J. Am. Chem. Soc. **2000,** *122,* 8087−8088

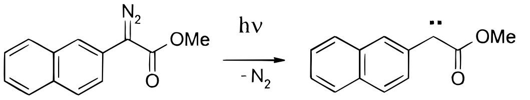
Ultrafast Carbonylcarbene Formation and Spin-Equilibration

Gina C. Hess, Bern Kohler,* Igor Likhotvorik,
Jorge Peon, and Matthew S. Platz*

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

Received March 31, 2000
Revised Manuscript Received July 6, 2000

The small energy gap between the lowest singlet and triplet states of many aryl carbenes leads to spin equilibration that is faster than the bimolecular reactions of either spin state.[1] Direct observation[2] of this equilibration has been difficult due to the elusive nature of singlet carbenes. Herein we report the detection of singlet and triplet carbenes following excitation of α-diazoester **D** with a 150 fs UV pump pulse in room-temperature solution. Singlet naphthyl carbene ester is formed within hundreds of femtoseconds following the laser pulse and is produced with excess vibrational energy. Thermalization occurs on a time scale of 10 ps. Singlet−triplet spin equilibration occurs at least as rapidly as thermalization, and thus takes place at least 1 order of magnitude faster than for diphenylcarbene or fluorenylidene.



D **^{1}C, ^{3}C**

Femtosecond pump−probe spectroscopy can be used to study the earliest dynamics of carbenes and their photoexcited precursors.[3,4] We chose the diazo ester **D** for this study due to the wealth of information recently obtained for this compound by nanosecond laser flash photolysis,[5] nanosecond transient infrared spectroscopy,[6] low-temperature matrix spectroscopy,[7] and ab initio calculations.[7,8] In particular, electronic spectra for both the singlet (**^{1}C**) and triplet carbene (**^{3}C**) derived from **D** were characterized in an argon matrix,[7] and the singlet−triplet gap was estimated to be just 0.2 ± 0.1 kcal mol^{-1} in CF$_2$ClCFCl$_2$ (Freon-113) at ambient temperature, with a triplet ground state.[6] Ketenes can be formed from α-diazocarbonyl compounds on the picosecond time scale,[9,10] but for **D** this reaction proceeds at a rate of $2-4 \times 10^6$ s^{-1}.[6] Thus, ultrafast investigation of **D** provides an excellent opportunity to observe the singlet/triplet spin equilibration dynamics in the absence of interfering rearrangements.

Solutions of **D** with an optical density of unity at 265 nm were studied in a 0.4-mm-thick jet. A femtosecond transient absorption spectrometer, described elsewhere,[11] was used to measure transient spectra and single-wavelength kinetics. The instrument response was approximately 200 fs. The solution under study was replaced frequently to minimize the build-up of photoproducts during data collection.

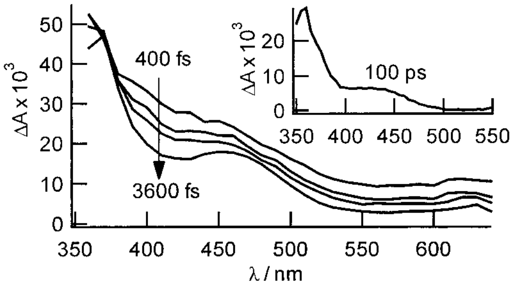


Figure 1. Transient spectra recorded 400, 800, 1200, and 3600 fs (from top to bottom) after excitation of the α-diazoester **D** in acetonitrile with a 265 nm, 150 fs pulse. All spectra have been corrected for probe chirp. The inset shows the transient spectrum recorded 100 ps after excitation of a solution of **D** in Freon-113.

Transient spectra recorded in acetonitrile (acn) and in Freon-113 are shown in Figure 1. Two broad bands are visible: an intense band near 360 nm and a weaker band at longer wavelengths. The long-wavelength band is better resolved and noticeably red-shifted in acn than in the less polar solvent Freon-113. Preliminary results in other solvents confirm a pronounced bathochromic shift of the long wavelength band with increasing solvent polarity. The long-wavelength absorption is assigned to the singlet carbene **^{1}C** by comparison with the results of Zhu et al.[7] These authors observed a broad absorption near 420 nm in an argon matrix, in good agreement with our spectrum in Freon-113. The pronounced sensitivity of this band to solvent polarity is consistent with singlet absorption due to the polar nature of singlet carbenes.[12,13]

