manner to give 220 mg (0.20 mmol, 80% based of starting material reacted) of **16**: R_f 0.15; ^{1}H NMR δ 1.27 ($H_{6'}$, $J_{5',6'} = 6.1$ Hz), 1.32 (H_6, $J_{5,6} = 6.1$ Hz), 1.48–1.91 ($H_{2a,2a'}$), 2.09 ($H_{2e'}$, $J_{1',2e'} = 2.0$ Hz, $J_{2e',3'} = 5.4$ Hz), 2.38 (H_{2e}, $J_{1,2e} = 2.9$ Hz, $J_{2e,3} = 5.0$ Hz), 3.12 (H_4, $J_{3,4} = J_{4,5} = 8.9$ Hz), 3.32 (OCH_3), 3.37–3.85 (H_3, $H_{3'}$, H_5, $H_{5'}$), 4.55 and 4.60 ($ArCH_2$), 4.58 ($H_{1'}$, $J_{1',2a'} = 10$ Hz), 4.76 (H_1), 5.03 ($H_{4'}$, $J_{4',5'} = J_{3',4'} = 9.3$ Hz), 7.16–7.56, 7.94–8.07 (aromatic). Anal. Calcd for $C_{27}H_{34}O_8$: C, 66.65; H, 7.04. Found: C, 66.81; H, 7.17. Compound **16** was reacted with *p*-toluenesulfonyl chloride, according to the procedure used for formation of **5**, to regenerate **13**.

Synthesis of Methyl 3-*O*-(4-*O*-Benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-4-*O*-(*p*-tolylsulfonyl)-α-D-*arabino*-hexopyranoside (17). Compound **13** (210 mg, 0.33 mmol) and 1.05 g of 5% Pd on carbon was stirred in 25 mL of ethyl acetate under 1 atm of hydrogen for 48 h. The suspension was filtered, and the filtrate evaporated to give 145 mg (0.26 mmol, 79% yield) of **17**: mp 154–155 °C; R_f 0.05; ^{1}H NMR δ 1.12 ($H_{6'}$, $J_{5',6'} = 6.1$ Hz), 1.43 (H_6, $J_{5,6} = 6.2$ Hz), 2.52 ($ArCH_3$), 3.31 (OCH_3), 4.74 (H_1, $J_{1,2a} = 3.0$ Hz, $J_{1,2e} = 1.0$ Hz), 7.25–8.07 (aromatic). Anal. Calcd for $C_{27}H_{34}O_{10}S$: C, 58.89; H, 6.22. Found: C, 59.98; H, 6.23. Reaction of compound **17** with benzyl triflate regenerated **13**.

Acknowledgment. We wish to thank Drs. J. C. Johnston and M. A. Meador for obtaining the 300-MHz NMR spectra of compounds **13** and **14** and the Research Challenge Program for financial support of this work.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for compound **15** (7 pages). Ordering information is given on any current masthead page.

Solvent Effects on the Ability of Amines To Physically Quench Singlet Oxygen As Determined by Time-Resolved Infrared Emission Studies

E. L. Clennan,* L. J. Noe,* T. Wen, and E. Szneler[1]

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82070

Received January 27, 1989

The rates of physical quenching of singlet oxygen by nine amines were determined by following the decrease in the singlet oxygen emission intensity at 1270 nm. The effect of solvents on these rates were shown to be related to the hydrogen bond donating ability of the solvent, α.

The ability of solvents to produce both subtle and dramatic effects in singlet oxygen reactions has been known for many years.[2] It was also recognized that analysis of these solvent effects was complicated by the multistep nature of singlet oxygen reactions. Solvent effects on the photophysics of the sensitizer[3] and lifetime of singlet oxygen[4] had to be separated from the solvent effect on the reaction of interest. Early reports were restricted to determining solvent effects on β[5] (rate of decay of $^1O_2$/rate of reaction with acceptor), and any successful study required a time-consuming and careful kinetic analysis.

