Laser Flash Photolysis Study of Carboethoxynitrene
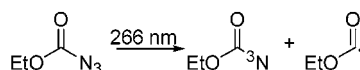
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ABSTRACT
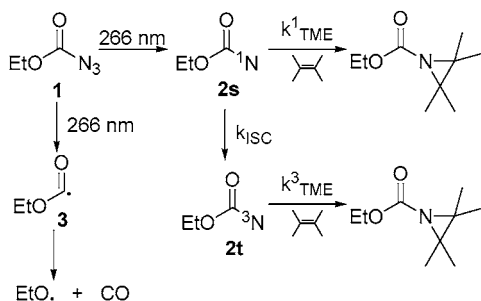

Laser flash photolysis (LFP, 266 nm) of carboethoxyazide produces a mixture of the ethoxycarbonyl radical (λ_{max} = 333 nm, τ = 0.4 μs, $CF_2ClCFCl_2$, ambient temperature) and triplet carboethoxynitrene (λ_{max} = 400 nm, τ = 1.5 μs, $CF_2ClCFCl_2$, ambient temperature). The carbon-centered radical is selectively scavenged by oxygen allowing sole observation of the triplet nitrene. We deduce that the singlet nitrene has a lifetime between 2 and 10 ns in $CF_2ClCFCl_2$ at ambient temperature.

Carboethoxynitrene is a molecule of fundamental interest that has important synthetic applications and has served to develop modern paradigms in mechanistic nitrene chemistry.[1] The pioneering work of Lwowski and co-workers demonstrate that photolysis of carboethoxyazide **1** generates singlet nitrene **2s** as the major product, although some triplet nitrene is formed concurrently as well. The singlet nitrene either reacts with a trap or relaxes to the lower energy triplet nitrene **2t** (Scheme 1).[1] Low-temperature ESR spectroscopy has

Scheme 1. Photolysis of Carboethoxy Azide

demonstrated the triplet nature of the ground state of carboethoxynitrene.[2] Nonconjugated triplet nitrenes have absorption maxima in a range that is convenient for direct observation by laser flash photolysis (LFP) techniques[3] (^{3}NH, 336 nm; ^{3}N−CH$_3$ 316.9 nm[4] (nitrogen matrix), 314.3 nm[5]

(gas phase); ^{3}N−CF$_3$, 342, 347.5, 354 nm[6]). These reports encouraged us to study carboethoxynitrene by LFP methods with the hope of determining the absolute rate constants of spin relaxation and reaction with alkenes of this important reactive intermediate.

LFP (Nd:YAG, 266 nm) of **1** in deoxygenated Freon-113 ($CF_2ClCFCl_2$) produces the transient spectrum shown in Figure 1 with maxima at 333 and 400 nm. The transient absorption bands are both formed within the 10 ns time resolution of the spectrometer and decay with lifetimes of 0.4 and 1.5 μs at 333 and 400 nm, respectively, suggesting the presence of two distinct intermediates. This was confirmed by recording the transient spectra in oxygenated Freon-113. As shown in Figure 1, only the 400 nm peak is present in oxygen-containing solution, demonstrating that

(1) (a) Lwowski, W.; Mattingly, T. W., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1947. (b) Lwowski, W.; Woerner, F. P. *J. Am. Chem. Soc.* **1965**, *87*, 5491. (c) McConaghy, J. S.; Lwowski, W. *J. Am. Chem. Soc.* **1965**, *87*, 5490. (d) McConaghy, J. S.; Lwowski, W. *J. Am. Chem. Soc.* **1967**, *89*, 4450. (e) Lwowski, W.; DeMauriac; Mattingly, T. W., Jr.; Schieffele, *Tetrahedron Lett.* **1964**, 3285.
(2) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.
(3) Gritsan, N. P.; Platz, M. S. *Adv. Phys. Org. Chem.* **2001**, *36*, 255.
(4) (a) Okabe, H.; Lenzi, M. *J. Chem. Phys.* **1967**, *47*, 5241. (b) Okabe, H. *J. Chem. Phys.* **1968**, *49*, 2726.
(5) (a) Carrick, P. G.; Engelking, P. C. *J. Chem. Phys.* **1984**, *81*, 1661. (b) Carrick, P. G.; Brazier, C. R.; Bernath, P. F.; Engelking, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 5100. (c) Chappell, C. E. L.; Engelking, P. C. *J. Chem. Phys.* **1988**, *89*, 6007. (d) Brazier, C. R.; Carrick, P. G.; Bernath, P. F. *J. Chem. Phys.* **1992**, *96*, 919.
(6) Gritsan, N. P.; Likhotvorik, I.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A.* **2001**, *105*, 3039.
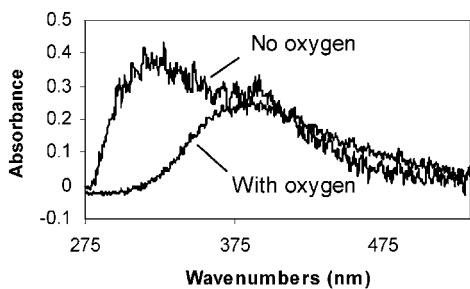
Figure 1. Transient UV spectrum produced by LFP (266 nm) of **1** in deoxygenated and oxygenated Freon. The spectrum was recorded immediately after the laser pulse over a window of 20 ns.

