J. Phys. Chem. A **2001,** *105,* 8413−8416

Matrix and Time-Resolved Infrared Spectroscopy of Chloro-*p*-nitrophenylcarbene and Related Species

Meng-Lin Tsao, Zhendong Zhu, and Matthew S. Platz*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

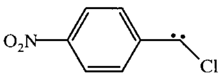
Received: May 14, 2001; In Final Form: July 11, 2001

Chloro-*p*-nitrophenyldiazirine (**2**) was deposited in an argon matrix. Photolysis (350 nm) releases chloro-*p*-nitrophenylcarbene (**1**) as a persistent species. The IR and UV−vis spectra of carbene **1** were obtained, and the IR spectrum was adequately simulated by density functional theory (DFT) calculations. The carbene has an intense IR vibration at 1206 cm^{-1} involving the carbene carbon and aromatic ring carbon. This band was observed by TRIR spectroscopy upon laser flash photolysis (355 nm) of **2** in heptane at ambient temperature. The presence of benzene did not influence the frequency of this vibration. The carbene lifetime as measured by TRIR spectroscopy (≈400 ns) is consistent with previous LFP studies utilizing UV−vis detection. Upon LFP of **2** in CCl_4 or $CF_2ClCFCl_2$ the photogenerated carbene abstracts chlorine atom from solvent to form α,α-dichloro-*p*-nitrobenzyl radical with a TRIR band at 1316 cm^{-1}. Upon LFP of **2** in acetonitrile, acetone, methyl acetate, pyridine, and tetrahydrofuran ylide species were produced. The ylides had similar TRIR spectra with bands at 1584, 1504, and 1312 cm^{-1}.

I. Introduction

Carbenes are important intermediates in organic chemistry.[1] As a consequence, they have been extensively studied as transient species in the liquid phase by laser flash photolysis methods with UV−vis detection.[2] Carbenes have also been studied as persistent species in solid argon at cryogenic temperatures.[3]

There has been recent dramatic progress in the development of time-resolved infrared (TRIR) spectroscopy. Prior to initiating studies of new carbenes by the TRIR technique, we thought it prudent to apply this methodology to a relatively well understood system. We also hoped to probe carbene−solvent interactions using IR spectroscopy, a potentially more sensitive probe than transient UV−vis spectroscopy. Herein we are pleased to report our TRIR investigation of chloro-*p*-nitrophenylcarbene (**1**) and radical and ylide species derived from it.



1

II. Experimental Section

Chloro-*p*-nitrophenyldiazirine (**2**) was synthesized as described in the literature.[4]

Time-Resolved Infrared (TRIR) Studies. TRIR experiments were conducted with a JASCO TRIR-1000 dispersive-type IR spectrometer with 16 cm^{-1} resolution following the method described in the literature.[5,6] Briefly, a reservoir of sample solution (10 mL of 8 mM of chloro-*p*-nitrophenyl diazirine with or without 10−500 mM of acetonitrile, acetone, methyl acetate, tetrahydrofuran, or pyridine) is continually circulated between two calcium fluoride salt plates with 0.5 mm path length. The sample was excited by 355 nm flash pulses of an Nd:YAG laser (97 Hz repetition rate, 0.5−0.7 mJ/pulse power), which is crossed with the broadband output of a $MoSi_2$ IR source (JASCO). The intensity change of the IR light induced by photoexcitation is monitored as a function of time by an MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1), with a 50 ns rise time amplified with a low-noise NF Electronic Instruments 5307 differential amplifier and digitized with a Tektronix TDS784D oscilloscope. The TRIR spectrum is analyzed by the IGOR PRO program (Wavematrics Inc.) in the form of a difference spectrum, $\Delta A_t = -\log(1 + \Delta I_t/I)$, where ΔI_t is the intensity change induced by photoreaction at time t, and I is the IR intensity with the sample without photoexcitation. Thus, depletion of reactant and formation of transient intermediates or products lead to negative and positive signals, respectively.