A second, stronger absorption band is observed near 360 nm. INDO calculations and matrix spectra[7] indicate that both **^{1}C** and **^{3}C** absorb in this region, and we assign this band to a mixture of both spin states. In the absence of absorption cross sections for **^{1}C** and **^{3}C**, it is difficult to quantify the contribution of each. Assignment is further complicated by the fact that the equilibrium constant for intersystem crossing is solvent dependent. In Freon-113, **^{3}C** is predicted to be the ground state, but the free energy difference is just 0.2 kcal mol^{-1},[6] and significant quantities of each spin state will be present at equilibrium. In the polar solvent acn, ab initio calculations indicate that **^{1}C** is the ground state.[8] In Figure 1, the ratio of the maximum absorbance of the long wavelength band to the short wavelength band decreases on going from acn to Freon-113. This is the expected trend if absorption in the long wavelength band is primarily due to **^{1}C**, and if the equilibrium constant for singlet−triplet spin equilibration increases in the less polar solvent. In neat methanol, both bands decay with the same first-order rate constant. Singlet carbenes react via OH insertion with alcohols to form far-UV-absorbing ethers.[1] The bimolecular reaction rate constant in acn/methanol mixtures is 1.6×10^8 M^{-1} s^{-1}, in reasonable agreement with the rate of 1.0×10^8 M^{-1} s^{-1} reported in Freon-113.[6] The reactivity in methanol confirms that the transient absorption bands are due to carbene intermediates.

In Figure 1, the carbene absorption bands in acn can already be seen 400 fs after the pump pulse, although they are significantly

---

* Address correspondence to these authors.

(1) Platz, M. S.; Maloney, V. M. *Laser flash photolysis studies of triplet carbenes*; Platz, M. S., Ed.; Plenum Press: New York, 1990.

(2) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A. J.; DuPuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6563.

(3) Hess, G. C. Ultrafast spectroscopy of 2-naphthylcarbomethoxycarbene in solution. M.S. Thesis, The Ohio State University, Columbus, OH, 1999.

(4) Portella-Oberli, M. T.; Jeannin, C.; Soep, B.; Zerza, G.; Chergui, M. *Chem. Phys. Lett.* **1998**, *296*, 323.

(5) Wang, J.-L.; Likhotvorik, I.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 2883.

(6) Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 2875.

(7) Zhu, Z.; Bally, T.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 2863.

(8) Toscano, J. P.; Hadad, C. M. Unpublished results.

(9) Vleggaar, J. J. M.; Huizer, A. H.; Kraakman, P. A.; Nijssen, W. P. M.; Visser, R. J.; Varma, C. A. G. O. *J. Am. Chem. Soc.* **1994**, *116*, 11754.

(10) Lippert, T.; Koskelo, A.; Stoutland, P. O. *J. Am. Chem. Soc.* **1996**, *118*, 1551.

(11) Peon, J.; Hess, G. C.; Pecourt, J.-M. L.; Yuzawa, T.; Kohler, B. *J. Phys. Chem. A* **1999**, *103*, 2460.

(12) Garcia-Garibay, M. A.; Theroff, C.; Shin, S. H.; Jernelius, J. *Tetrahedron Lett.* **1993**, *34*, 8415.

(13) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed.* **1972**, *11*, 92.

10.1021/ja0011358 CCC: $19.00

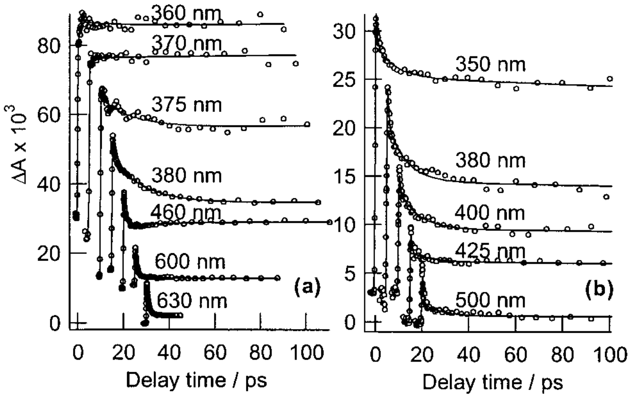


Figure 2. Absorbance change (circles) at the indicated probe wavelengths induced by a 150 fs, 265 nm pump pulse for **D** in (a) acetonitrile and (b) Freon-113. Solid curves are from global fitting. The transients have been offset for clarity.

broadened. Rapid narrowing occurs in a few picoseconds, followed by more subtle changes on a time scale of tens of picoseconds. All spectral evolution ceases after approximately 50 ps. Single-wavelength traces in acn and in Freon-113 (Figure 2) confirm these dynamics. The solid curves in Figure 2 are from a global, nonlinear least-squares-fitting analysis.[14] The transients were fit to the sum of three exponentials convoluted with a Gaussian that represents the instrument response function. The amplitudes of the exponential functions were varied independently for each probe wavelength, but the exponential time constants were globally linked for traces in the same solvent. In both solvents, one time constant has a value of many nanoseconds, consistent with the essentially constant signals seen at delay times >50 ps. The other time constants and two σ uncertainties are 0.70 ± 0.09 and 13.8 ± 2.5 ps (acn) and 0.44 ± 0.07 and 8.0 ± 1.3 ps (Freon-113).

