to induce such a large change in the carbene ISC rate, we must consider reassigning both bands (360 and 470 nm) in acetonitrile (and Freon-113) solely to the singlet carbene $^1NpCCO_2CH_3$. In the case of $BpCCO_2CH_3$, the singlet has only one absorption band (λ_{max} = 350 nm) within our wavelength detection window and it is well separated from the triplet carbene absorption (λ_{max} = 320 nm).[23] Unfortunately, in $NpCCO_2CH_3$ both singlet and triplet carbene absorb at 360 nm. The matrix studies by ZBSM indicated that $^3NpCCO_2CH_3$ has a strong absorption band at 360 nm, and the singlet carbene has a broad absorption at 340 nm and in the region of 400−450 nm.[24] TD-DFT calculations predict that $^1NpCCO_2CH_3$ absorbs at both 354 and 409 nm (f = 0.141 and 0.071, respectively), in good agreement with the assignment of both the promptly formed 360 and 470 nm bands to $^1NpCCO_2CH_3$ (Table S1, Supporting Information). Further, compelling evidence for this assignment will be given in the ultrafast infrared section (section IV).

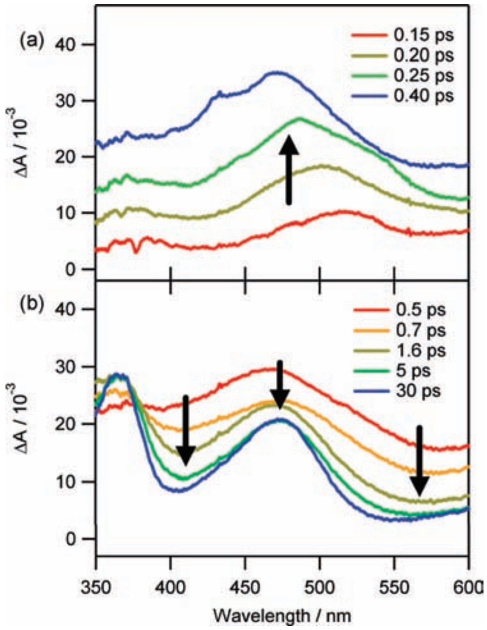

Figure 1. Transient spectra obtained by photolysis of 2-$NpCN_2CO_2CH_3$ in acetonitrile. Spectra were generated by ultrafast laser flash photolysis (LFP) (310 nm) with time windows of (a) 0.15−0.40 and (b) 0.5−30 ps.

III.2. Cyclohexane. In cyclohexane the singlet carbene $^1NpCCO_2CH_3$ absorption intensity decays to 50% of its initial value at 3 ns after the laser pulse (Figure 2). We cannot accurately determine the singlet carbene lifetime in this solvent, but our best estimate is ~2 ns (Figure S1, Supporting Information). WHT performed calculations on the solvent dependence of the $NpCCO_2CH_3$ singlet−triplet energy gap[14] and found that in nonpolar solvents such as cyclohexane that the ground state is triplet while in polar solvent the singlet state is favored. The ultrafast UV−vis results show that $^1NpCCO_2CH_3$ carbene decays to the ground-state triplet in cyclohexane and that in acetonitrile no decay is seen. This is consistent with this calculation[14] and indicates that in cyclohexane the carbene ester has a triplet ground state but that in acetonitrile $^1NpCCO_2CH_3$ is the ground state as deduced by WHT.[14] Our study of $^1BpCCO_2CH_3$ showed the same trend.[23]

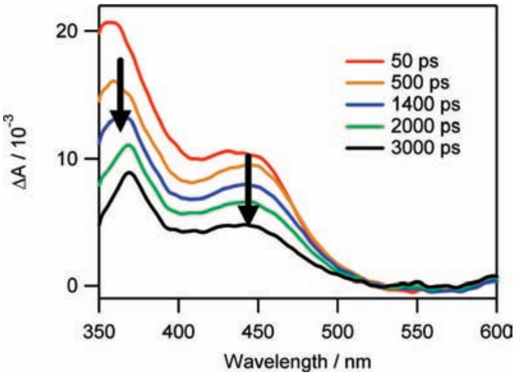

Figure 2. Transient spectra obtained by photolysis of 2-$NpCN_2CO_2CH_3$ in cyclohexane. Spectra were generated by ultrafast LFP (310 nm) with a time window of 50−3000 ps.