In 1979 Krasnovskii[6] and Khan and Kasha[7] reported for the first time the observation of the phosphorescence from $^1O_2[^1\Delta_g(\nu = 0) \rightarrow {}^3\Sigma_g^-(\nu = 0)]$ in solution at 1270 nm. The technique of following the time rate of change of the $^1O_2$ phosphorescence intensity results in a simple, direct, and accurate measure of the $^1O_2$ lifetime in comparison to earlier indirect methods based on competitive kinetics. The lifetime of the $^1\Delta_g$ state is a function of competitive processes which include physical quenching, chemical quenching, and electronic to vibronic energy transfer to the solvent. Early studies by investigators[4,8] with this now popular and improved technique focused on examinations of the effect of solvents on the nonradiative lifetime of $^1O_2$.

Table I. Solvent Effects on Singlet Oxygen Lifetimes[a]

solvent	$1/(k_d + k_s[S])$[b]	$1/k_d$[b]
(±)-2-butanol	16.1 ± 0.2	19.7
2-propanol	22.4 ± 0.4	22.1
CF_3CH_2OH	24.3 ± 0.4	
benzene[c]	25.8 ± 0.7	31.2,[d] 32,[e] 28[f]
acetone	38.2 ± 1.1	40,[e] 46.5[f]
acetone[g]	43.4 ± 0.2	
$(CF_3)_2CHOH$	52.5 ± 0.3	
CH_3CN	55.3 ± 0.5	61,[e] 54.4[f]
acetone-d_6	585 ± 5.0	640,[d] 690[f]

[a] 9.0×10^{-5} to 1.0×10^{-6} M Rose Bengal. [b] In microseconds. [c] Sensitizer acridine. [d] Reference 4c. [e] Reference 4b. [f] Reference 4a. [g] 1×10^{-4} M tetraphenylporphyrin.

We report here a study of the physical quenching ability of several amines (Figure 1) using this technique. The quenching of singlet oxygen by amines has been extensively examined.[9] Several workers[10] have observed that

---

(1) Jagiellonian University, Krakow, Poland.

(2) Schenck, G. O.; Gollnick, K. *Forschungsbericht des Landes Nordrhein-Westfalen*, Nr. 1256; Westdeutscher Verlag: Koln and Opladen, 1963

(3) Cramer, L. E.; Spears, K. G. *J. Am. Chem. Soc.* **1978**, *100*, 221.

(4) (a) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423. (b) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756. (c) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201. (d) Schmidt, R.; Brauer, H.-D *J. Am. Chem. Soc.* **1987**, *109*, 1987.

(5) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5168.

(6) Krasnovskii, A. A. *Photochem. Photobiol.* **1979**, *29*, 29.

(7) Khan, A.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6074.

(8) Byteva, I. M. *Zh. Prikl. Spektrosk.* **1979**, *31*, 333.

(9) (a) Ouannes, C.; Wilson, T. *J. Am. Chem. Soc.* **1968**, *90*, 6527. (b) Smith, W. F. *J. Am. Chem. Soc.* **1972**, *94*, 186.

(10) (a) Ogryzlo, E. A.; Tang, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 5034. (b) Young, R. H.; Martin, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 5183. (c) Young, R. H.; Martin, R. L.; Feriozi, D.; Brewer, D.; Kayser, R. *Photochem. Photobiol.* **1973**, *17*, 233. (d) Young, R. H.; Brewer, D.; Kayser, R.; Martin, R.; Feriozi, D.; Keller, R. A. *Can. J. Chem.* **1974**, *52*, 2889. (e) Saito, I.; Matsuura, T.; Inoue, K. *J. Am. Chem. Soc.* **1981**, *103*, 188. (f) Manring, L. E.; Foote, C. S. *J. Phys. Chem.* **1982**, *86*, 1257. (g) Saito, I.; Matsuura, T.; Inoue, K. *J. Am. Chem. Soc.* **1983**, *105*, 3200.

0022-3263/89/1954-3581$01.50/0

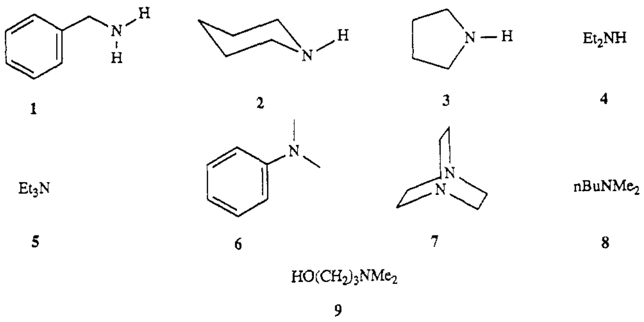


Figure 1.

