J. Am. Chem. Soc. **1996,** *118,* 3527−3528 3527

The Lifetime of Formylcarbene Determined by Transient Absorption and Transient Grating Spectroscopy

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Received November 13, 1995

Aromatic carbenes have been thoroughly studied by transient absorption spectroscopy.[1,2] In condensed phases simple arylcarbenes do not undergo intramolecular rearrangements which might otherwise limit their lifetimes. The aromatic component also provides a convenient chromophore for UV−vis detection.

Recently much attention has been directed toward the study of alkylcarbenes[3] and acylcarbenes.[4] These species do undergo facile rearrangements and thus are much shorter lived than typical arylcarbenes. They also lack convenient chromophores. We have reported lifetimes of various alkyl- and acylcarbenes using the pyridine ylide-nanosecond laser flash photolysis technique.[5] This technique utilizes a competition between all first-and pseudo-first-order carbene reactions with a pyridine-dependent second-order reaction which produces a useful UV−vis active probe (ylide **1**, Scheme 1).

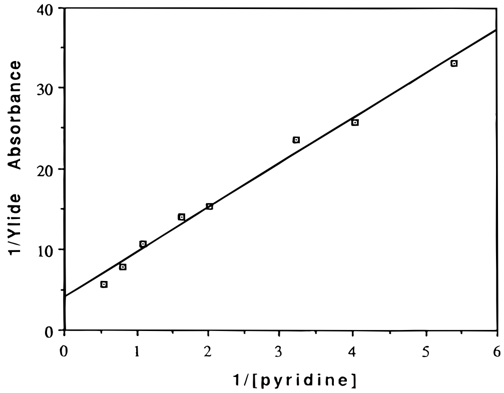
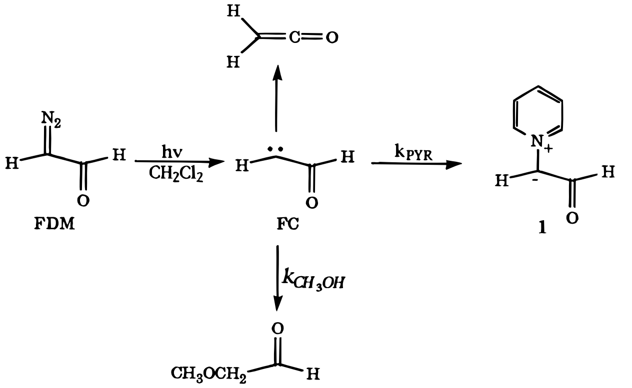


Figure 1. Double reciprocal treatment of the yield of ylide **1** produced by LFP (308 nm) of FDM in methylene chloride at ambient temperature.

Scheme 1



Laser flash photolysis (LFP) of formyldiazomethane (FDM) produces singlet formylcarbene (FC) which can isomerize,[6] or react with solvent or pyridine (Scheme 1).[4] It is not possible to resolve the rate of formation of ylide **1** in methylene chloride with the spectrometer available in Columbus (20 ns time resolution). However, standard double reciprocal analysis (Figure 1) of the optical yield of ylide with pyridine concentration yields the ratio k_{PYR}/k_0 (or $k_{PYR}\tau$) equal to 0.73 M^{-1} where k_0 is the sum of all first-order and pseudo-first-order rate constants of all processes which consume the carbene in the absence of pyridine and τ ($1/k_0$) is the carbene lifetime as defined in Scheme 1.[3] The value of k_{PYR} is typically taken as $1-5 \times 10^9$ M^{-1} s^{-1} which indicates that the lifetime of singlet formyl carbene lies in the range of 0.15−0.73 ns in methylene chloride. This is consistent with our previous estimate of τ as 0.5−2.3 ns in Freon-113 ($CF_2ClCFCl_2$).[4c,d] The ratio $k_{CH_3OH}/k_{PYR} = 4.6$, in Freon-113, was determined by Stern−Volmer analysis of the quenching of the yield of **1** as a function of methanol concentration at a constant concentration (3.1 M) of pyridine (Figure 2) (Scheme 1). At this concentration of pyridine in Freon-113, all FC produced in the laser pulse is captured by pryridine. Thus, in Freon-113 we can deduce that $k_{CH_3OH}\tau = 3.4$ M^{-1}. This analysis assumes that all of the chemistry of FC in solution proceeds through the singlet state of the carbene.