Figure 2. Plot of the observed rate constant of transient decay (400 nm) versus the concentration of tetramethylethylene and triethylsilane produced by LFP (266 nm) of **1** in Freon.

only the carrier of 333 nm absorption reacts rapidly with oxygen. Triplet nitrenes are known to react with oxygen, but with absolute rate constants that are much smaller than diffusion control.[3] Therefore, it seems unlikely that the oxygen-sensitive transient species is triplet carboethoxynitrene.

To identify the carriers of the transient spectra, the UV–vis spectra of various possible reactive intermediates were predicted using time-dependent density functional theory (TD-DFT, Supporting Information). On the basis of the calculations and the reactivity of the intermediates toward oxygen, the transient species absorbing at 333 and 400 nm are attributed to radical **3** and triplet nitrene **2t**, respectively (Table 1). Lwowski and co-workers' product-based studies[1]

Table 1.

2t
λ_{max}: 415 nm, f= 0.0095
367 nm, f=0.0060

3
λ_{max}: 311 nm, f= 0.0046
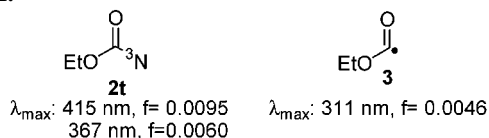
demonstrated that nitrene-derived products are formed in approximately 70% yield upon photolysis of **1**. Thus, we conclude that the ratio of **2t/3** is at least 70/30.

Consistent with these assignments, we find that the observed rate constant of decay of **2t** (1/lifetime, τ_{2t}) is linearly dependent on the concentration of tetramethylethylene (TME, $k^3_{TME} = 3 \times 10^8$ M^{-1} s^{-1}, Figure 2) and triethylsilane (TES $k^3_{TES} = 1 \times 10^6$ M^{-1} s^{-1}, Figure 2). Both TME and TES quench the yield of transient absorption at 400 nm in addition to shortening the triplet nitrene lifetime. Stern–Volmer treatment of the data yields values of $k_Q\tau_{2s}$ = 10 and 0.4, respectively (Figures 3). Methanol hardly quenches the yield of **2t**, except at very high concentration ($k_Q\tau_{2s} \le 0.1$), but does not shorten the lifetime of **2t** (Figure 3).