Matrix Isolation Spectroscopy. The diazirine precursor **2** was placed in a glass U tube that was directly connected to a closed cycle cryogenic system cooled by helium (Air Products). Argon gas blew over the precursor and condensed on the surface of a CsI window. The argon matrix formed was maintained at 14 K during the entire experiment. UV−vis spectra were measured with a Lambda 6 UV−vis spectrophotometer, and the IR spectrum was recorded with an FT-IR 2000 Perkin-Elmer spectrometer with 2 cm^{-1} resolution. Ray-O-Net 350 nm lamps were used to photolyze the sample and the resulting IR and UV−vis spectra were recorded sequentially in each step of the photolysis cycle.

Density Functional Theory Calculations. Geometries of singlet chloro-*p*-nitrophenylcarbene (**1**) and its radical (**3**) and ylide (**4**−**8**) derivatives were fully optimized at the B3LYP level of theory using the 6-31G* basis set.[7] Vibrational frequencies of these species were performed at the same level, and no imaginary frequencies were found. All the calculations were performed using the GAUSSIAN 98 program.[8]

III. Results and Discussion

Chloro-*p*-nitrophenyldiazirine (**2**) was deposited in an argon matrix at 14 K. Photolysis (350 nm, 6 h) led to disappearance

10.1021/jp011841a CCC: $20.00

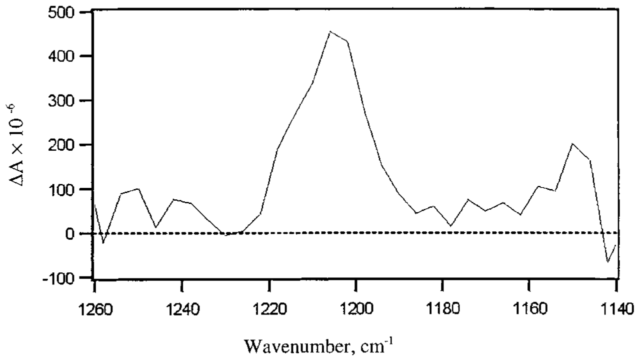
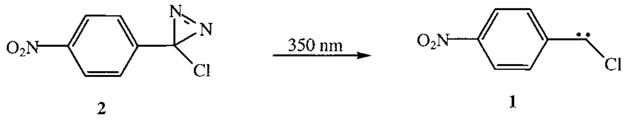


Figure 1. TRIR spectrum produced upon LFP (355 nm) of **2** from 0 to 200 ns in heptane at ambient temperature.

of the IR and UV−vis of the diazirine and the appearance of new spectral features summarized in the Supporting Information. These new features will be assigned to carbene **1** on the basis of calculations and by analogy to related compounds.



The IR spectrum of the product of photolysis of **2**, given in Supporting Information Figure S1(A), is in agreement with the previous study of Wierlacher et al.[9] The vibrational spectrum of carbene **1** calculated using density functional theory (DFT) at the B3LYP level of theory using the 6-31G* basis set is shown in Figure S1(B) after application of a scaling factor of 0.96. The agreement is satisfactory. The carbene has an intense absorption at 1206 cm^{-1}, in a spectral region where the diazirine absorbs weakly. This vibration largely (∼95%) consists of a C−C stretch involving the carbene carbon and aromatic ring (see Table S2, Supplementary Information). Unsubstituted chlorophenylcarbene has a similar absorption band at 1225 cm^{-1}.[10] The large band of carbene **1** at 830 cm^{-1} is the mixing of the bending of the nitro group and the asymmetric stretching of C−C−Cl.

The UV−vis spectrum of the product of photolysis of **2** has a strong absorption at 320 nm, in reasonable agreement with the reported absorption maximum of carbene **1** observed in laser flash photolysis experiments.[4,11] In addition to the strong absorption in the UV region there is a weak broad band in the visible above 700 nm. This is a characteristic band of closed shell singlet carbenes. Chlorophenylcarbene, for example, absorbs at 700 nm. This band is essentially a HOMO−LUMO transition in which an electron is promoted from the in-plane hybrid orbital to the out-of-plane p orbital.[12]

