

Dynamics of α -CH Deprotonation and α -Desilylation Reactions of Tertiary Amine Cation Radicals

Xiaoming Zhang,[†] Syun-Ru Yeh,[†] Seok Hong,^{†,1} Mauro Freccero,[‡] Angelo Albini,[‡] Daniel E. Falvey,[†] and Patrick S. Mariano^{*,†}

Contribution from the Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, Department of Organic Chemistry, University of Pavia, Pavia, Italy I-27100, and Institute of Organic Chemistry, University of Torino, Torino, Italy I-10125

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Abstract: Time-resolved laser spectroscopy has been used to generate and characterize a series of tertiary amine cation radicals and to determine the rates of their α -CH deprotonation and α -desilylation reactions with bases and silophiles. Laser excitation (308 nm) of a 60:40 MeOH:MeCN solution of PhNMe₂ (DMA) and 1,4-dicyanobenzene (DCB) promotes SET-induced formation of the DMA cation radical (460 nm) and DCB anion radical (340 nm), which undergo decay by back electron transfer at nearly equal rates and with respective second-order rate constants of 1.1×10^{10} and $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (25 °C). The decay rate is lowered (ca. 4-fold) by the inclusion of salts (ca. 0.1 M) such as nBu₄NClO₄, LiClO₄, nBu₄NCl, nBu₄NBF₄, and nBu₄NO₂SCF₃ in MeOH–MeCN and by changing the solvent from MeCN to MeOH and to EtOH. The cation radical of PhNMeCH₂(TMS) (480 nm) and the simultaneously generated DCB anion radical undergo second order decay in MeCN with respective rate constants of 1.2×10^{10} and $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C). The silylamine cation radical decay rate was found to be governed by the concentration of silophiles (MeOH, H₂O, and nBu₄NF) in MeCN solutions. The observations are consistent with a silophile-induced desilylation process with second-order rate constants of 8.9×10^5 (MeOH), 1.27×10^6 (H₂O), and $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (nBu₄NF). The rate of DMA cation radical decay is a function of base concentration. Both nBu₄NOAc and nBu₄NO₂CCF₃ react with the DMA cation radical (in 60:40 MeOH:MeCN containing 0.1 M nBu₄NClO₄) with second-order rate constants for α -CH deprotonation of 3.1×10^5 and $8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C), respectively. Measurements with PhN(CD₃)₂ and nBu₄NOAc gave a $k_{\text{H}}/k_{\text{D}}$ for α -CH deprotonation of 3.6 (60:40 MeOH:MeCN, 25 °C). Para-substituents have a pronounced effect on the rate of α -CH deprotonation by nBu₄NOAc; second-order rate constants of 2.3×10^4 , 1.1×10^5 , and $2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ were determined for the *p*-OMeC₆H₄NMe₂, *p*-MeC₆H₄NMe₂ and *p*-CF₃C₆H₄NMe₂ cation radicals. Studies with Ph₂NMe demonstrated that its cation radical (645 nm) can be generated by SET to DCB and that its decay through α -CH deprotonation by nBu₄NOAc has a second-order rate constant of $9.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and a $k_{\text{H}}/k_{\text{D}}$ value of 2.8 (25:75 MeOH:MeCN, 25 °C). Finally, the effects of α -substituents on the rates of nBu₄NOAc-induced α -CH deprotonation of tertiary amine cation radicals were evaluated by use of the amines Ph₂NCHR₁R₂. The second-order rate constants (25 °C, 25:75 MeOH:MeCN) are 2.3×10^5 (R₁ = Me, R₂ = H), 1.7×10^5 (R₁ = R₂ = Me), 3.2×10^6 (R₁ = Ph, R₂ = H), 2.6×10^6 (R₁ = CH=CH₂, R₂ = H), and $7.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (R₁ = C≡CH, R₂ = H).

Introduction

Interest continues to expand in the area of electron-transfer (SET) photochemistry. The overlapping issues of reaction mechanism and synthetic potential² have stimulated efforts to gain detailed information about the individual steps involved in the overall SET-reaction pathways and to develop methods to successfully predict new and efficient photochemical processes. Much attention has been given to understanding the properties of ion radicals owing to the key role these intermediates play in SET-induced photochemical reactions. In general, ion radicals formed by SET between neutral donors and acceptors can either decay by back electron transfer to produce ground-state reactants or undergo chemical reaction to produce radical or ionic precursors of photoproducts. Consequently, the efficiencies (chemical and quantum) and nature of SET-photochemical processes are governed to a large extent by the rates and types of reaction pathways open to the ion radical intermediates. Owing to this,

it is understandable why much attention has been focused on assessing ion radical reactivity. A number of photochemical^{2,3} and electrochemical⁴ studies have been designed to gain information about this issue through the analysis and interpretation of product distributions arising from processes proceeding *via* the intermediacy of charged radicals. In contrast, only a few investigations have employed direct methods to determine ion radical reaction rates and to evaluate how they are influenced by structural, substituent, and medium variations.⁵

In early efforts⁶ concentrating on the SET photochemistry of iminium cation–neutral donor pairs, indirect methods based on product distribution and quantum efficiency data were used by one of us to define the unique and high chemical reactivity of allyl- and benzylsilane cation radicals.^{3,7} In more recent

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[†] University of Maryland.

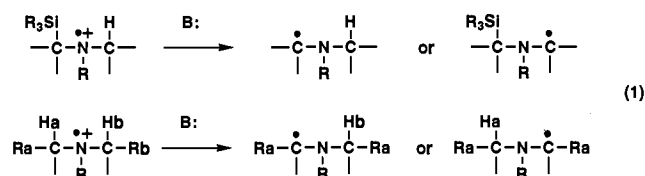
[‡] Universities of Pavia and Torino.