III.3. Halogenated Solvents. In Freon-113, the singlet carbene $^1NpCCO_2CH_3$ is produced from the diazo excited state (Figure S2, Supporting Information) within the laser pulse (0.3 ps), and then the carbene spectral evolution reveals the typical narrowing and blue shifting behavior associated with vibrational cooling with a time constant of 31 ps (Figure S3, Supporting Information).[32] $^1NpCCO_2CH_3$ does not decay up to 3 ns in this solvent and in acetonitrile, which is consistent with HKLPP's observation that spectral evolution ceases after 50 ps.[16] WHT derived a ΔE_{ST} of $NpCCO_2CH_3$ as 0.2 kcal/mol in Freon-113 based on their nanosecond time-resolved IR data and ZBSM's matrix studies. WHT's study monitored the C═O stretch of both singlet and triplet $NpCCO_2CH_3$ in Freon-113. They assumed that the ratio of the IR oscillator strengths for singlet and triplet $NpCCO_2CH_3$ in Freon-113 are the same as that determined in the cryogenic matrix and concluded that triplet $NpCCO_2CH_3$ is the ground state in Freon-113 and favored by 0.2 kcal/mol. We favor a singlet ground state for $NpCCO_2CH_3$ in Freon-113 because the singlet carbene population shows no decay over 3 ns, as in acetonitrile. It is clear that the triplet state of $NpCCO_2CH_3$ must be within a few hundred calories/mole of the energy of the singlet ground state; thus, our disagreement with WHT is truly over very small numbers. In support of our interpretation we note that our recent studies show that halogenated solvents can more effectively stabilize a singlet carbene through complexation than its triplet counterpart.[15]

In chloroform the diazo ester excited state $NpCN_2CO_2CH_3$ grows and decays within the laser pulse (0.3 ps, Figure S4). The carbene $^1NpCCO_2CH_3$ is formed with an apparent time constant of 21 ± 6 ps due to vibrational cooling, and no spectral evolution is observed after 100 ps (Figure S5, Supporting Information).

III.4. Alcohols. In methanol, the transient absorption bands of $^1NpCCO_2CH_3$ at 370 and 490 nm undergo a red shift between 3 and 20 ps (Figure 3). This shift is not due to vibrational cooling, which typically involves a blue shift.[32] Following our previous studies of *p*-biphenylyltrifluoromethylcarbene, this observation is interpreted as the dynamics of carbene solvation.[29] Both bands decay with the same lifetime of 189 ps in methanol and 385 ps in methanol-*O-d*, respectively (Figure S6, Supporting Information). There is no evidence that reaction of the carbene with methanol leads to a significant yield of cation. Thus, the kinetic isotope effect (KIE) of 2.1 indicates that the carbene primarily reacts with methanol by a concerted insertion into the O−H bond. Similarly, $^1BpCCO_2CH_3$ has a lifetime of 185 ps in methanol and the KIE is 2.3,[26] which is in excellent agreement with this result.