On the basis of the extensive product studies of Lwowski and co-workers,[1] it is well-known that singlet carboethoxynitrene **2s** will both add to alkenes such as TME to form
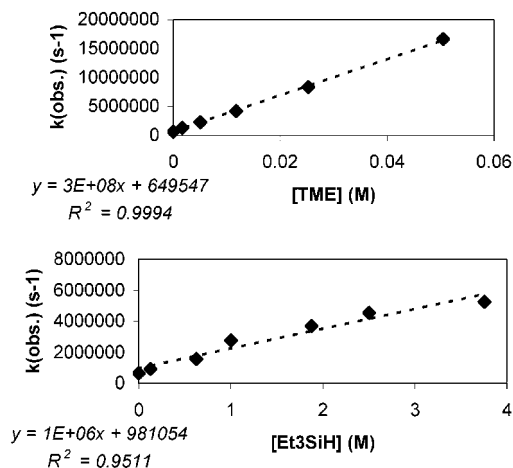
aziridine and insert into an allylic C–H bond to form urethane, insert into an unactivated C–H or Si–H bond as in TES, and insert into the O–H bond of methanol.[1] We speculate that the O–H insertion reaction of the singlet nitrene is slower than the C–H insertion reactions of the singlet nitrene because of lone pair–lone pair repulsive interactions between the nitrogen and oxygen atoms of the reactants. Triplet nitrene **2t** is expected to add in a stepwise fashion to the alkene[1] to eventually form aziridine and to slowly abstract hydrogen atoms even from generally good donors.[3]
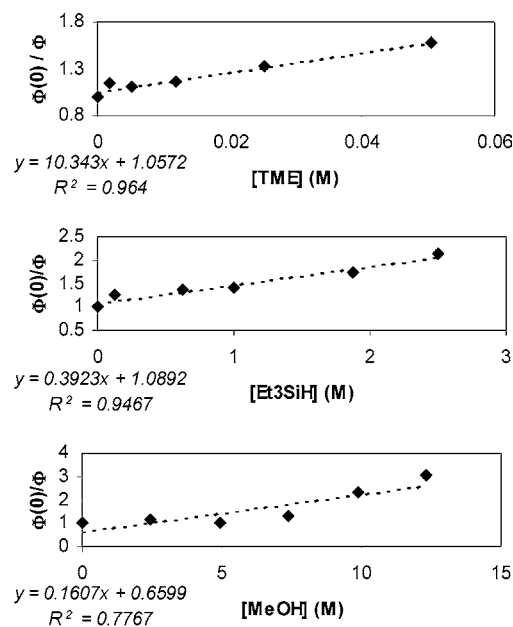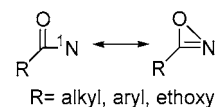

Figure 3. A plot of $\Phi(0)/\Phi$ versus the concentration of tetramethylethylene, triethylsilane, and methanol produced by LFP (266 nm) of **1** in Freon.

Assuming that $k^1_{TME} \leq 5 \times 10^9$ M^{-1} s^{-1} and recalling that triplet nitrene **2t** is formed within the 10 ns time resolution of the spectrometer, one deduces that the lifetime of **2s** in Freon-113 at ambient temperature is between 2 and 10 ns and that k_{ISC} is approximately $(1-5) \times 10^8$ s^{-1}. This value of k_{ISC} is 2 orders of magnitude greater than the corresponding intersystem crossing rate constant of singlet phenyl nitrene.[3]

The difference in intersystem crossing rates can be understood with the aid of theory. DFT calculations of closed-shell singlet nitrene **2s** place the energy of this state 12.3 kcal/mol above the corresponding triplet nitrene (Supporting Information). However, this level of calculation overestimates the stability of triplet methylene relative to singlet methylene by ∼4 kcal/mol and that of triplet formylnitrene relative to singlet formylnitrene by about 9 kcal/mol with the 6-31G* basis set.[7,8] If the same error applies to carboethoxynitrene, we can estimate that the triplet state of this nitrene is 3.3−8.3 kcal/mol more stable than the singlet. Unlike singlet aryl nitrenes, singlet acylnitrenes prefer closed-shell rather than open shell configurations[8] due to a bonding interaction between the nitrene nitrogen and carbonyl oxygen bonding interaction (Figure 4).

Figure 4. Electronic interactions in acylnitrenes.

Thus, we suspect that in nitrene **2s**, the lowest singlet also has a closed-shell singlet configuration, which unlike open-shell singlets (e.g., phenyl nitrene[3]) has allowed spin−orbit intersystem crossing (ISC).[9] A similar interpretation has been used to understand rapid ISC in phosphorylnitrenes.[10]

Supporting Information Available: Optimized geometries, energies, zero-point and thermal corrections, and IR frequencies of several possible intermediates generated upon photolysis of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Scott, A. P.; Platz, M. S.; Radom, L. *J. Am. Chem. Soc.* **2001**, *123*, 6069.

(8) Pritchina, E. A.; Gritsan, N. P.; Maltsev, A.; Bally, T.; Autrey, T.; Liu, Y.; Wang, Y.; Toscano, J. P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1010.

(9) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3568. (c) Zimmerman, H. E.; Kutateladze, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 249. (d) Zimmerman, H. E.; Kutateladze, A. G. *J. Org. Chem.* **1995**, *60*, 6008.

(10) Gohar, G.; Platz, M. S. *J. Phys. Chem. A* **2003**, *107*, 3704.