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(1) Permanent address: Department of Chemistry, Kungnam National University, Masan, Korea.

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investigations⁸ probing the SET photochemistry of tertiary amine–enone systems, mechanistically intriguing and synthetically useful reactions driven by tertiary aminium radical α -CH deprotonation and α -desilylation (eq 1) were uncovered. The complimentary



influences of solvent type and base strength on the relative rates (assessed by product analysis) of these competing α -heterolytic fragmentation processes were delineated⁹ and then used as strategy elements in the design of chemoselective and regioselective photoaddition and photocyclization reactions.^{10,11}

Even earlier, interest in tertiary aminium radical α -CH deprotonation reactions revolved about intense investigations^{12,13} of amine–olefin, –arene, and –ketone SET-induced photoaddition reactions. Thorough product analyses of tertiary amine–stilbene photoaddition reactions by Lewis and his co-workers¹³ first brought to light the effects of α -substituents on the relative rates of these α -CH deprotonation processes. Similarly, the selectivities observed in tertiary amine anodic oxidation reactions were also interpreted in terms of substituent effects on the rates of α -CH deprotonation of aminium radicals derived by one-electron oxidation.¹⁴

Continuing interest in this area of cation radical chemistry¹⁵ has led to several recent efforts which have employed direct measurements to determine tertiary aminium radical α -CH deprotonation rates. Included here are the pulse radiolysis study of von Sonntag,¹⁶ the stopped-flow investigation of Dinnocenzo,¹⁷ and the derivative cyclic voltammetry determinations of Parker¹⁸ (see below). Our attempts to understand how substituents and media govern the chemoselectivities (eq 1, $\sim\text{H}^+$ vs $\sim\text{SiR}_3^+$) and regioselectivities (eq 1, $\sim\text{H}_a^+$ vs $\sim\text{H}_b^+$) of tertiary aminium radical α -heterolytic fragmentation reactions guided us to the current investigation in which laser spectroscopic techniques were used to generate, characterize, and determine the decay rates of tertiary amine cation radicals. In this way, we have obtained α -CH deprotonation rates for cation radicals derived from para-substituted *N,N*-dimethylanilines 1–5 and α -substituted *N,N*-diphenyl-*N*-methylamines 7–13 and the rates of desilylation of the aminium radical from *N*-methyl-*N*-((trimethylsilyl)methyl)-aniline (6). These results along with observations of solvent, salt, and base strength effects are summarized and discussed below.

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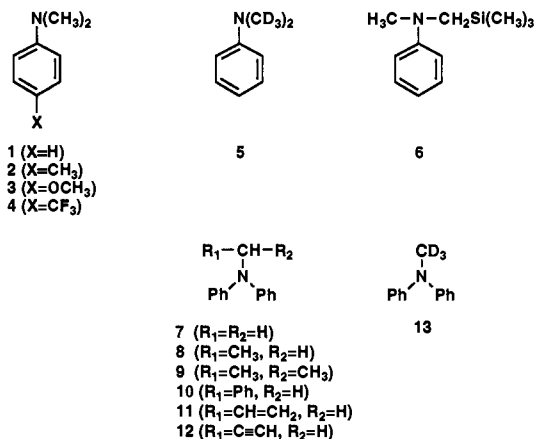
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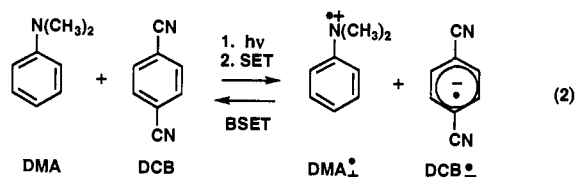
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Results

Generation, Detection, and Decay Kinetics of the *N,N*-Dimethylaniline (DMA) Cation Radical. The first phase of our studies focused on the SET-photoinduced generation and detection of the DMA cation radical. As anticipated, laser excitation (308 nm, 6 ns, 50–60 mJ) of a deoxygenated solution of DMA (0.5 mM) and 1,4-dicyanobenzene (DCB) (50 mM) in 60:40 MeOH:MeCN (by volume) leads to generation of two transient absorption bands assigned as that for the DCB anion radical (DCB^{•-}) (340 nm) and that for the DMA cation radical (DMA^{•+}) (460 nm) (see eq 2 and Figure 1). These absorption maxima match those



previously reported^{19,20} for these species. Further, both bands decay with overall second-order kinetics (power dependence on the rate observed). Owing to the nature of our planned studies, it was important to determine the process responsible for decay of these ion radical intermediates. Analysis of the decay curves (Figures 2 and 3) in conjunction with the known²⁰ molar extinction coefficient of DCB^{•-} ($3.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 340 nm) and the calculated²¹ molar absorptivity of DMA^{•+} ($6.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ at 460 nm) gives second-order rate constants of 1.29×10^{10} and $1.11 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for decay of the respective DCB^{•-} and DMA^{•+} species. The DCB^{•-} and DMA^{•+} decay rates are not dependent on α -CD substitution in the amine (*i.e.* from PhN(CD₃)₂). Thus, the equivalence of the decay rates and the lack of an isotope dependence suggest that the predominant mode of decay of these ion radicals is diffusion-controlled back electron transfer.