Time-Resolved Infrared Spectroscopy. The IR band of **1** at 1206 cm^{-1} is attractive for TRIR spectroscopy because it is an intense band unique to the carbene system. Laser flash photolysis (LFP) of **2** in heptane produces the TRIR spectrum of Figure 1, which clearly shows the presence of the 1206 cm^{-1} vibration. The carrier of this signal decays exponentially with a time constant of 400 ns at ambient temperature, a result consistent with LFP studies of carbene **1** with UV−vis detection.[4,11] The lifetime of **1**, measured at 1210 cm^{-1} in CCl_4, is slightly sensitive to the presence of oxygen. The observed rate constant of disappearance of the carbene increases ($k = 1.5 \times 10^6$ and 1.8×10^6 s^{-1}) when bubbling the solution with argon and oxygen, respectively, as expected from published reports.[2,11c]

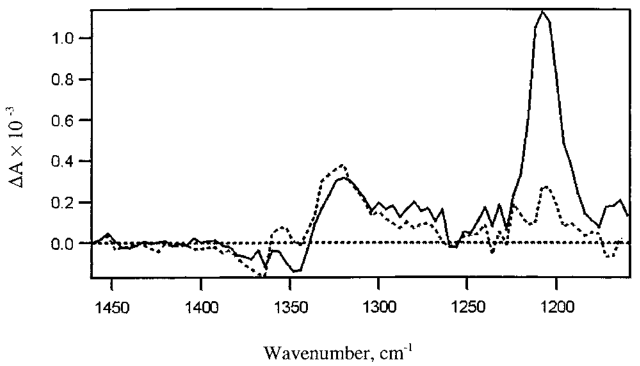


Figure 2. TRIR spectrum produced upon LFP (355 nm) of **2** from 0 to 500 ns (solid line) and 1500 to 2000 ns (dashed line) in CCl_4 at ambient temperature.

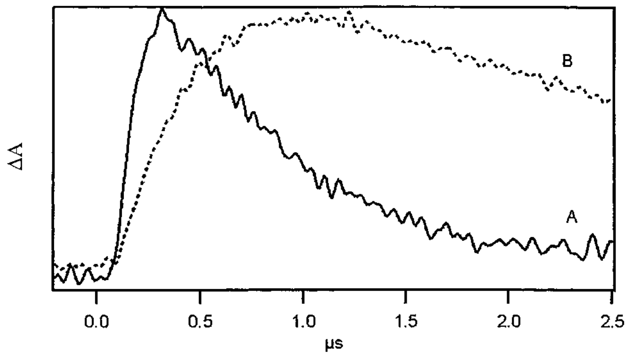
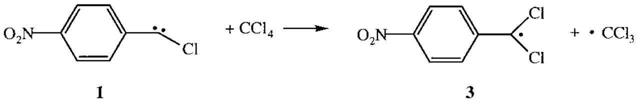


Figure 3. Decay of transient absorption at 1206 cm^{-1} (A) and the growth of transient absorption at 1316 cm^{-1} (B) following LFP (355 nm) of **2** in CCl_4.

The frequency of the carbene vibration at 1206 cm^{-1} is not influenced by the presence of 0.1−1 M benzene. Thus, there is no evidence of complexation of this carbene with benzene from vibrational spectroscopy. This is in accord with our kinetic studies of this system.[13]

LFP of **2** in either Freon-113 ($CF_2ClCFCl_2$) or carbon tetrachloride (Figure 2) leads to the presence of a new transient species absorbing at 1316 cm^{-1}. This species grows and decays with comparable time constants. If k_1 and k_2 are the rate constants for the formation and decomposition of this intermediate, we find that their apparent values are $k_1 = 1.5 \times 10^6$ s^{-1} and $k_2 = 4.8 \times 10^5$ s^{-1}. These values are only approximate because of the complex nature of the signal (Figure 3).