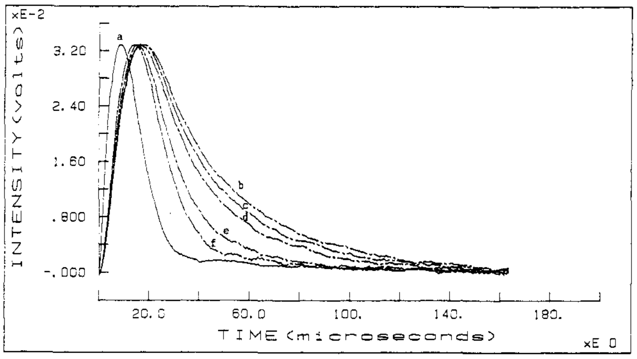


Figure 2. Normalized $^1O_2$ phosphorescence decay curves in the absence (b) and in the presence of increasing amounts of DABCO (c–f). The detector response curve is given by a. All data collected in benzene using acridine as the sensitizer.

quenching is enhanced with decreasing ionization potentials of the amines. This observation has led to the suggestion that quenching occurs by a charge-transfer mechanism (eq 1). As a result of this study we have discovered

$$^1O_2 + R_3N \rightarrow [\overset{\delta^-}{^1O_2}\cdots\overset{\delta^+}{NR_3}] \rightarrow {}^3O_2 + R_3N \qquad (1)$$

that in addition to ionization potential, the ability of amines to quench $^1O_2$ is related to a specific solvent property, its hydrogen bond donating ability, α.[11] Our results have important implications in biological systems where amines can exist in either hydrophilic or hydrophobic environments.

Results and Discussion

Oxygen-saturated solutions containing varying amounts of amines and sensitizers were irradiated at either 355 or 532 nm with a Nd:YAG laser (see the Experimental Section), and the $^1O_2$ phosphorescence intensities were monitored as a function of time at 1270 nm. Sample data for DABCO 7 is shown in Figure 2. Each exponential decay curve in Figure 2 is first-order and is adequately described by eq 2. The rate constants k_d, k_s, and k_a represent the

$$-\frac{d[^1O_2]}{dt} = k_{obsd}[^1O_2]$$

$$k_{obsd} = k_d + k_s[S] + k_a[A] \qquad (2)$$

solvent-, sensitizer-, and amine-induced deactivation of singlet oxygen, respectively, and [S] the concentration of the sensitizer, either Rose Bengal excited at 532 nm or acridine at 355 nm, and [A] the concentration of the amine. The rate constants k_s and k_a are composites of both physical (k_q) and chemical (k_r) processes which remove singlet oxygen from solution. Plots of k_{obsd} versus [A] produce linear curves from which both the rate constants k_a (slope) and the quantity $[k_d + k_s[S]]$(intercept) can be extracted. Examination of Table I, which compares our value of $1/(k_d + k_s[S])$ to published data for $1/k_d$, demonstrates that within experimental error $k_s[S] = 0$ under our conditions except in acetone-d_6. Experiments in acetone-d_6 in which [A] = 0 and the concentration of Rose Bengal is varied give $1/k_d$ = 641 μs and $k_s = 9.93 \times 10^6$ M^{-1} s^{-1}, in excellent agreement with literature results.[12]

Table II. Rates of Reactions of Amines with Singlet Oxygen as a Function of Solvent