Having shown that DMA^{•+} can be generated and detected and that its decay kinetics can be accurately analyzed, we addressed the issue of medium effects on the ion radical lifetimes. Our purpose here was only to gain information about solvent and salt effects which would aid in our later (see below) interpretation of α -heterolytic fragmentation reactions of amine cation radicals. Accordingly, rate constants were determined for back electron transfer induced decay of DMA^{•+} and DCB^{•-} in media comprised of the solvents MeCN, EtOH, MeOH, and H₂O and in 60:40 MeOH:MeCN containing 0–0.1 M nBu₄NClO₄, LiClO₄, nBu₄NCl, nBu₄NBF₄, nBu₄NO₃SCF₃, and nBu₄NF. As the data in

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(21) The molar absorptivity of DMA^{•+} at 460 nm was determined by using the ratio of the absorbance at 340 nm for DCB^{•-} to that at 460 nm and the known extinction coefficient of $6.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for DCB^{•-} assuming a 1:1 ratio of these ion radicals are formed.

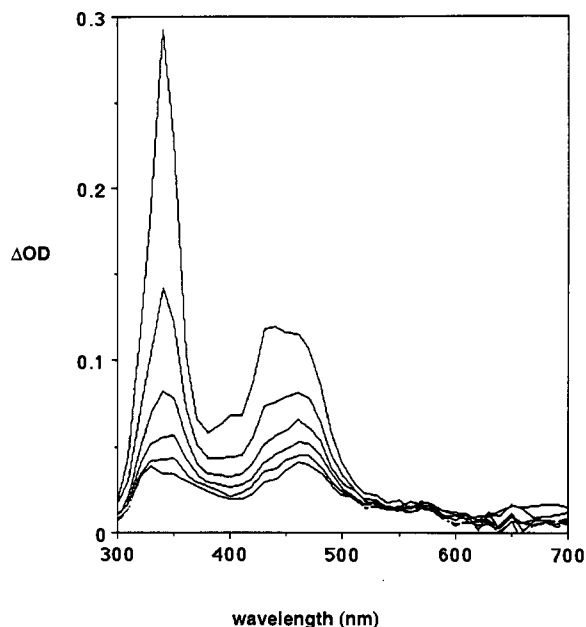


Figure 1. Transient absorption spectra following 308-nm excitation of 0.5 mM DMA and 50 mM DCB in 60:40 (volume) MeOH:MeCN at 2, 4, 6, 8, 10, 12, and 14 μ s.

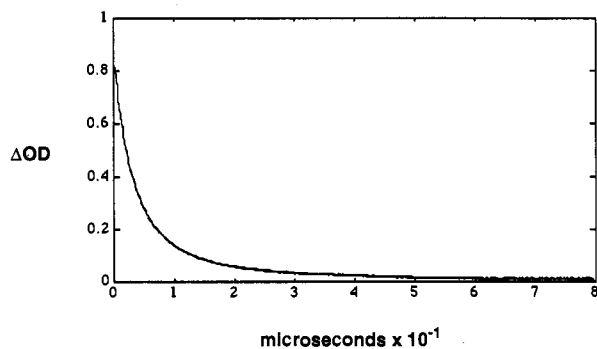


Figure 2. Decay of DCB^- at 340 nm after excitation of a solution of 0.5 mM DMA and 50 mM DCB in 60:40 $\text{CH}_3\text{OH}:\text{CH}_3\text{CN}$. Points are experimental data, and the solid curve represents kinetics calculated upon the basis of second-order decay.

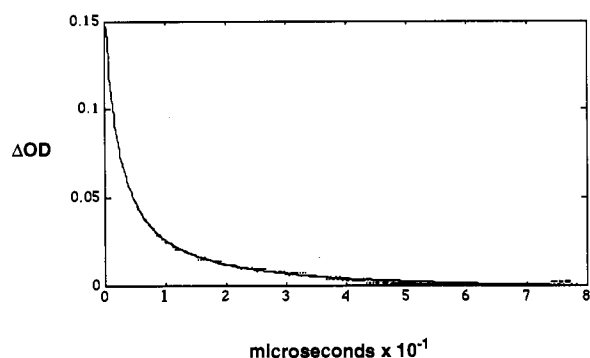


Figure 3. Decay of DMA^+ at 460 nm after excitation of a solution of 0.5 mM DMA and 50 mM DCB in 60:40 $\text{CH}_3\text{OH}:\text{CH}_3\text{CN}$. Points are experimental data, and the solid curve represents kinetics calculated upon the basis of second-order decay.

Figures 4 and 5 and summarized in Table 1 show, the rate constants ($k\epsilon^{-1}$) for DMA^+ decay decrease by nearly 1 order of magnitude with increasing concentrations of the salts listed above. The magnitude of this effect associated with LiClO_4 and $\text{nBu}_4\text{NClO}_4$ is equal and larger than that for the other tetra-*n*-butylammonium salts. Also, the attenuating effects of the salts

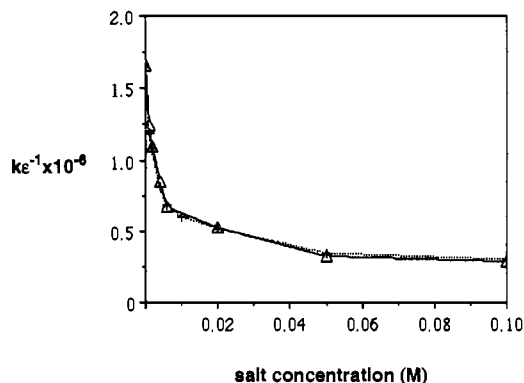


Figure 4. Rate ($k\epsilon^{-1}$) of DMA^+ decay at 460 nm vs salt concentrations following excitation of solutions of DMA and DCB in 60:40 MeOH:MeCN containing $\text{nBu}_4\text{NClO}_4$ (solid line) and LiClO_4 (dotted line).