The species absorbing at 1316 cm^{-1} is associated with radical **3**, produced by chlorine atom abstraction reaction of the carbene with solvent, because the lifetime of the carrier of the 1316 cm^{-1} vibrational band is sensitive to the presence of oxygen and because DFT calculations predict that **3** will have an intense absorption at 1328 cm^{-1} (Supporting Information). Chlorine atom abstraction reactions of arylhalocarbenes have been studied previously by laser flash photolysis methods with UV−vis detection.[14]



Because of absorption by the solvent, carbene **1** cannot be monitored in Freon-113. Both the carbene and radical can be observed in CCl_4 (Figure 2). The formation of the radical appears to be faster than the decay of the carbene (Figure 3). We suspect this is an artifact of the poor separation of the growth and decay dynamics of the radical.

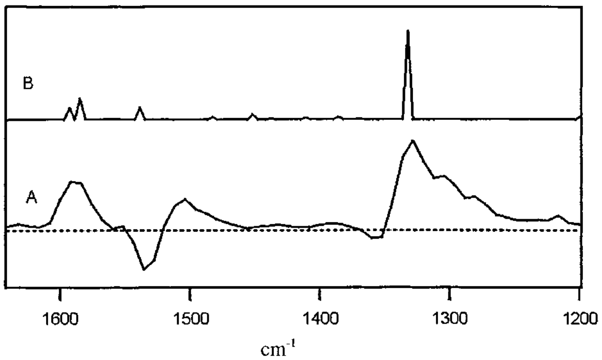


Figure 4. TRIR spectrum produced upon LFP of **2** from 500 to 1000 ns in CD_3CN at ambient temperature (A). IR spectrum of ylide **4** calculated by DFT with the B3LYP/6-31G* basis set after scaling by 0.96 (B).

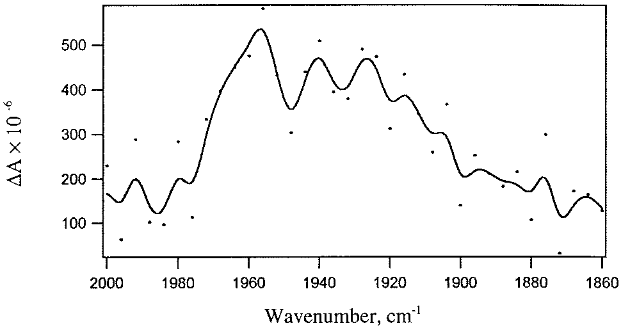
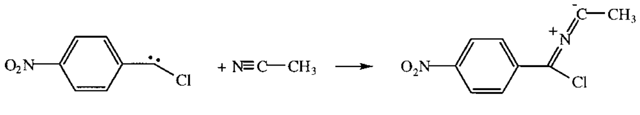


Figure 5. TRIR spectrum produced upon LFP of **2** from 500 to 1000 ns in CH_3CN at ambient temperature.

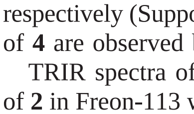
Laser flash photolysis of **2** in CD_3CN and CH_3CN produces the TRIR spectrum of Figures 4 and 5. This spectrum is attributed to ylide **4**, previously observed by UV–vis spectroscopy.[4,11,13] The ylide is formed with observed rate constant 5.8 × 10^6 s^{-1} and has a lifetime of several microseconds at ambient temperature.



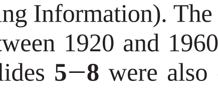
4

DFT calculations adequately simulate the IR spectrum of **4** (Figures 4 and 5) and clearly favor a cumulene-like structure of the ylide. The ylide absorbs at 1584, 1504, and 1312 cm^{-1}. These vibrations are associated with deformation of the aromatic ring and asymmetric and symmetric stretching of the nitro group, respectively (Supporting Information). The cumulene vibrations of **4** are observed between 1920 and 1960 cm^{-1} (Figure 5).

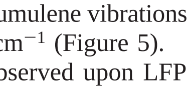
TRIR spectra of ylides **5**–**8** were also observed upon LFP of **2** in Freon-113 with the presence of acetone, methyl acetate, pyridine, and tetrahydrofuran, respectively.



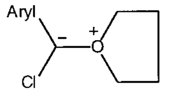
5



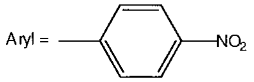
6



7



8



The TRIR spectra of ylides **5**–**8** are given in the Supporting Information. The spectra are adequately simulated by DFT calculations. The TRIR spectra of ylides **4**–**8** are all rather similar.

