JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Direct Observation of a Carbene-Alcohol Ylide

Jiadan Xue, Hoi Ling Luk, and Matthew S. Platz*

Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210

S Supporting Information

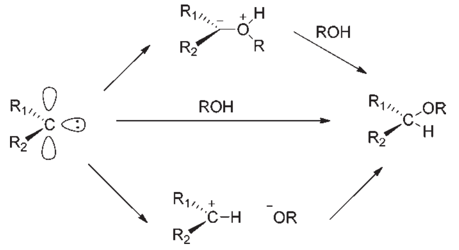
ABSTRACT: Carboethoxycarbene reacts with methanol-OD to form an ylide. The formation and decay of this ylide was monitored by ultrafast time-resolved IR spectroscopy. The formation and decay of the ylide is linearly dependent on the concentration of methanol-OD in acetonitrile with second-order rate constants of ylide formation $(8.4 \times 10^9\ M^{-1}\ s^{-1})$ and decay $(1.4\times10^9\ M^{-1}\ s^{-1})$. Similar results were obtained with 1-butanol.

Carbene chemists have long been fascinated by the range of mechanisms by which carbenes can react with alcohols to form ethers.[1] Carbenes can abstract protons from solvents to form ion pairs, can react with the oxygen atom of alcohols to form ylides, or undergo direct insertion into an OH bond in a manner akin to CH bond insertion (Scheme 1).[2]

Kirmse and co-workers[3] were the first to directly detect the carbocations formed by the proton transfer mechanism. This was followed by Goodman's,[4] Kohler's,[5] and our own ps/fs time-resolved studies[6] of this reaction mode. Our strategy for detecting carbene-alcohol ylides, described herein, is to use a carbonyl carbene for the following two reasons. First, the electron-withdrawing nature of the carbonyl group will destabilize a carbocation but will stabilize an alcohol derived ylide, and thus should favor the latter mechanistic pathway. Second, the carbonyl group provides a convenient vibrational band to monitor using fs/ps time-resolved infrared spectroscopy.

Ultrafast photolysis (270 nm) of ethyl diazoacetate **1** was performed in acetonitrile (ACN) and tetrahydrofuran (THF). This produced transient infrared (IR) bands at 1640 and 1636 cm^{-1}, respectively (Figure 1a,b). The carriers of these bands are assigned to nitrile and ether ylides **2** and **3**. These assignments are based on literature precedent[7,8] and the good agreement of experiment with DFT[9] calculations that predict the carbonyl vibrations of **2** and **3** at 1664 and 1651 cm^{-1}, respectively (Supporting Information (SI) Tables S1 and S2). The ylides are formed within 2 ps of the laser pulse, dynamics which are associated with the reaction of a nascent, vibrationally excited carbene with a solvent molecule.[10] The ylides formed from hot carbenes are also born with excess vibrational energy, as evidenced by their broad carbonyl vibrational bands. The ylide is thermalized by vibrational cooling (VC)[11] in 6 ps as evidenced by band narrowing and blue shifting. The relaxed ylide lifetimes are in excess of 3 ns, the time resolution of the spectrometer.

Scheme 1



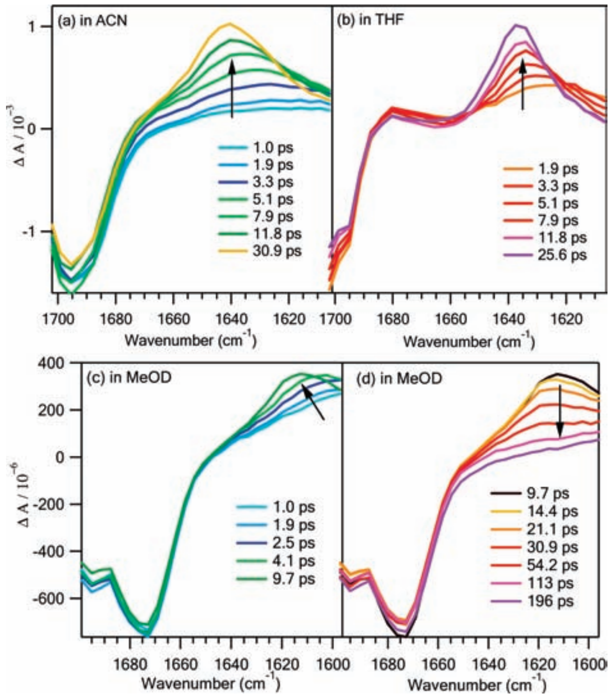
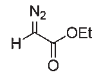
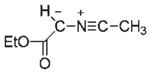


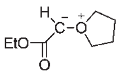
Figure 1. Transient IR spectra produced by photolysis of ethyl diazoacetate in ACN (a), THF (b), and MeOD (c, d).