amine	solvent^a	k_a, M^{-1} s^{-1}	α^b
1	CH$_3$CN	1.71×10^6	
	(CH$_3$)$_2$CHOH	9.62×10^4	
2	acetone	7.82×10^7	0.08
	CH$_3$CN	5.61×10^7	0.19
	CHCl$_3$^{c}	3.62×10^6	0.44
	(±)-2-butanol	1.03×10^6	0.73
	(CH$_3$)$_2$CHOH	9.05×10^5	0.76
	CF$_3$CH$_2$OH	6.5×10^3	1.51
3	CH$_3$CN	1.4×10^8	
	(CH$_3$)$_2$CHOH	2.15×10^6	
	CF$_3$CH$_2$OH	1.46×10^4	
4	CH$_3$CN	1.48×10^8	
	(CH$_3$)$_2$CHOH	3.84×10^6	
5	CH$_3$CN	3.33×10^8	
	(CH$_3$)$_2$CHOH	3.64×10^7	
	CF$_3$CH$_2$OH	1.73×10^4	
6	CH$_3$CN	4.77×10^8	
	(CH$_3$)$_2$CHOH	1.72×10^7	
7	CH$_3$CN	4.9×10^8	
	(CH$_3$)$_2$CHOH	3.6×10^6	
	CF$_3$CH$_2$OH	4.42×10^4	
8	benzene^d	4.35×10^8	0.0
	acetone	3.45×10^8	
	CH$_3$CN	2.68×10^8	
	(CH$_3$)$_2$CHOH	4.51×10^7	
	CF$_3$CH$_2$OH	1.9×10^5	
9	benzene^d	6.82×10^7	
	acetone	1.88×10^8	
	CH$_3$CN	1.35×10^8	
	CF$_3$CH$_2$OH	1.82×10^5	

^{a}(3–9) × 10^{-5} M Rose Bengal. ^{b}Reference 10. ^{c}1.6 × 10^{-4} M tetraphenylporphyrin. ^{d}(2–3) × 10^{-5} M acridine.

The rates constants k_a measured by this direct kinetic method for the reactions of amines 1–9 with singlet oxygen are tabulated in Table II. Consistent with suggestions[9,10] that amine quenching occurs by charge-transfer interactions is the reactivity sequence in CH$_3$CN: primary amine 1 < secondary amines **2**, **3**, and **4** < tertiary amines **5**, **6**, **7**, and **8**.

The solvent effect data in Table II reveals that for amines 2, 3, 5, and 7 there is a decrease of 4 orders of magnitude in the quenching rates as the solvent is changed from CH$_3$CN to 2,2,2-trifluoroethanol (CF$_3$CH$_2$OH). This solvent-induced rate ratio ($k_{fastest}/k_{slowest}$) of 10^4 is much larger than that reported by Gollnick for the singlet oxygen ene (20)[13] or 2 + 2 cycloaddition reactions (350).[14] The rates of these ene and cycloaddition reactions were successfully correlated to the Dimroth Reichardt[15] $E_T(30)$ and the Kirkwood–Laidler–Eyring[16] $(\epsilon - 1)/(2\epsilon + 1)$ solvent polarity scales. In contrast, the rate of reaction of amine 2 is best predicted (eq 3) by the Taft α scale, which de-

$$\log k_A = -2.87\alpha + 8.10 \qquad r = -0.995 \qquad (3)$$

---

[11] Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

[12] Tanielian, C.; Golder, L.; Wolff, C. *J. Photochem.* **1984**, *25*, 117.

[13] Gollnick, K.; Griesbeck, A. *Tetrahedron* **1984**, *40*, 3235.

[14] Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1984**, *725*.

[15] Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98.

[16] Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; J. Wiley: New York, 1961.