The pump pulse populates an electronically excited state of the diazo precursor, **D**. Very little information is available about the photodissociation dynamics of diazo compounds. The transient spectra seen at the earliest delay times (Figure 1) are broadened, but otherwise similar to the carbene spectra seen at longer delay times, suggesting that **^{1}C** is formed within our time resolution. There is no evidence for an additional absorption band at short times that could be assigned to electronically excited **D**. Excited-state absorption of **D** should be distinct from the carbene spectra on account of the very different electronic structure of carbenes and their diazo precursors. Thus, our results support the notion that N_2 loss occurs promptly, perhaps on the time scale of a single C−N stretching period. Ab initio calculations have located a variety of conical intersections for electronically excited diazomethane that could give rise to rapid N_2 loss.[15]

A rapid decay with a time constant of several hundred femtoseconds at most probe wavelengths is seen in both solvents. This time constant does not appear to be associated with spin equilibration since rising signals are not observed,[16] even at wavelengths near 360 nm in the nonpolar solvent Freon-113, where **^{3}C** is likely to be the dominant absorber. Instead, we assign this fast time constant to structural relaxation in the newly formed carbenes. Whatever its exact nature, the subpicosecond decay seen here and in diphenyldiazomethane[4] appears to be characteristic of the ultrafast dynamics of diazo compounds.

The intermediate time constant of 8−14 ps is again not clearly identifiable with singlet−triplet intersystem crossing since globally decaying signals are seen in Freon-113.[16] The results in acn provide the key to assigning this time constant. Small-amplitude signal rises are observed at wavelengths near the long-wavelength band maximum in acn, while decays are observed on the red edge. The decays become progressively faster at longer probe wavelengths. Both observations are hallmarks of vibrational cooling processes in ultrafast pump−probe experiments,[17−19] and the measured time constants of 8−14 ps are reasonable for intermolecular energy transfer from vibrationally hot solutes to the solvent. Typical bond dissociation energies for the carbon−nitrogen bond in diazo compounds are 20−30 kcal mol^{-1},[8,20] so excitation of **D** with a 265-nm photon (108 kcal mol^{-1}) prepares an initial excited state with substantial excess energy. We propose that photodissociation of **D** gives rise to **^{1}C** with considerable excess vibrational energy. The precise amount of excess energy will depend sensitively on the photodissociation reaction coordinate. Even if most of the excess energy appears as kinetic energy of the N_2 photoproduct, collisions between rotationally or translationally hot N_2 and the solvent cage could provide an indirect mechanism for solute heating.

We return finally to the question of spin equilibration. Since spectral evolution ceases 50 ps after the pump pulse in both solvents, the carbene populations must be completely spin-equilibrated before this time. The rapid appearance of the double-peaked transient spectra (Figure 1) strongly suggests that spin equilibration occurs more rapidly, perhaps during the initial photodissociation and thermalization of the hot photoproducts.

In summary, these results indicate that appreciable quantities of singlet and triplet carbenes are formed on the time scale of several hundred femtoseconds with a large amount of excess internal energy. Nitrogen loss occurs on a subpicosecond time scale and a lower limit for the rate of intersystem crossing is 10^{11} s^{-1}. This is roughly an order of magnitude faster than for previously studied diarylcarbenes.[2,21−24] Ab initio calculations reveal that **^{3}C** has a planar structure like its diazo precursor, while the ester group in **^{1}C** is rotated by 90°. Thus, rotation about the single bond between the carbene carbon and the ester moiety in the vibrationally excited nascent carbene provides a rapid mechanism for spin interconversion consistent with our observations.

Acknowledgment. M.S.P. thanks the National Science Foundation for partial support (CHE-9613861). The authors thank Professors Hadad and Toscano for permission to cite their unpublished work.

JA0011358

---

(14) Knutson, J. R.; Beechem, J. M.; Brand, L. *Chem. Phys. Lett.* **1983**, *102*, 501.

(15) Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1994**, *116*, 2064.

(16) Globally decaying pump−probe signals could be consistent with spin equilibration, only if the extinction coefficient of **^{1}C** were greater than that of **^{3}C** at all probe wavelengths.

(17) Elsaesser, T.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1991**, *42*, 83.

(18) Sension, R. J.; Szarka, A. Z.; Hochstrasser, R. M. *J. Chem. Phys.* **1992**, *97*, 5239.

(19) Schwarzer, D.; Troe, J.; Votsmeier, M.; Zerezke, M. *J. Chem. Phys.* **1996**, *105*, 3121.

(20) Bethel, D.; Whittaker, D.; Callister, J. B. *J. Chem. Soc.* **1965**, 2466.

(21) Dupuy, C.; Korenowski, G. M.; McAuliffe, M.; Hetherington, W. M. I.; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *77*, 272.

(22) Langan, J. G.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1984**, *110*, 521.

(23) Sitzmann, E. V.; Langan, J. G.; Griller, D.; Eisenthal, K. B. *Chem. Phys. Lett.* **1989**, *161*, 353.

(24) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.