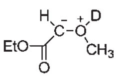
1



2



3

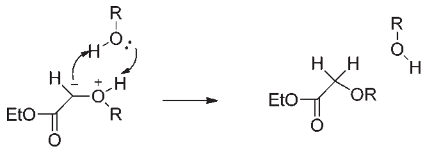


4

The decay of an alcohol ylide is expected to be bimolecular (Scheme 2) as the intramolecular 1,2-shift is forbidden by orbital symmetry and thus will exhibit a first-order dependence on the concentration of alcohol.[1,2]

Received: December 8, 2010
Published: January 25, 2011

Scheme 2



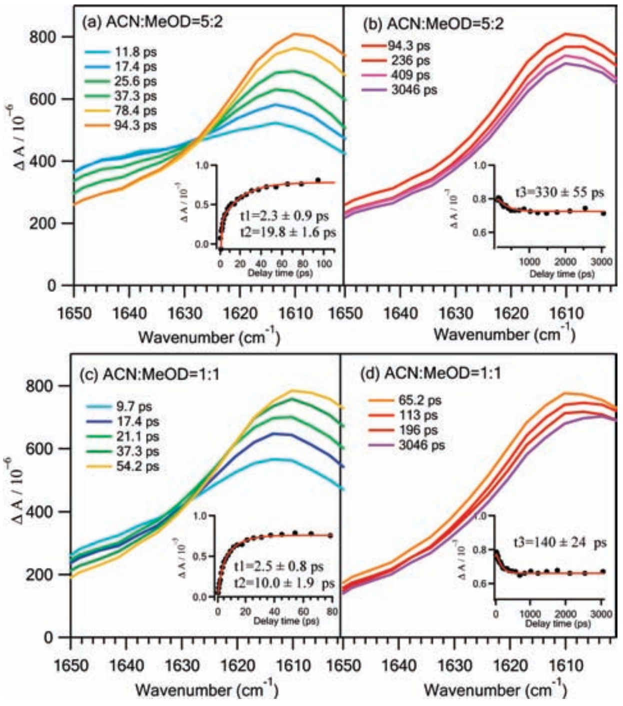


Figure 2. Transient IR spectra produced by photolysis of ethyl diazoacetate in ACN/MeOD = 5:2 (a,b) and ACN/MeOD = 1:1 (c,d) by volume. Inset: kinetics at 1610 cm^{-1}; formation fit to a biexponential function and decay fit to a monoexponential decay function.

Ultrafast photolysis of **1** in neat methanol-OD (MeOD)[12] produces the transient spectra of Figure 1c,d. The 1616 cm^{-1} absorbing transient is formed in 2 ps with excess energy (broad band that narrows and blue shifts as before) and is then thermalized by VC. The transient has a decay lifetime of 35 ps in neat MeOD. DFT calculations predict the carbonyl vibration of **4** (**H** instead of **D** in the calculation) to be at 1642 cm^{-1} (SI Table S3). Experiments were conducted in ACN/MeOD mixtures. It is clear that the kinetics of ylide **4** formation can be fit to a biexponential function and its decay fit to a monoexponential function (Figure 2). The pseudo-first-order rates of formation (slow part) and decay of ylide **4** are linearly dependent on the concentration of MeOD with second-order rate constants of ylide formation (8.4×10^9 M^{-1} s^{-1}) and decay (1.4×10^9 M^{-1} s^{-1}) (Figure 3).

The carbene singlet and triplet vibrational bands are predicted to be at 1561 and 1587 cm^{-1}, respectively, after scaling (SI, Table S4). Although the IR of the triplet carbene is predicted to be close to the observed 1616 cm^{-1} transient, the triplet carbene rate of formation should not show a first-order dependence on alcohol concentration; thus another assignment is required. Reaction of a carbene with MeOD to form a carbocation would show a first-order dependence of growth and decay on alcohol concentration. Theory, however, predicts that the cation carbonyl vibrational band will be at 1811 cm^{-1}, after scaling (SI, Table S5). As this is so far removed from experiment the alcohol ylide assignment of the transient spectrum is preferred.

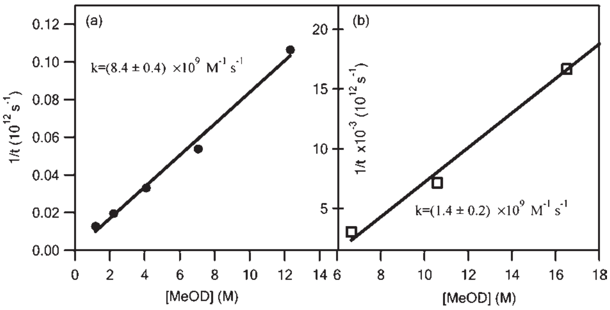


Figure 3. Plots of the formation (a) and decay (b) rates of MeOD-ylide as a function of the MeOD concentration in ACN/MeOD mixed solvent, fitted to a linear function respectively.