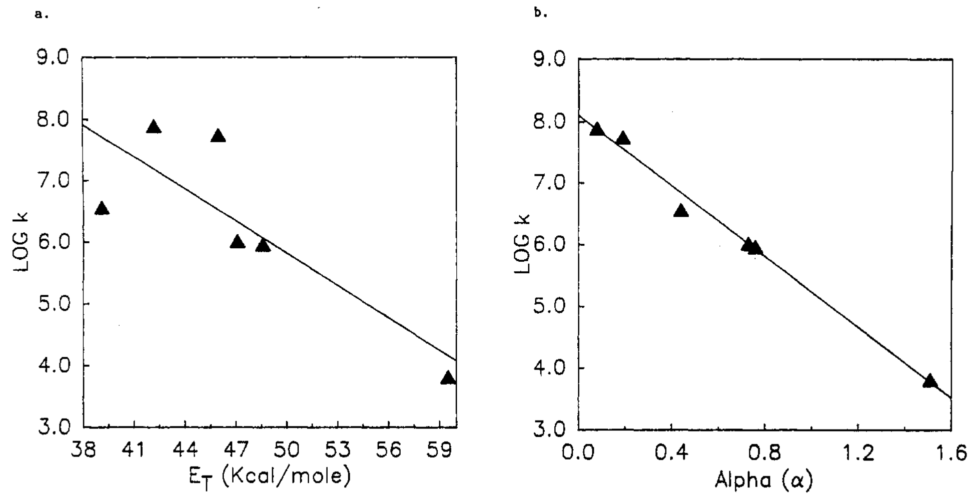


Figure 3. (a) log k_a versus E_T, and (b) log k_a versus α for the reactions of amine **2** with singlet oxygen.

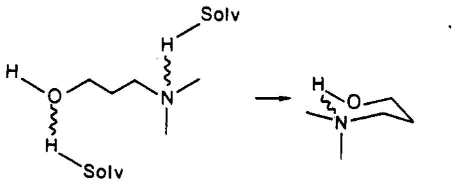
$$R_3N + HSolv \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3N\cdots H\cdots Solv$$

$$R_3N + {}^1O_2 \xrightarrow{k_a(\text{intrinsic})} R_3N + {}^3O_2$$

Figure 4.

scribes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond (Figure 3). The observation of this correlation demonstrates that the solvents dipolarity/polarizability play little if any role in the stabilization of the transition states for these reactions. We suggest that measured rate constants for amine singlet oxygen quenching reactions in solvents where α is not zero are given by $k_a = k_a(\text{intrinic})/K_{eq}$, where $K_{eq} = k_1/k_{-1}$ (Figure 4).

The behavior of *n*-butyldimethylamine (**8**) is compared to its hydroxy analogue **9** in Figure 5. In the potent hydrogen bonding solvent 2,2,2-trifluoroethanol, both amines are extensively hydrogen bonded, at nitrogen in **8** and at both nitrogen and oxygen in **9**. In this solvent both compounds react at the same rate as a result of the near identical electronic environment at nitrogen. As the hydrogen bond donating ability of the solvent decreases, the rate of reaction of **8** responds as observed previously for amines **1**–**7**. In contrast, the hydroxy amine **9** increasingly reacts slower than predicted based on electronic considerations alone. This behavior reflects the increasing availability of the hydroxy group to participate in an intramolecular hydrogen bond and to lower the effective concentration of free amine (eq 4). The difference in rates of reaction of **8** and **9** in benzene, given the mechanism depicted in Figure 4, translates into a free energy for reaction 4 of 1.2 kcal/mol at 298.16 K.



(4)

The observed rate constant for the ene reaction[17] of tetramethylethylene also decreases with increasing hydrogen bond donating ability in the series, CH_3CN (3.84×10^7 M^{-1} s^{-1}); $(CH_3)_2CHOH$ (2.8×10^7 M^{-1} s^{-1}); CF_3CH_2OH (9.8×10^6 M^{-1} s^{-1}). The much reduced rate ratio ($k_{fastest}/k_{slowest}$) of only 3.9 reflects the much reduced propensity of π-electrons to participate in hydrogen bonding[18] in comparison to amines. Breslow[19] has reported a rate-enhancing effect of H_2O ($\alpha = 1.17$) on the rates of 2 + 4 cycloadditions. In this case the rate enhancement is likely to be due to the hydrophobic tendency to diminish the hydrocarbon–water interfacial area, an effect which is more important than the rate-retarding hydrogen bonding.

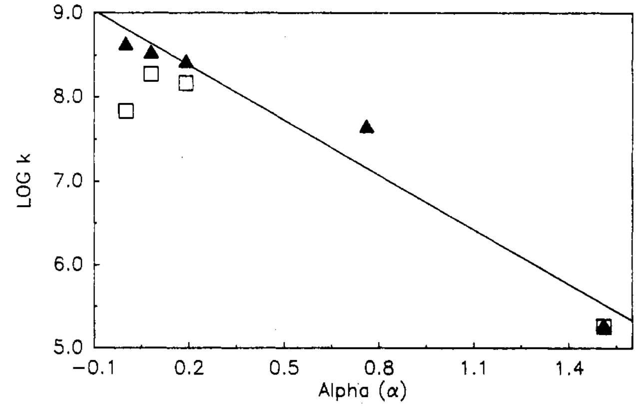


Figure 5. log k_a versus α for **8** (filled triangles) and **9** (open squares).