To confirm this analysis and its implicit assumptions, a technique with superior time resolution, transient grating spectroscopy, was utilized. Transient grating based calorimetric techniques provide sufficient time resolution to determine transient lifetimes of 1 ns or less.[7] Gratings were generated in $1.5-2.0 \times 10^{-3}$ M solutions of FDM in CH_2Cl_2 by crossing two 279-nm pulses (45 ps fwhm, <1 μJ, 400 μm) at a 37° angle in a 1 mm suprasil flow cell. The time dependence of the resulting thermal phase grating was probed using a 633-nm dye laser pulse (60 ps fwhm, <0.5 μJ, 250 μm) incident on the sample at the Bragg angle. The photochemically induced diffraction waveform was adequately fit (Figure 3) using a model containing only two heating terms: a kinetically unresolvable (fast) heat release and one resolvable (slow) exponential heat release.[7d] No dispersive or absorptive terms in the model were required to fit the data.[7b] The rate constant of

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(1) Platz, M. S.; Maloney, V. M. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 239.

(2) Moss, R. A.; Turro, N. J. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 213.

(3) Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R.; Mullins, M.; Celebi, S.; Toscano, J. P. *Prog. React. Kinet.* **1994**, *19*, 93.

(4) (a) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popic, V. *J. Am. Chem. Soc.* **1994**, *116*, 8146. (b) Wang, J. L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477. (c) Toscano, J. P.; Platz, M. S.; Nikolaev, V. *J. Am. Chem. Soc.* **1995**, *117*, 4712. (d) It was not possible to saturate the yield of ylide in methylene chloride, thus, Stern−Volmer experiments were performed in Freon-113.

(5) Jackson, J. E.; Platz, M. S. *Advances in Carbene Chemistry*; Vol. 1, Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol 1, p 89.

(6) (a) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Krieger: Malabar, FL, 1983; Vol. I. (b) Moss, R. A.; Jones, M., Jr. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981, p 61. (c) Moss, R. A.; Jones, M., Jr. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; p 95. (d) Marchand, A. P.; Brockway, N. M. *Chem. Rev.* **1974**, *74*, 431. (e) Kirsme, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1978. (f) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. (g) Torres, M.; Lown, E. M.; Gunning, H. E.; Strausz, O. P. *Pure Appl. Chem.* **1980**, *52*, 1623. (h) Zeller, K.-P. *Tetrahedron Lett.* **1977**, 707. (i) Zeller, K.-P.; Meier, H.; Kolshor, H.; Muller, E. *Chem. Ber.* **1972**, *105*, 1875. (j) Timm, U.; Zeller, K.-P.; Meier, H. *Tetrahedron* **1977**, *33*, 453.

(7) (a) Miller, R. J. D. In *Advances in Spectroscopy*; Clark, R. J., Hester, R. E. Eds.; John Wiley and Sons: New York, 1989; Vol. 18, p 1. (b) Morais, J.; Zimmt, M. B. *J. Phys. Chem.* **1995**, *99*, 8863. (c) Ma, J.; Dutt, B.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 10619. (d) 74% of the detected expansion is prompt, the remaining 26% occurs with a time constant of 900 ps.

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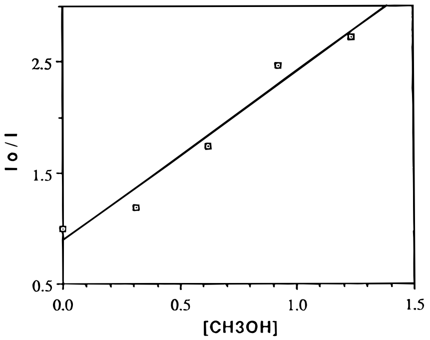


Figure 2. Stern–Volmer analysis of the quenching of the yield of ylide **1** as a function of methanol concentration at constant (3.1 M) concentration of pyridine in $CF_2ClCFCl_2$.