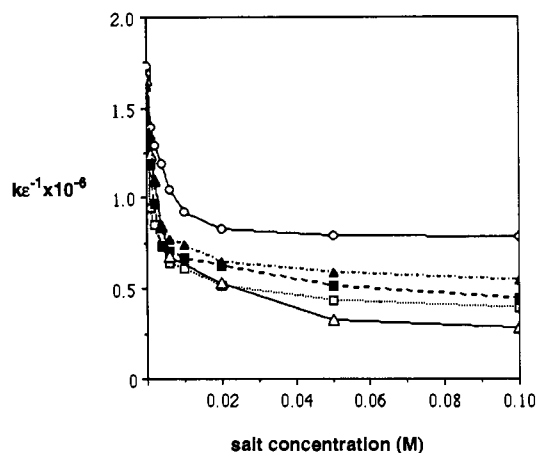


Figure 5. Rate ($k\epsilon^{-1}$) of DMA^+ decay at 460 nm vs salt concentrations following excitation of solutions of DMA and DCB in 60:40 MeOH:MeCN containing $\text{nBu}_4\text{N}-\text{ClO}_4$ (empty triangles), $-\text{Cl}$ (empty squares), $-\text{BF}_4$ (filled squares), $-\text{O}_3\text{SCF}_3$ (filled triangles), and $-\text{F}$ (empty circles).

Table 1. Solvent and Salt Effects on the Second-Order Rate Constants (25 °C) for Decay of the Dimethylaniline Cation Radical

solvent	salt (0.1 M)	$k \times 10^{-10}$ ($\text{M}^{-1} \text{s}^{-1}$)	$\eta \times 10^{-2}$ (P) ^a	$k_{\text{diff}} \times 10^{10}$ ($\text{M}^{-1} \text{s}^{-1}$) ^b
EtOH		0.70	1.08	0.61
MeOH		1.05	0.55	1.21
MeCN		2.05	0.35	1.91
60:40 MeOH:MeCN		1.11		
60:40 MeOH:MeCN	LiClO_4	0.17		
60:40 MeOH:MeCN	$\text{nBu}_4\text{NClO}_4$	0.17		
60:40 MeOH:MeCN	nBu_4NCl	0.25		
60:40 MeOH:MeCN	nBu_4NBF_3	0.28		
60:40 MeOH:MeCN	$\text{nBu}_4\text{NO}_3\text{SCF}_3$	0.34		
60:40 MeOH:MeCN	nBu_4NF	0.49		

^a Viscosity in Poise ($\text{g}/(\text{s}\cdot\text{cm})$) at 25 °C (ref 22). ^b Calculated by use of $k_{\text{diff}} = 8RT/3000\eta$ at 25 °C.

are the same for decay of both the DMA^+ and DCB^- transients. Finally, the salt effects display a saturation behavior; that is, the ion radical decay rates reach minimum values above salt concentrations of ca. 0.05–0.1 M.

The absorption spectral profiles for the DMA^+ and DCB^- transients generated by laser excitation of MeCN, EtOH, MeOH, and H_2O solutions of DMA and DCB are identical to those for these radical ions in 60:40 MeOH:MeCN. Also, both of these species have equivalent decay rates in these solvents. However, as demonstrated by the data accumulated in Figure 6 and Table 1, the nature of the solvent has a definite effect on the second-order rate constants for simultaneous decay of DMA^+ and DCB^- . The decrease in the DMA^+ decay rate in proceeding from MeCN ($2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), to MeOH ($1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) to EtOH ($7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) appears to be best correlated with the bimolecular

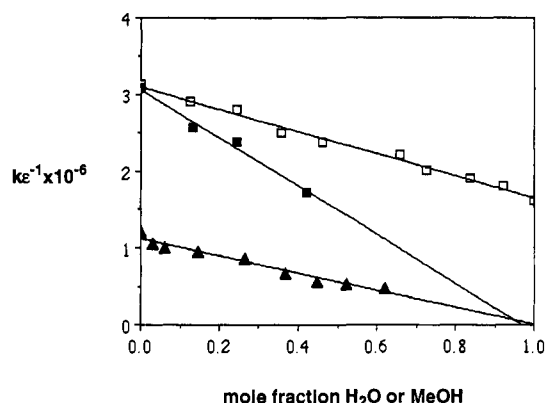


Figure 6. Rate ($k\epsilon^{-1}$) of DMA⁺⁺ decay at 460 nm vs mole fractions of MeOH in MeCN (empty squares), H₂O in MeCN (filled squares), and H₂O in EtOH (filled triangles) following excitation of solutions of DMA and DCB.

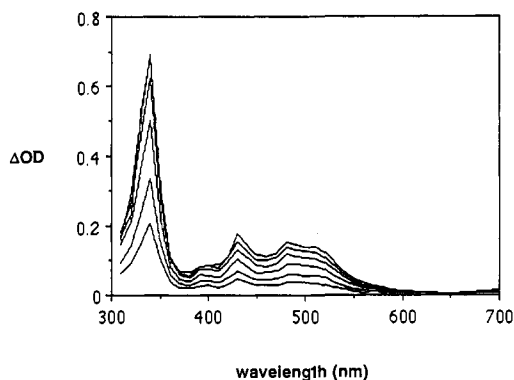
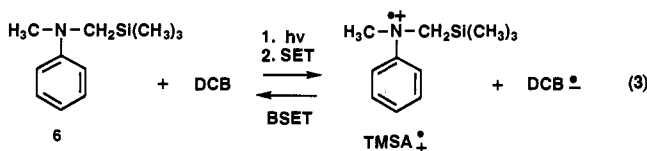


Figure 7. Transient absorption spectra following 308-nm excitation of 0.5 mM TMS-substituted aniline **6** and 50 mM DCB in MeCN at 0.2, 0.5, 1, 2, 4, 7, and 10 μ s.

diffusion rates in these solvents, which are governed by their viscosity (Table 1).