1-Butanol is a factor of 4.6 more viscous than MeOD.[13] The molarities of neat MeOD and 1-butanol are 24.6 and 10.9 M, respectively. As a result carboethoxy carbene should have a longer time constant of reaction with *neat* 1-butanol, relative to neat MeOD. Ultrafast photolysis of **1** in neat 1-butanol again leads to transient absorption at 1616 cm^{-1}, assigned to an alcohol ylide, which rises in 20 ps and decays in 130 ps (SI Figure 4S). The alcohol ylide pseudo-first-order formation rate is an order of magnitude faster in neat MeOD relative to 1-butanol and the pseudo-first-order decay rate is almost 4 times faster in neat MeOD than in 1-butanol, consistent with expectations.

The second-order rate constants of 1-butanol-ylide formation and decay (determined in ACN cosolvent) are 4.2×10^9 and 1.4×10^9 M^{-1} s^{-1} (SI Figures 5S, 6S), respectively. Note that dilution of 1-butanol with ACN decreases the viscosity differences between the neat solvents[13b] and thus reduces the reactivity difference between MeOD and 1-butanol on a per molar basis.

Strausz and co-workers[14] reported a 37% yield of O−H insertion product after photolysis of **1** in 2-propanol; thus we are not surprised that photolysis of **1** leads to significant carbene capture in neat methanol-OD or 1-butanol. This result is consistent with our steady-state FT-IR studies that reveal that a persistent product band is formed after photolysis of **1** in MeOD (Figure 7S in SI). The position of this band is consistent with that of a simple nonconjugated ester. In final support of the proposed assignment of the transient we note that the data (Figure 8S in SI) demonstrate that the formation (41± 11 ps, 64%) of the expected stable product correlates with the decay of the MeOD-ylide, as required by the proposed assignment.

In summary, evidence is presented for the first direct observation of a carbene-alcohol ylide. As expected, the ylide is formed in a near diffusion controlled process and its decay is governed, as predicted, by a near diffusion controlled bimolecular reaction with an additional alcohol molecule or hydrogen bonded network of molecules.

■ ASSOCIATED CONTENT

S Supporting Information. DFT calculations, ultrafast kinetic traces, complete ref 9. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
platz.1@osu.edu

ACKNOWLEDGMENT

Support of this work by the National Science Foundation is gratefully acknowledged. The experiments were performed at the OSU Center for Chemical and Biophysical Dynamics, established with the support of the NSF. The authors thank Prof. R. A. Moss and Drs. G. Burdzinski and J. Kubicki for useful conversations.

REFERENCES

(1) (a) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964. (b) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (c) Jones, M., Jr., Moss, R. A., Eds. *Carbenes*, Vol. 1; Wiley-Interscience: New York, 1973. (d) Moss, R. A. Jones, M., Jr., Eds. *Carbenes*, Vol. 2; Wiley-Interscience: New York, 1975. (e) Platz, M. S., Ed. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990. (f) Moss, R. A., Platz, M. S., Jones, M., Jr., Eds. *Reactive Intermediate Chemistry*; John Wiley & sons, Inc.: Hoboken, NJ, 2004.

(2) (a) Bethell, D.; Newall, A. R; Whittaker, D. *J. Chem. Soc. B* **1971**, 23. (b) Bethell, D.; Newall, A. R.; Stevens, G.; Whittaker, D. *J. Chem. Soc. B* **1969**, 749. (c) Bethell, D.; Howard, R. D. *J. Chem. Soc. B* **1969**, 745.

(3) Kirmse, W.; Kilian, J. *J. Am. Chem. Soc.* **1990**, *112*, 6399.

(4) Dix, E. J.; Goodman, J. L. *J. Phys. Chem.* **1994**, *98*, 12609.

(5) Peon, J.; Polshakov, D.; Kohler, B. *J. Am. Chem. Soc.* **2002**, *124*, 6428.

(6) Wang, J.; Burdzinski, G.; Kubicki, J.; Platz, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 11195.

(7) Naito, I.; Nakamura, K.; Kumagai, T.; Oku, A.; Hori, K.; Matsuda, K.; Iwamura, H. *J. Phys. Chem. A* **1999**, *103*, 8187.

(8) Tippmann, E. M.; Platz, M. S.; Svir, I. B.; Klymenko, O. *J. Am. Chem. Soc.* **2004**, *126*, 5750.

(9) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(10) (a) Wang, J.; Burdzinski, G.; Kubicki, J.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 5418. (b) Zhang, Y.; Burdzinski, G.; Kubicki, J.; Platz, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 9646.

(11) VC: The initially observed vibration for both species is broad, but the band sharpens and blue shifts in 20 ps and produces a clear isosbestic point. Moreover, the decay at 1615 cm^{-1} is correlated with the growth monitored at 1640 cm^{-1}. Therefore the 1615 cm^{-1} band carrier should come from its corresponding hot state.

(12) MeOD is used instead of MeOH, as the former but not the latter is transparent in the critical region of the IR.

(13) (a) The viscosities of MeOH and 1-butanol are 0.55 and 2.57 mPa·s respectively. (b) Nikam, P. S.; Shirsat, L. N.; Hasan, M. *J. Chem. Eng. Data* **1998**, *43*, 732.

(14) Strausz, O. P.; DoMinh, T.; Gunning, H. E. *J. Am. Chem. Soc.* **1968**, *90*, 1660.