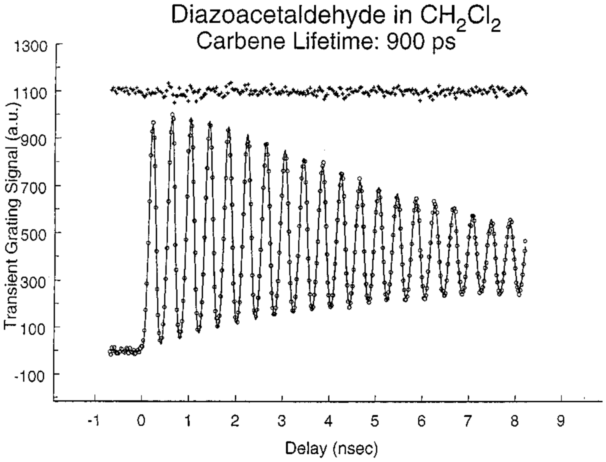


Figure 3. Transient grating waveform generated by irradiation of diazoacetaldehyde in CH_2Cl_2 (see text for details). The circles denote every third data point used in the fitting. The solid line is the calculated fit. The (+) indicate the residuals. The increase in the peak signal within the first three oscillations is the result of a "slow" heat release.

the slow heat release determined from three independent samples was 1.1 (±0.1) × 10^9 s^{-1}, or $\tau = 0.9$ ns.

To correlate the transient absorption and transient grating experiments, the effect of a quencher on the kinetics was studied. Although pyridine would have been the quencher of choice, its strong absorption at 279 nm precludes its use in these grating experiments. Instead, the effect of added methanol on the slow heat release rate constant was determined. As shown in Figure 4, the slow heat release rate constant, k_{obs}, increased in the presence of methanol. Analysis of the data using equation 6 yields a value for k_{CH_3OH} of 4.3 (±0.4) × 10^9 M^{-1} s^{-1}.

$$k_{obs} = k_0 + k_{CH_3OH}[CH_3OH] \qquad (6)$$

Thus the value of $k_{CH_3OH}\tau$ in CH_2Cl_2 determined by transient grating spectroscopy is 3.9 M^{-1} which is in excellent agreement with the value determined by optical methods in Freon-113.

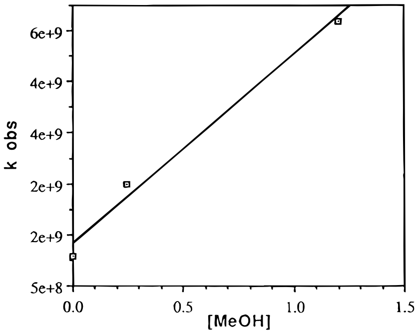
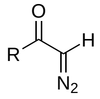


Figure 4. A plot of k_{obs}, the "slow" heat release time constant, as a function of MeOH concentration in the grating experiments. The solid line is the linear regression fit.

The preceding analysis demonstrates that the same species has been studied by two independent techniques. However, the transient intermediate can in principle be either singlet FC or the excited singlet state of the diazo precursor. We believe that we have characterized singlet FC for two reasons. First, it is clear that the yield of ketocarbene from the diazo excited state depends on the conformation[4,8] of the diazo precursor, and FDM gives a much larger yield of trappable carbene than does LFP of **2**–**4**.



R = CH_3 (**2**); $CH(CH_3)_2$ (**3**); $C(CH_3)_3$ (**4**)

Significantly, for **1**–**4** only irradiation of FDM produces sufficient "slow" ($\tau > 200$ ps) heat release as to be detectable by transient grating spectroscopy.

Furthermore, FDM is non-fluorescent in our hands. This prevents the use of fluorescence spectroscopy for determination of whether pyridine or methanol react with the singlet excited state of the diazo precursor. Nevertheless, the transient lifetime of 0.9 ns determined in this study seems much too long for a non-fluorescent excited state which efficiently extrudes nitrogen.[9]

In conclusion, transient grating spectroscopy directly provides lifetime data for formylcarbene which is consistent with the results deduced from more indirect laser flash photolysis studies. The consistency in the results validates our previous assumptions of the magnitude of k_{pyr} and the exclusively singlet state reactivity patterns of the transient carbene.

Acknowledgment. Support of this work in Columbus (CHE-8814950) and Providence (CHE-9206765) by the NSF is gratefully acknowledged. J.P.T. gratefully acknowledges NIH post doctoral fellowship support. M.B.Z. acknowledges support from the Camille and Henry Dreyfuss Foundation.

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[9] To our knowledge the quantum yield of disappearance of FDM is not known.