Decay Kinetics for the *N*-Methyl-*N*-((trimethylsilyl)methyl)-aniline Cation Radical. The SET-photochemical methodology described above was used to generate the *N*-methyl-*N*-((trimethylsilyl)methyl)aniline (**6**) cation radical (TMSA⁺⁺) (eq 3)



and to analyze its decay kinetics. The spectrum produced by irradiation (308 nm) of a deoxygenated MeCN solution of **6** (0.5 mM) and DCB (13 mM) is comprised of bands for TMSA⁺⁺ (480 nm, $\epsilon = 7.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) and DCB⁻ (340 nm) (Figure 7). Analysis of the decay profiles (Figures 8 and 9) gives the second-order rate constants 1.2×10^{10} and $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C) for decay of the respective transients.

The rate of decay of TMSA⁺⁺ (and not of DCB⁻, see Figure 10) is greatly accelerated by the presence of silophilic substances such as MeOH, H₂O, and nBu₄NF. Disappearance of the TMSA⁺⁺ absorption at 480 nm displays a pseudo-first-order kinetic dependence on these substances in MeCN solutions. A plot (Figure 11) of the TMSA⁺⁺ decay rate vs MeOH concentration (ca. 2–25 M) in MeCN is linear with a positive slope. The data yield a second-order rate constant of $8.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for MeOH-induced decay of TMSA⁺⁺. In contrast, a two-component dependence (Figure 12) of TMSA⁺⁺ decay on water concentration (ca. 1–20 M) in MeCN is observed. By using data in the near linear ([H₂O] = 0–5 M) region of this plot, it is possible to calculate

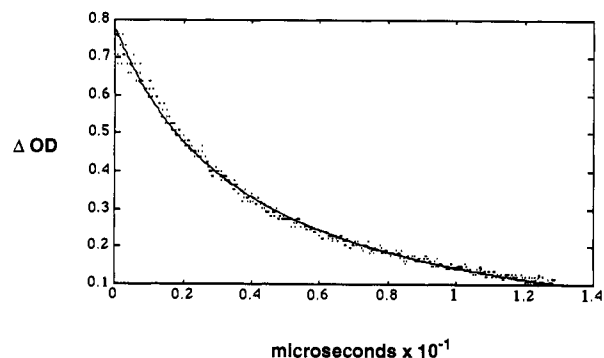


Figure 8. Decay of DCB⁻ at 340 nm after excitation of a solution of 0.5 mM **6** and 50 mM DCB in MeCN. Points are experimental data, and the solid curve represents kinetics calculated upon the basis of second-order decay.

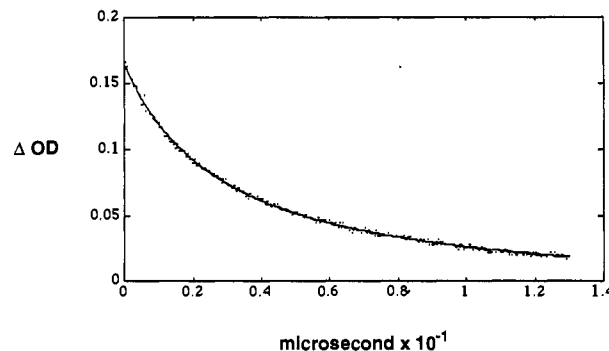


Figure 9. Decay of TMSA⁺⁺ at 480 nm after excitation of a solution of 0.5 mM **6** and 50 mM DCB in MeCN. Points are experimental data, and the solid curve represents kinetics calculated upon the basis of second-order decay.

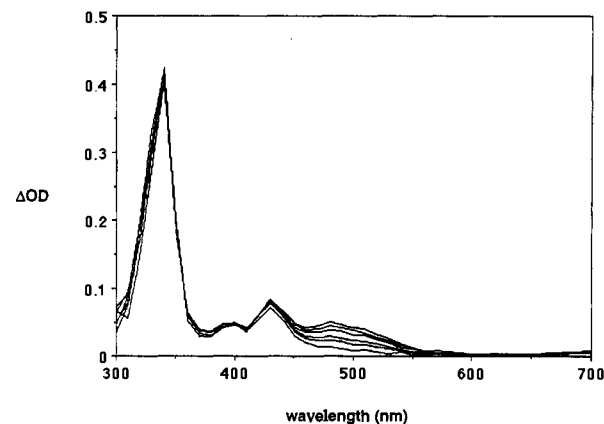


Figure 10. Transient absorption spectra following 308-nm excitation of 0.5 mM **6**, 13 mM DCB, and 5 M H₂O in MeCN at 0.2, 0.5, 1, 1.5, 2, and 5 μ s.

a second-order rate constant of $1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the H₂O + TMSA⁺⁺ decay process. Finally, a more dramatic effect is seen with the potent silophile nBu₄NF. The decay rate vs [nBu₄NF] (ca 0–1 mM) data plotted in Figure 13 yield a rate constant of $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for fluoride-promoted TMSA⁺⁺ decay.