Experimental Section

Triethylamine (99+% Gold Label), piperidine (99%), pyrrolidine (99%), and benzylamine (99%) were obtained from Aldrich, and dimethylaniline and diethylamine from Baker. These reagents were used without further purification. 1,4-Diazabicyclo[2.2.2]octane was obtained from Aldrich and was sublimed twice under vacuum.

Preparative gas chromatography was conducted with a GOW-MAC Series 550 thermal conductivity instrument equipped with a 20 ft × $^1/_4$ in. column packed with 20% Carbowax 20M on Chromosorb W.

Proton and carbon NMR spectra were obtained on a JEOL FX270 instrument operating at 270 and 67.83 MHz, respectively, and the chemical shifts are referenced to Me_4Si.

***N*,*N*-Dimethyl-*N*-butylamine**[20] (**8**) was prepared from butylamine by reductive methylation.[21] It was purified at 60 °C by gas chromatography, flow rate 25 mL/min He, detector 150 °C, injector 120 °C, and collector 150 °C: ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7 Hz, 3 H), 1.25–1.5 (m, 4 H), 2.21 (s, 6 H), 2.24 (t,

---

[17] Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809.

[18] Baker, A. W.; Shulgin, A. T. *J. Am. Chem. Soc.* **1958**, *80*, 5358.

[19] Rideout, D. C.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 7816.

[20] Ma, J. C. N.; Warnhoff, E. W. *Can. J. Chem.* **1965**, *43*, 1849.

[21] Borch, R. F.; Hassid, A. I. *J. Org. Chem.* **1972**, *37*, 1673.

$J = 7.3$ Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 14.0, 20.6, 30.0, 45.5, 59.7.

***N*,*N*-Dimethyl-*N*-(3-hydroxypropyl)amine (9)** was prepared from *N*,*N*-dimethyl-*N*-(3-chloropropyl)amine by alkaline hydrolysis. It was purified at 120 °C by gas chromatography, flow rate 25 mL/min He, detector 180 °C, injector 180 °C, and collector 190 °C: ^{1}H[22] NMR (CDCl$_3$) δ 1.69 (m, 2 H), 2.26 (s, 6 H), 2.54 (t, $J = 6$ Hz, 2 H), 3.81 (t, $J = 5$ Hz, 2 H), 5.46 (b s, 1 H).

Rate Constant Determinations. The kinetic apparatus consisted of (a) a Spectra-Physics DCR11 Nd:YAG pulsed laser with second and third harmonic (532 and 355 nm) capability which delivers 10-ns pulses at rates up to 10 pps, (b) a germanium (Judson 2 or 5 mm ϕ) diode detector/customized preamplifier, (c) various optics, the most important of which is a 10-nm narrow band pass nonfluoresceing filter centered at 1.27 μm placed just ahead of the detector, (d) a 100-MHz LeCroy transient digitizer/signal averager interfaced to a 80386 based PC/AT computer, and (e) an energy meter. Since the experimental decay is a convolution of the detector response (fwhm of approximately 10 μs for the 5 mm ϕ-detector; 5 μs for the 2 mm ϕ-detector) and the sample decay, it was necessary to implement a numerical deconvolutional analysis in order to accurately extract measured lifetimes 2 μs $\leq \tau \leq$ 100 μs from the recorded data. With this treatment lifetimes as low as 2 μs for certain nondeuterated solvent–sensitizer–amine combinations were available. The numerical deconvolution analysis of Demas[23] for exponential decays also corrects artifacts caused by scattered excitation light that may reach the detector was used. This analysis was implemented on our laboratory computer by using a general scientific/engineering analysis/data acquisition program called ASYST. Signal averaging 100 experiments, each with laser pump energies $\leq$5 mJ gave 8192-point decay curves each of which produced pseudo-first-order rate constants with correlation coefficients (square root) better than 0.99.

