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Direct Observation of Carbene and Diazo Formation from Aryldiazirines by Ultrafast Infrared Spectroscopy

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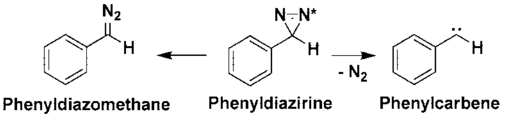
Diazirines are useful precursors for mechanistic studies of carbenes.[1,2] The photoisomerization of diazirines to diazo compounds and their light induced fragmentation to form carbenes (Scheme 1) has motivated matrix isolation and nanosecond (ns) time-resolved spectroscopic studies.[3]

Scheme 1. Photochemical Reactions of Phenyldiazirine



Ultrafast time-resolved (fs, ps) laser flash photolysis (LFP) studies with UV−vis and IR detection are needed to understand early events in the photochemistry of carbene precursors. We have recently reported the use of ultrafast UV−vis spectroscopic studies of arylhalodiazirines[4] and IR studies of carbonyl diazo compounds and their related carbenes.[5] Herein, the application of ultrafast IR spectroscopy to the study of the photochemistry of simple aryldiazirines and the observation of singlet carbenes is described.

Ultrafast LFP (270 nm) of chlorophenyldiazirine in chloroform produces the transient IR spectrum shown in Figure 1. Two broad bands are observed within a few picoseconds of the laser pulse. These bands narrow and shift to the blue over 100 ps, then center at 2040 and 1583 cm^{-1}, and do not decay within the detection window (3 ns).

These transient absorption bands can be readily assigned to the diazo band of chlorophenyldiazomethane ($PhCN_2Cl$) and a C═C vibrational band of singlet chlorophenylcarbene (^1PhCCl), respectively, on the basis of matrix IR[3] and solution phase ns time-resolved IR[6] spectroscopic studies and computational[7] work. The blue shift and band narrowing are characteristic of vibrational cooling (VC) of intermediates born with excess vibrational energy.[8] The diazo band integration reveals that the majority of diazo compound is formed instantaneously (<1 ps, Figure S1). The growth of carbene ^1PhCCl can not be accurately determined because the C═C band of hot carbene $^1PhCCl^{\#}$ severely overlaps bleaching centered at 1568 cm^{-1}. We have reported that ultrafast photolysis (350 nm) of chlorophenyldiazirine produces a zwitterionic species, detected by UV−vis spectroscopy, which undergoes biexponential decay. The fast process has a time constant of 0.9 ps in acetonitrile.[4,9] In the interest of economy we associate the growth of the diazo compound with the "fast" decay of the zwitterion (Supporting Information (SI), Scheme S1).

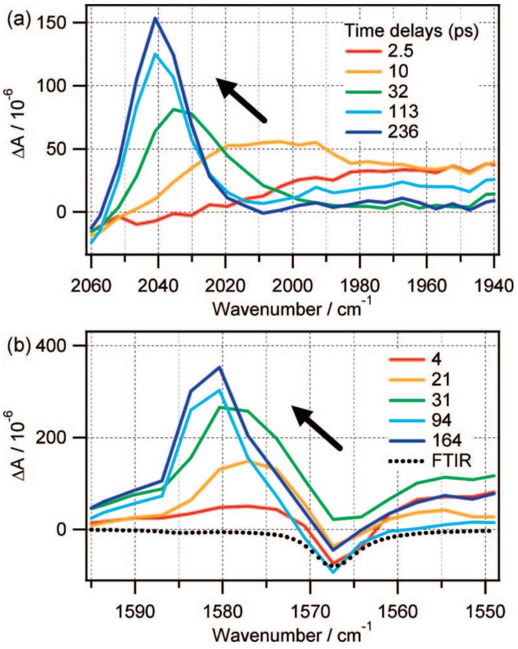


Figure 1. Transient IR spectra produced by photolysis of chlorophenyldiazirine (λ_{ex} = 270 nm) in chloroform at selected time delays; (a) The diazo band in the region 2060−1940 cm^{-1} and (b) the carbene band in the region 1600−1550 cm^{-1}.

Ultrafast photolysis of phenyldiazirine in acetonitrile produces the transient IR spectra shown in Figure S2 (SI). A broad band in the region 1900−2100 cm^{-1} was formed within a few picoseconds of the laser pulse. It narrows and shifts to the blue at 2064 cm^{-1} over ∼100 ps. This band does not decay within the detection window (3 ns) and is confidently assigned to the diazo band of phenyldiazomethane which is born with excess energy and undergoes VC.

Another transient band, centered at 1582 cm^{-1}, was observed in the region 1640−1550 cm^{-1} in chloroform (Figure 2). This initially broad band is also formed within a few picoseconds of the laser pulse, and it grows and narrows with a blue shift and reaches its maximum intensity at 50 ps, post laser pulse. This band (monitored at 1582 cm^{-1}) decays with a lifetime of 414 ps in chloroform (SI, Figure S3). Three negative bands at 1625, 1608, and 1580 cm^{-1} were also observed immediately after the laser pulse due to depletion of the ground-state diazirine. The carrier of the transient absorption band at 1582 cm^{-1} can be assigned to singlet phenylcarbene (^1PhCH). DFT calculations predict that singlet ^1PhCH has a C═C vibration at 1571 cm^{-1} (SI, Table S1), in good agreement with experiment. This is also consistent with the observed singlet chlorophenylcarbene (^1PhCCl) C═C vibration at 1583 cm^{-1} and singlet $^1NpCCO_2CH_3$ which has a C═C vibrational band at 1584 cm^{-1}.[5] This is the first direct spectroscopic observation of singlet ^1PhCH, and it provides the first direct measurement of its lifetime.