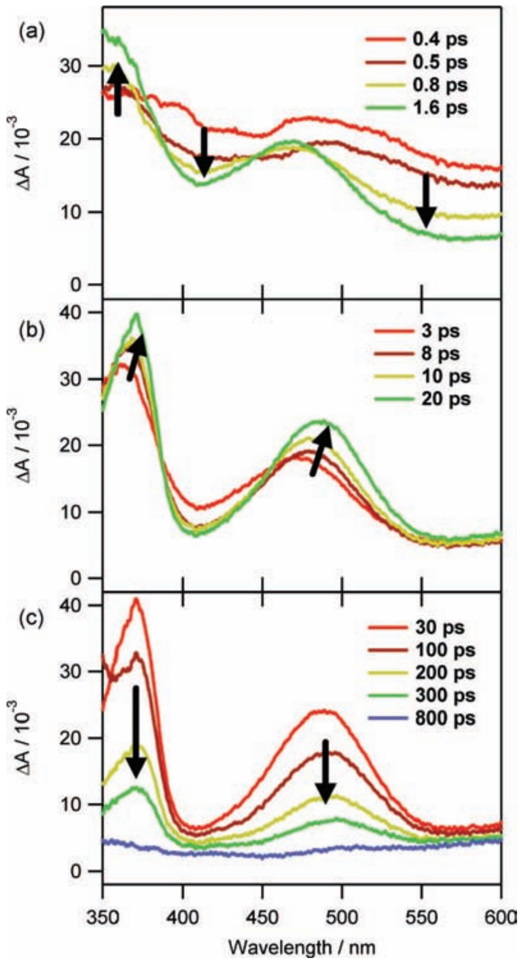

Figure 3. Transient spectra obtained by photolysis of 2-$NpCN_2CO_2CH_3$ in methanol. Spectra were generated by ultrafast LFP (310 nm) with time windows of (a) 0.4−1.6, (b) 3−20, and (c) 30−800 ps.

A different story is told in α,α,α-trifluoroethanol (TFE). In the acidic solvent, the decay of $^1NpCCO_2CH_3$ is accompanied by growth of a transient absorption at 415 nm (Figure S7, Supporting Information). This transient absorption is attributed to cation $NpCHCO_2CH_3^+$. TD-DFT calculations predict that the cation absorbs at 362 nm ($f = 0.42$, Table S1, Supporting Information), in fair agreement with our experiment. The lifetime of $^1NpCCO_2CH_3$ is 27 ps probed at 370 nm (Figure S8, Supporting Information). The lifetime of $NpCHCO_2CH_3^+$ in TFE is too long to be accurately measured on our spectrometer, and our best estimate is 2 ns. Thus, we conclude that the lifetime of singlet carbene $^1NpCCO_2CH_3$ is controlled by O−H insertion in methanol and cation formation in TFE.

IV. Ultrafast IR Spectroscopy

Ultrafast photolysis ($\lambda_{ex} = 270$ nm) with infrared detection was performed to monitor the 1560−1670 cm^{-1} region in chloroform (Figure 4a), acetonitrile (Figure 4b), cyclohexane (Figure 4e), and Freon-113 (Figure S9, Supporting Information). In chloroform three bands at 1584, 1620, and 1645 cm^{-1} were observed within 1 ps after the laser pulse (Figure 4a). The 1645 cm^{-1} band is very broad and may considerably overlap with the 1620 cm^{-1} band. Similar bands were also observed in Freon-113 (Figure S9, Supporting Information) and acetonitrile (Figure 4b); the differences are that in acetonitrile the 1584 cm^{-1} band was not observed because it is in the solvent obscured region of acetonitrile and that the 1645 and 1620 cm^{-1} bands are red