Sample preparation was conducted by adding varying amounts of a stock solution of the amine to a stock solution of oxygen saturated sensitizer. This method insured the same sensitizer concentration in each experiment. At least five pseudo-first-order rate constants were collected for each amine. This experiment was repeated at least twice with fresh stock solutions for every amine–sensitizer–solvent combination.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, Grants CHE-8722088 and RII-8610680. We also thank Professor Peter Ogilby (University of New Mexico) for his helpful advice on the construction of our germanium preamplifier/detector.

---

(22) Proton NMR reported in *The Aldrich Library of NMR Spectra*, ed. 2; Vol. 1, spectrum 299C.

(23) Love, J. C.; Demas, J. N. *Anal. Chem.* **1984**, *56*, 82.

Solvent and Aryl-Substituent Effects on the Rates of Thermal Decomposition of α-Azidostyrenes

David Jordan

Department of Chemistry, Potsdam College, Potsdam, New York 13676

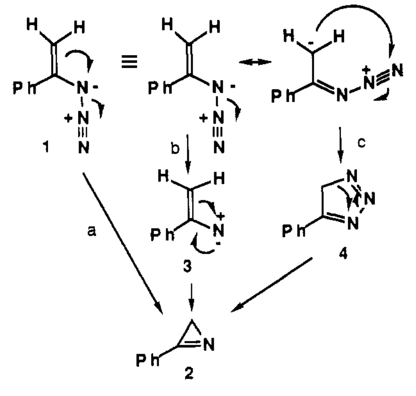
Received February 17, 1989

The effect on the rates of first-order thermolysis of α-azidostyrenes by aryl substitution have been measured in benzyl alcohol and 1-butanol in the temperature range 60–100 °C. Values for ΔH^{*} are in the range 24–28 kcal/mol, and for ΔS^{*}, +1 to −9 eu. The rate constants of the meta and para substituents are correlated with σ^{+} substituent constants where $\rho = -0.7$ ($r = 0.98$) in both solvents. Relative to α-azidostyrene, 2-methyl-α-azidostyrene and 2,4,6-trimethyl-α-azidostyrene experience retardation of thermolysis by factors of 0.97 and 0.58, respectively, in 1-butanol at 80 °C. The activation parameters, ρ value, σ^{+} rate correlation, and the steric retardation support a concerted mechanism where, in the transition state, positive charge is delocalized to the aryl ring, coplanarity of the developing azirine ring and the aryl ring being required. Thermolysis rates of α-azidostyrene at 80.2 °C are little affected by changes in solvent polarity, but are markedly accelerated in methyl acrylate, in which $\Delta H^{*} = 20$ kcal/mol and $\Delta S^{*} = -17$ eu, supporting a hypothesis by others that this reaction does not produce a nitrene intermediate, as was first suggested, but is likely a 1,3-dipolar cycloaddition mechanism of the azide function of α-azidostyrene with methyl acrylate to give a triazoline, which rapidly loses nitrogen.

Mechanistic studies have sought to determine whether thermal decomposition of α-azidostyrene (**1**) proceeds via concerted migration of a hydrocarbon group with dinitrogen loss (Scheme I, path a), involves the intermediacy of a nitrene species (path b), followed by ring closure to an azirine or other nitrene reactions, or involves the possibility (path c) that an intramolecular [3 + 2] cycloaddition yields an unstable isotriazole which extrudes dinitrogen to provide azirine as product, mechanistic pathways proposed by Smolinsky.[1] Arguments for one or the other paths have been reviewed.[2]

Azirine **2** is clearly established as the major thermolysis product of **1**. It has been isolated as the gas phase pyrolysis product of **1**,[1a] it is the major product of thermolysis in various hydrocarbons, acetonitrile, and dimethyl sulfoxide,[3] and it is formed in high yield, as are various other para-

Scheme I



---

(1) (a) Smolinsky, G. *J. Am. Chem. Soc.* **1961**, *83*, 4483. (b) Smolinsky, G. *J. Org. Chem.* **1962**, *27*, 3557.

(2) (a) Hassner, A. In *Azides and Nitrenes, Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984, Chapter 2. (b) L'abbe, G. *Angew. Chem., Int. Ed. Eng.* **1975**, *14*, 775.

(3) Woerner, F. P.; Reimlinger, H. *Chem. Ber.* **1970**, *103*, 1908.

0022-3263/89/1954-3584$01.50/0