IV. Conclusions

The IR and UV–vis spectra of chloro-*p*-nitrophenylcarbene (**1**) as a persistent species have been obtained in argon at 14 K. The spectra are adequately simulated by DFT calculations. Carbene **1** has a prominent vibration at 1206 cm^{-1} that involves a C–C stretch between the carbene carbon and adjacent aromatic ring carbon. This band of **1** is readily detected upon LFP of diazirine **2** in heptane because the precursor and stable reaction products have little absorption in this region. The frequency of this vibration is not influenced by the presence of benzene. There is no TRIR evidence of complexation of this carbene with benzene. Upon LFP of **2** in CCl_4 or $CF_2ClCFCl_2$ the TRIR spectrum of the α,α-dichloro-*p*-nitrobenzyl radical is detected at 1316 cm^{-1}. Upon LFP of **2** in acetonitrile, acetone, methyl acetate, pyridine, or tetrahydrofuran, the TRIR spectra of ylides are observed. The TRIR spectra of the radical and ylides derived from chloro-*p*-nitrophenyl carbene are well simulated by DFT calculations. The spectra of the ylides are all quite similar and have prominent bands of 1584, 1504, and 1312 cm^{-1}. These vibrations are all associated with the *p*-nitrophenyl ring. It is demonstrated that TRIR spectroscopy, in parallel with DFT calculations, is a useful way of studying carbenes and related reactive intermediates.

Acknowledgment. We are indebted to Professor Gustafson for training on the TRIR spectrometer. Financial support of the National Science Foundation (NSF CHE-9613861) is gratefully acknowledged.

Supporting Information Available: Figures of IR and UV–vis spectra of **1** and **2** and TRIR spectra of **5**–**8**. Tables of optimized geometries and vibrational frequencies of **1** and its radical and ylide derivatives. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971.

(2) Bucher, G.; Scaiano, J. C.; Platz, M. S. *Landolt-Bornstein*; Springer: Berlin, Germany, 1998; Group II, Volume 18, Subvolume E2, p 141.

(3) Sander, W.; Bucher, G.; Wierlacher. *Chem. Rev.* **1993**, *93*, 1583.

(4) Bonneau, R.; Liu, M. T. H. *J. Am. Chem. Soc.* **1990**, *112*, 744.

(5) (a) Yuzawa, T.; Kato, C.; George, M. W.; Hamaguchi, H. *Appl. Spectrosc.* **1994**, *48*, 684. (b) Toscano, J. P. *Adv. Photochem.* **2001**, *26*, 41.

(6) For recent reviews, see: (a) Ford, P. C.; Bridgewater, J. S.; Lee, B. *Photochem. Photobiol.* **1997**, *65*, 57. (b) Schoonover, J. R.; Strouse, G. F. *Chem. Rev.* **1998**, *98*, 1335. (c) George, M. W.; Turner, J. J. *Coord. Chem. Rev.* **1998**, *177*, 201. (d) Geroge, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551.

(7) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M.

W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision x.x; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) Wierlacher, S.; Sander, W.; Liu, M. T. H. *J. Org. Chem.* **1992**, *57*, 1051.

(10) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

(11) (a) Liu, M. T. H.; Toriyama, K. *Can. J. Chem.* **1972**, *50*, 3009. (b) Chateauneuf, J. E.; Liu, M. T. H. *J. Am. Chem. Soc.* **1991**, *113*, 6585. (c) Liu, M. T. H.; Bonneau, R.; Jefford, C. W. *J. Chem. Soc., Chem. Commun*. **1990**, *21*, 1482.

(12) Pliego, J. R., Jr.; DeAmedia, W. B.; Celebi, S.; Zhu, Z.; Platz, M. S. *J. Phys. Chem.* **1999**, *103*, 7481.

(13) Celebi, S.; Tsao, M.-L.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 1158.

(14) Jones, M. B.; Maloney, V. M.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 2163.