α -CH Deprotonation Rates for Dimethylaniline Cation Radicals.

A number of preliminary experiments were performed to demonstrate that this methodology can be reliably employed in the determination of tertiary aminium radical α -CH deprotonation rates. The effects of base (nBu₄NOAc) on the decay of the DMA⁺⁺ and DCB⁻ transients were evaluated. As seen by viewing the spectra in Figure 14 and plots in Figure 15, the presence of nBu₄NOAc in 60:40 MeOH:MeCN results in an increase in the rate of DMA⁺⁺ decay and not in that of DCB⁻. Also, the effects of nBu₄NOAc and the weaker base nBu₄NO₂CCF₃ on the rate of DMA⁺⁺ decay are linear (Figure 15). Plots of rate vs base

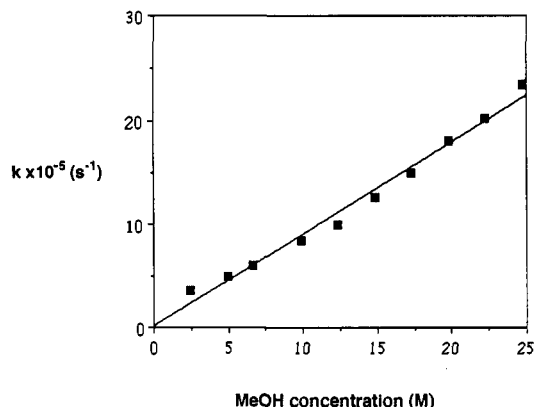


Figure 11. Rate of TMSA⁺⁺ decay at 480 nm vs concentration of MeOH in MeCN.

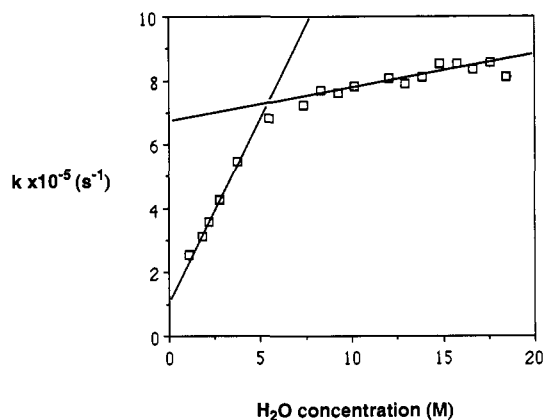


Figure 12. Rate of TMSA⁺⁺ decay at 480 nm vs concentration of H₂O in MeCN.

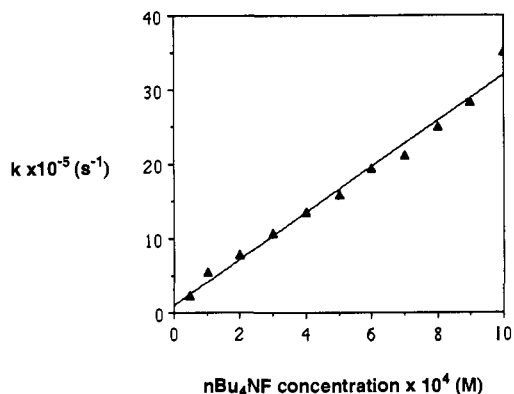


Figure 13. Rate of TMSA⁺⁺ decay at 480 nm vs concentration of nBu₄NF in MeCN.

concentration give second-order rate constants of 3.1×10^5 and $8.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the respective bases. In order to avoid problems associated with salt effects on the DMA⁺⁺ lifetime, the solutions used for these measurements containing base concentrations in the range 0–0.6 M were maintained at a constant salt concentration of 0.6 M by the addition of corresponding amounts of nBu₄NClO₄. Finally, similar measurements made on the cation radical derived from the aniline-*d*₆ **5** give a k_H/k_D value of 3.6 (25 °C, 60:40 MeOH:MeCN, nBu₄NOAc as the base). The combined results (Table 2) show that the carboxylate-promoted decay of DMA⁺⁺ is associated with an α -CH bond cleavage process involving proton transfer to the base.

To probe the effects of para-substituents on DMA⁺⁺ α -CH kinetic acidity, the rates of nBu₄NOAc-dependent decay of cation radicals, derived from the dimethylanilines **2–4** with *p*-CH₃, *p*-OCH₃, and *p*-CF₃ groups, were determined. Rate constants

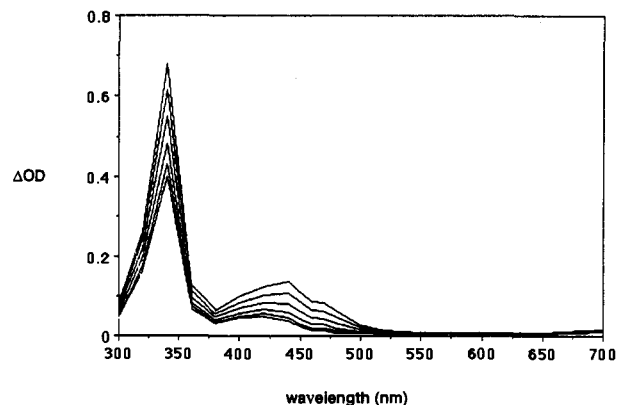


Figure 14. Transient absorption spectra following 308-nm excitation of 0.5 mM DMA and 50 mM DCB in 60:40 MeOH:MeCN containing 0.6 M nBu₄NOAc at 1, 2, 3, 5, 7, 10, and 15 μs .