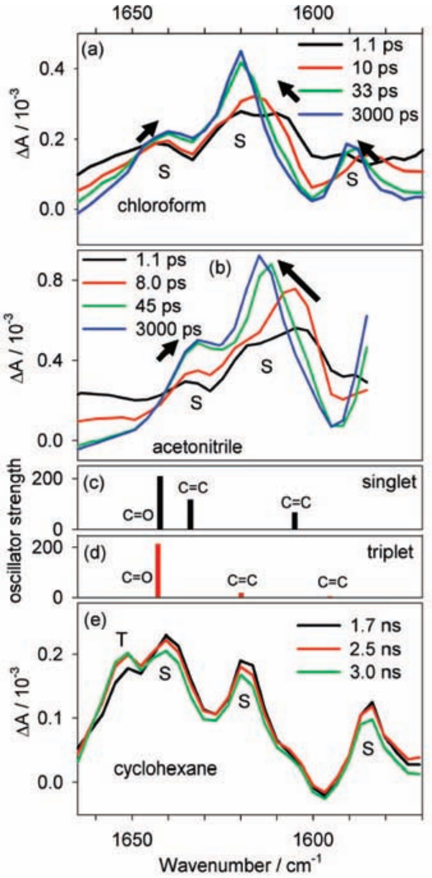

Figure 4. Transient IR spectra obtained by ultrafast ($\lambda_{ex} = 270$ nm) photolysis of 2-$NpCN_2CO_2CH_3$ in (a) chloroform, (b) acetonitrile, and (e) cyclohexane along with the predicted spectra of the (c) singlet and (d) triplet carbene by B3LYP/6-31+G(d) and scaled by 0.98.

shifted by about 7 and 3 cm^{-1}, respectively. In these three solvents (chloroform, Freon-113, and acetonitrile) all the bands grow and narrow within a few tens of picoseconds and then maintain the same intensity up to 3 ns. However, in cyclohexane (Figure 4e), the decay of the three bands at 1645, 1620, and 1584 cm^{-1} is accompanied by growth of a 1655 cm^{-1} centered band. On the basis of our DFT calculations (Figure 4c and 4d) and the studies of ZBSM,[24] WYHT,[17] and WHT,[14] the three bands observed in chloroform, Freon-113, and acetonitrile are assigned to singlet carbene $^1NpCCO_2CH_3$ (1645 cm^{-1} C=O stretch, 1620 cm^{-1} aromatic C=C stretch, 1584 cm^{-1} aromatic C=C stretch). The 1655 cm^{-1} band observed in cyclohexane is assigned to triplet carbene $^3NpCCO_2CH_3$ (C=O stretch).

ZBSM[24] reported that the singlet carbene has a typical triad of absorption bands at 1641, 1626, and 1591 cm^{-1} in an argon matrix. Both the typical triad absorption and the relative intensities agree very well with the singlet carbene bands observed in this study. Thus, in chloroform all three bands can be confidently assigned to $^1NpCCO_2CH_3$. Similarly, the three bands (1645, 1620, and 1584 cm^{-1}) observed in Freon-113 are also assigned to $^1NpCCO_2CH_3$ (Figure S9a, Supporting Information).

We note that WYHT observed three bands (1650, 1620, and 1584 cm^{-1}) in the singlet−triplet carbene mixture (50 ns after the laser pulse) in Freon-113 using nanosecond IR spectroscopy.[17] The 1620 (aromatic C=C stretch) and 1584 cm^{-1} (aromatic C=C stretch) bands were again assigned to $^1NpCCO_2CH_3$, while the 1650 cm^{-1} band (C=O stretch) is assigned to the $^3NpCCO_2CH_3$ by them (Figure S9, Supporting Information).[14,17] WYHT reported that the singlet carbene C=O stretch band at 1641 cm^{-1} observed by ZBSM in an argon matrix was not observed as a distinct band in their nanosecond IR study in Freon-113, a result they attributed to its low intensity and the relative broadness of solution IR bands and limitation of their spectral resolution (8 cm^{-1}). As we observed the triad peaks of the singlet carbene in Freon-113 with similar resolution (∼7 cm^{-1}), we believe the 1650 cm^{-1} band observed by WYHT is actually that of the singlet C=O stretch at 1645 cm^{-1}. Although we cannot completely rule out a triplet contribution to the 1645 cm^{-1} band observed within a few picoseconds of the laser pulse (Figure S9a, Supporting Information), we think the triplet carbene concentration is negligible a few picoseconds after the laser pulse for the following reasons. First, the 1645 cm^{-1} band observed in this study is broader and lower in intensity than the 1620 cm^{-1} (aromatic C=C stretch) band, but the 1650 cm^{-1} band observed by WYHT is much sharper and has higher intensity than the 1620 cm^{-1} (Figure S9b, Supporting Information) band. Thus, these two bands are considerably different. Second, the 1645 cm^{-1} band is formed along with the other two bands (1620 and 1584 cm^{-1}) within 1 ps after laser pulse, and they all grow and narrow over a few tens of picoseconds and maintain the same intensity up to 3 ns. This is consistent with our ultrafast UV−vis (Figure S2, Supporting Information) and the HKLPP[16] report that spectral evolution is complete 50 ps after the laser pulse. Thus, this is consistent with assigning the promptly formed IR bands to the singlet carbene. Third, our recent study on $BpCCO_2CH_3$ indicated that the triplet carbene is not observed 2 ns after laser pulse. Thus, we do not think it reasonable that the triplet carbene $^3NpCCO_2CH_3$ is formed within a few tens of picoseconds. We conclude that the promptly formed 1645 cm^{-1} band observed in Freon-113 is purely that of the singlet and that singlet carbene is ground state in chloroform, Freon 113, and acetonitrile. Our data permits the possibility that a small amount of triplet carbene is present at equilibrium and contributes to the IR spectrum recorded by WYHT (Figure S9b, Supporting Information).