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Matrix ESR[10] and infrared[11] spectroscopy and computational studies[12−14] confirm that PhCH has a triplet ground state. Thus, the decay of singlet ^{1}PhCH in this solvent will lead to either triplet ^{3}PhCH or a chlorobenzyl radical (PhCHCl) produced by Cl abstraction from chloroform. DFT calculations predict that triplet ^{3}PhCH has its C═C vibration at 1543 cm^{-1} and the radical PhCHCl C═C band will be observed at 1550 cm^{-1}. Neither triplet ^{3}PhCH nor radical PhCHCl was observed in this experiment, presumably because of their low intensity (calculated to be 0.2 for ^{3}PhCH and PhCHCl), compared with that of singlet ^{1}PhCH (99.3) (SI, Table S1).

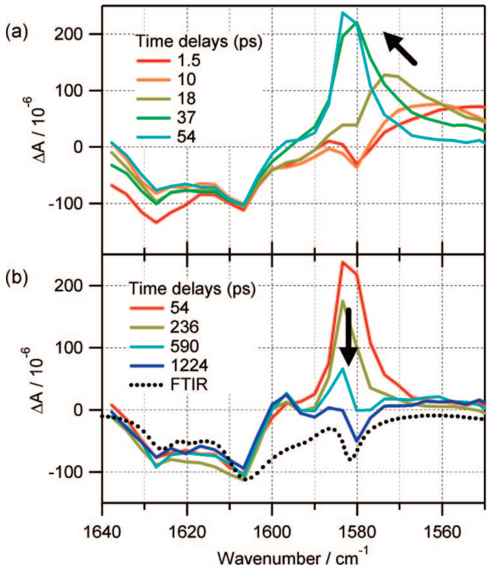

Figure 2. Transient IR spectra produced by photolysis of phenyldiazirine (270 nm) in chloroform. (a) Formation of the carbene ^{1}PhCH band, and (b) decay of carbene ^{1}PhCH band at 1582 cm^{-1}.

Phenylcarbene undergoes rearrangement to form 1,2,4,6-cycloheptatetraene under certain conditions, and this molecule absorbs at 1842 cm^{-1}.[15,16] We did not observe the formation of this species by ultrafast IR spectroscopy.

Phenylmethyldiazirine (PhCN$_2$CH$_3$) was also studied by ultrafast IR spectroscopy, but the intensity of the carbene vibrational bands is greatly reduced (SI, Figure S4a) relative to the parent system. This may result from lower IR oscillator strength (SI, Figure S4b).

Calculations predict that *p*-biphenylcarbene (^{1}BpCH) has a stronger C═C vibrational band than does ^{1}PhCH (SI, Table S1); thus we have studied the photochemistry of *p*-biphenyldiazirine (BpCN$_2$H) and *p*-biphenylmethyldiazirine (BpCN$_2$CH$_3$) in the same fashion (SI, Figure S5) as the parent system. The transient spectra of both the ^{1}BpCH and ^{1}BpCCH$_3$ singlet carbenes are observed and are stronger than the ^{1}PhCH and ^{1}PhCCH$_3$ C═C bands as predicted.

The ^{1}BpCH carbene band integration (SI, Figure S6) reveals that the majority of ^{1}BpCH is formed within a few ps of the laser pulse, but the growth time constant can not be accurately determined. Both ^{1}BpCH and ^{1}BpCCH$_3$ carbenes are formed with excess energy and undergo VC over 60 ps and then decay with lifetimes of 599 and 667 ps, respectively, recorded at 1585 cm^{-1} (SI, Figures S6 and S7a). The singlet ^{1}BpCH and ^{1}BpCCH$_3$ carbene lifetimes are both longer than that of ^{1}PhCH (414 ps), indicating a *para*-phenyl kinetic stabilization effect on the singlet carbene. As the decay times of relaxed ^{1}BpCH and ^{1}BpCCH$_3$ are similar it is clear that the 1,2 H shift does not control the disappearance of these singlet carbenes in chloroform.[17] The lifetime of carbene ^{1}BpCH in chloroform is longer than that in dichloromethane (382 ps, SI, Figure S7b) and much longer than that in cyclohexane (77 ps).[18] Singlet carbene lifetimes are known to be extended by halogenated solvents due to complexation of the empty *p* orbital of the carbene with nonbonding electron pairs of solvent atoms which accounts for the data obtained in this study.[19] In two highly reactive solvents, methanol-O-*d* and cyclohexene, the ^{1}BpCH carbene lifetimes are reduced to 19 and 38 ps (SI, Figure S7c,d) respectively, consistent with the assignment of the transient IR band to the singlet carbene.

Biphenyldiazomethane formation was also observed by ultrafast IR spectroscopy (SI, Figure S8), and the diazo band integration indicates that the majority of the diazo compound is formed in the isomerization process within a few picoseconds of the laser pulse, consistent with the results obtained with chlorophenyldiazirine.

In conclusion, ultrafast IR spectroscopy is a valuable tool for studying the photochemistry of aryldiazirines and allows study of the dynamics of its photoisomerization to diazo compounds and the first direct observation of singlet phenylcarbene. Both the diazo compound and the majority of carbene are formed within a few picoseconds of the laser pulse.

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Supporting Information Available: Descriptions of the ultrafast spectrometer, the zwitterion structure (Scheme S1), details of calculations (Table S1), and the transient spectra and kinetics (Figures S1–S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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