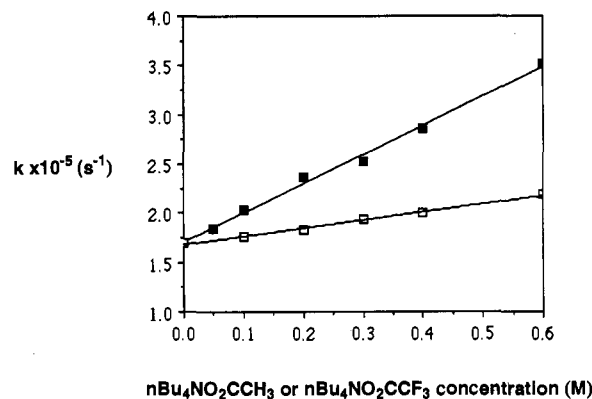


Figure 15. Rate of DMA⁺⁺ decay at 460 nm vs concentrations of nBu₄NOAc (filled squares) and nBu₄NO₂CCF₃ (empty squares) in 60:40 MeOH:MeCN.

Table 2. Rate Constants for Base-Promoted Decay of the Dimethylaniline Cation Radical in 60:40 MeOH:MeCN

aniline precursor	base	$k \text{ (M}^{-1} \text{ s}^{-1})$ at 25 °C
PhN(CH ₃) ₂	nBu ₄ NOAc	3.1×10^5
PhN(CD ₃) ₂	nBu ₄ NOAc	8.6×10^4
PhN(CH ₃) ₂	nBu ₄ NO ₂ CCF ₃	8.0×10^4

Table 3. Rate Constants for nBu₄NOAc-Promoted Decay of Para-Substituted Dimethylaniline Cation Radicals in 60:40 MeOH:MeCN

para-substituent	$k \text{ (M}^{-1} \text{ s}^{-1})$ at 25 °C	$E_{ox}^a \text{ (V vs SCE)}$	$\lambda_{max} \text{ (nm)}$
OMe	2.0×10^4	+0.49	480
CH ₃	1.1×10^5	+0.65	460
H	3.1×10^5	+0.71, +0.65	460
CF ₃	2.5×10^6		440

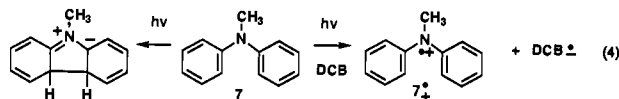
^a Taken from ref 23.

resulting from decay rate vs [nBu₄NOAc] data for 60:40 MeOH:MeCN solutions at 25 °C and constant (0.6 M) salt concentration are given in Table 3 along with the known oxidation potentials of the precursor anilines and the absorption maxima of the corresponding cation radicals.

α -Substituent Effects on Tertiary Amine Cation Radical α -CH Kinetic Acidity. The *N*-substituted-*N,N*-diphenylamines **7–13** were used to assess the effects of α -substituents on the rates of α -CH deprotonation of amine cation radicals. While these amines are properly structured for the designed purpose, their documented²⁴ propensity to undergo excited-state electrocyclicization to produce azomethine ylids (eq 4) was an initial concern. Indeed,

(23) Seo, E. T.; Nelson, R. F.; Frtisch, J. M.; Marcoux, L. S.; Leddy, O. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498.

(24) Forster, E. W.; Grellman, K. H. *J. Am. Chem. Soc.* **1973**, *95*, 3108.



excitation (308 nm) of Ph_2NMe (7) in 25:75 MeOH:MeCN does lead to formation of a 610-nm absorbing transient (Figure 16), identified previously²⁴ as the ylide shown in eq 4. This transient undergoes slow, $[\text{nBu}_4\text{NOAc}]$ -independent decay. In contrast, irradiation of a mixture of 0.1 M DCB and 7 (0.5 mM) leads instead to simultaneous production of $\text{DCB}^{\bullet-}$ and a new transient absorbing at 645 nm ($7.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) (Figure 17). The 645-nm species is assigned as the cation radical of 7 (i.e., $7^{\bullet+}$). As expected, $\text{DCB}^{\bullet-}$ and $7^{\bullet+}$ decay at equivalent ($1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, 25 °C) diffusion-controlled rates (Figures 18 and 19). Moreover, the rate of $7^{\bullet+}$ decay is a linear function of $[\text{nBu}_4\text{NOAc}]$ with a derived second-order rate constant of $9.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, 25:75 MeOH:MeCN) and a $k_{\text{H}}/k_{\text{D}}$ value (comparing $7^{\bullet+}$ and $13^{\bullet+}$ decay) of 2.81. Finally, cation radicals from the variously α -substituted diphenylamines 8–12 were generated by this SET-photochemical method and their decay kinetics were measured. The rate constants for nBu_4NOAc -induced decay of these transients (given along with their absorption maxima in Table 4) show a pronounced dependence on the nature and degree of α -substitution.

Discussion

Pathways for Amine Cation Radical Generation and Decay.

The overall mechanistic sequence for amine cation generation used in these laser spectroscopic studies involves photoinduced electron transfer from the aniline derivatives to the singlet excited state²⁶ of DCB. The prediction that these processes should be thermodynamically ($\Delta G_{\text{SET}} < 0$) and, consequently, kinetically ($k_{\text{SET}} = ca. k_{\text{diff}}$)²⁷ favorable is based on a consideration of the redox potentials of the amine donors (e.g. $E_{1/2}(+) = ca. +0.7 \text{ V}$ for DMA^{4a} and $\text{DCB}^{\text{S1}}(E_{1/2}(-) = ca. +2.6 \text{ V})$.²⁸ It is likely that SET in these donor-acceptor pairs results in direct formation of either solvent-separated (SSIRP) or contact (CIRP) ion radical pairs,²⁵ both with singlet multiplicity. Prior to the onset of transient detection in the laser experiments (ca. 10 ns), competitive reactions of the ion radical pairs can occur to produce neutral ground-state reactants (back electron transfer in SSIRP and/or CIRP) or fully solvated free ion radicals. The latter pathway is favorable in highly polar media like the MeCN–MeOH solvent systems employed in these experiments. Thus, it is reasonable to expect that the ion radicals whose kinetics are scrutinized in these laser spectroscopic studies are free species.