In cyclohexane we observed the decay of singlet carbene and growth of triplet carbene at 1655 cm^{-1}. This is consistent with our ultrafast UV−vis observation that the singlet carbene decays by 50% within 3 ns (Figure 2). ZBSM[24] observed triplet carbene at 1660 cm^{-1} in argon, in good agreement with our results. The decay of singlet to triplet carbene indicates that in cyclohexane the triplet carbene is the ground state. This is consistent with the nanosecond IR spectroscopy and calculations of WHT.[14]

We noticed that the 1620 and 1584 cm^{-1} (aromatic C=C stretch) bands grow and narrow with a blue shift over a few tens of picoseconds, but the 1645 cm^{-1} (C=O) band shifts to the red in chloroform (Figures 4a and S10a (Supporting Information)). The same trend is also observed in Freon-113 (Figure 9a, Supporting Information) and acetonitrile (Figure 4b). We posit that the different behaviors of the three bands originate from three different vibrational modes. A blue shift of promptly formed species in ultrafast infrared spectroscopy is very common and characteristic of vibrational cooling.[25,30,32−35] The vibrational cooling time constant as probed at 1620 cm^{-1} is 28 ps, which correlates very well with the time constant of carbene vibrational cooling (21 ± 6 ps) determined by ultrafast UV−vis spectroscopy in the same solvent. The observation of a red shift, however, is very rare in ultrafast infrared spectroscopy. It is possible that the red shift is an indication of carbene solvation that is specific to the carbonyl stretch.[36,37] This would be reminiscent of our UV−vis studies of this work and with our study of an aryl trifluoromethyl carbene.[31] Such solvation effects are usually much pronounced in alcohols but are modest in chloroform, which argues against this interpretation.

It is well known that singlet carbene ^{1}NpCCO$_2$CH$_3$ has a preferred geometry in which the carbonyl group is perpendicular to the naphthalene ring while the triplet carbene ^{3}NpCCO$_2$CH$_3$ has a planar molecular geometry, the same as that in the precursor diazo ester 2-NpCN$_2$CO$_2$CH$_3$.[17,26,38] Thus, we postulate that upon excitation the excited state of diazo ester 2-NpCN$_2$CO$_2$CH$_3$ in the Franck−Condon geometry decomposes into singlet carbene 2-NpCN$_2$CO$_2$CH$_3$ within 300 fs. The initially formed singlet carbene 2-NpCN$_2$CO$_2$CH$_3$ would have the same planar geometry as in its precursor in which the carbene lone pair is coplanar with the carbonyl group. This geometry is not stable and relaxes to the more stable orthogonal geometry in which the carbene lone pair conjugates with the π^* orbital of the C═O bond. As rotation to the preferred geometry proceeds the C═O band would become weaker as a result of the conjugation with the antibonding orbital. Consequently, the force constant of the bond becomes weaker and the C═O bond becomes elongated. This explains the uncommon behavior of the red shift of the C═O stretching band at 1645 cm^{-1}. Our DFT calculations predict that the planar singlet carbene is a transition state with a C═O stretch at 1667 cm^{-1} and that the C═O stretch of the orthogonal singlet carbene occurs at 1643 cm^{-1} (Table S2, Supporting Information); indeed, the C═O stretch undergoes a red shift on relaxation to the minimum, consistent with our observations. The calculations also indicate that the carbene C═O stretching band occurs at a lower frequency compared to the C═O stretching band of the diazo ester precursor. The calculated carbene C═O bond (1.231 Å) is longer than the diazo ester C═O bond (1.219 Å) because donation of carbene lone pair into the C═O π^* orbital weakens this bond in a manner consistent with the stretching frequencies.

Rapid internal conversion from an excited state of a diazo compound to the ground state reduces the quantum yield of irreversible photochemistry. Ultrafast IR can provide quantitative information in this regard. We observed that the ground state of 2-NpCN$_2$CO$_2$CH$_3$ was partially recovered, after excitation, by monitoring at the carbonyl (1704 cm^{-1}, Figure S10, Supporting Information) and diazo (2089 cm^{-1}, Figure S11, Supporting Information) bleaching bands. The negative peak observed at 1704 cm^{-1} upon excitation is due to the depletion of ground state 2-NpCN$_2$CO$_2$CH$_3$ by the laser pulse (Figure S10, Supporting Information). This negative peak partially recovers its original intensity with a time constant of 16 ps and stays constant after 50 ps with ~60% of the original intensity. Thus, ~40% of the originally excited diazo molecules return to the ground state via internal conversion, indicating a quantum yield of denitrogenation of 0.6. Similarly, a recovery ratio of 48% is observed by the diazo bleaching band (Figure S11, Supporting Information, quantum yield of denitrogenation of 0.52) in fair agreement. These results indicate that internal conversion (IC) is an important pathway of the decay of excited state 2-NpCN$_2$CO$_2$CH$_3$, which competes with carbene formation. Since the diazo excited-state lifetime is less than 300 fs as shown by ultrafast UV−vis spectroscopy, the 16 ps time constant obtained from growth of the carbonyl bleaching band at 1704 cm^{-1} and the diazo bleaching band at 2089 cm^{-1} is assigned to vibrational cooling of the vibrationally hot ground state 2-NpCN$_2$CO$_2$CH$_3$. In acetonitrile and Freon-113 similar results were obtained.

V. Conclusions

The ultrafast UV−vis studies of this work confirm and complement the work of HKLPP.[16] However, the assignment of one transient absorption band is changed from a mixture of singlet and triplet carbene to that of purely singlet carbene in Freon-113. Ultrafast IR studies in chloroform, acetonitrile, and Freon-113 confirm that only singlet ^{1}NpCCO$_2$CH$_3$ can be observed in these solvents 3 ns after the laser pulse and also that the concentration of the triplet state is negligible in these solvents. Thus, the triplet carbene cannot be observed by ultrafast UV−vis spectroscopy 50 ps after the laser pulse in these two solvents, contrary to HKLPP's conclusion.[16] It is now clear that the UV−vis transient absorption bands observed prior to 3 ns after the laser pulse must be assigned entirely to ^{1}NpCCO$_2$CH$_3$. In addition, our studies show that ~50% of the excited-state diazo precursor molecules produced in a laser pulse return to the ground state via internal conversion. Excitation of planar diazo ester in chloroform produces a planar excited state, which we posit fragments to make the planar singlet carbene ester. The planar singlet relaxes to the preferred perpendicular singlet over a few tens of picoseconds, as evidenced by the red shift of the carbonyl stretching vibration.

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Supporting Information Available: Figures S1−S11 and Tables S1−S7 and complete reference 27. This material is available free of charge via the Internet at http://pubs.acs.org.

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