Several observations support both this proposal and the conclusion that the major pathway for decay of the free ion radicals in the absence of added bases or nucleophiles involves diffusion-controlled back electron transfer. Specifically, the second-order nature and equal rate constants for decay of each of the amine cation radicals and the DCB anion radical are consistent with involvement of free, charged radical intermediates. Furthermore, the strict dependence of these rates on solvent viscosity is another indicator of diffusion-controlled decay of free transients. Finally, the ion radical decay rates in the absence of added base show no *d*-isotope dependence, a result not expected if decay were by

(25) (a) The absorption maximum for this cation radical in MeCN, derived by irradiation of benzophenone *N*-methyl-*N,N*-diphenylamine mixtures, has been reported to be 635 nm (ref 25b). (b) Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452.

(26) (a) ISC from DCB^{S1} is known to be slow (ref 26b). (b) Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785.

(27) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(28) (a) Calculated on the basis of $E_{1/2}(-) = ca. -1.6 \text{ V}$ and $E_{00}^{\text{S1}} = ca. 98 \text{ kcal/mol}$ (ref 28b,c) for DCB. (b) Wayner, D. D. M. *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. 2, p 395. (c) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1985**, *66*, 3012.

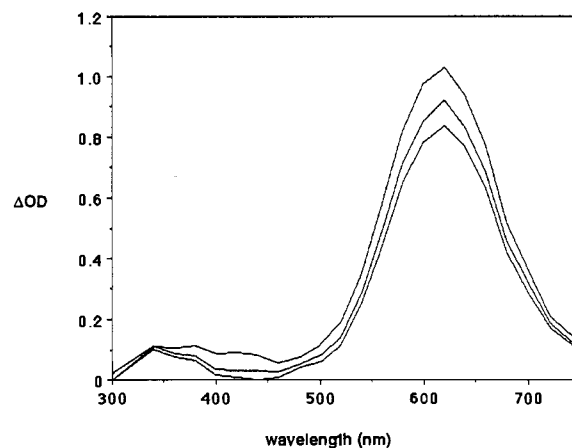


Figure 16. Transient absorption spectra following 308-nm excitation of 0.5 mM 7 in 25:75 MeOH:MeCN at 10, 100, and 400 μs .

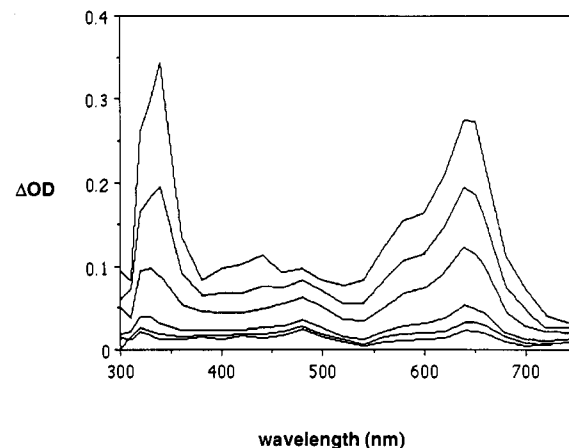


Figure 17. Transient absorption spectra following 308-nm excitation of 0.5 mM 7 and 0.1 M DCB in 25:75 MeOH:MeCN at 1, 2, 4, 10, 15, and 20 μs .

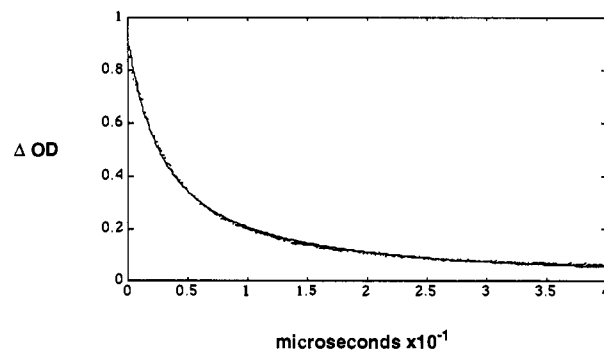
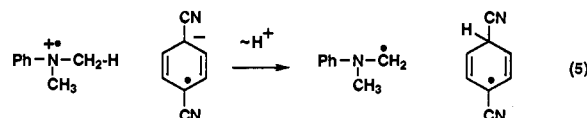


Figure 18. Decay of $\text{DCB}^{\bullet-}$ at 340 nm after excitation of a solution of 0.5 mM 7 and 0.1 M DCB in 25:75 $\text{CH}_3\text{OH}:\text{CH}_3\text{CN}$. Points are experimental data, and the solid curve represents kinetics calculated upon the basis of second-order decay.

proton transfer²⁹ from the amine cation to the cyanoarene anion radical (eq 5).



As part of experimentation to define conditions under which amine cation radical α -CH deprotonation rates could be accurately measured, the effects of nonbasic salts on the rates of $\text{DMA}^{\bullet+}$

(29) Proton transfer from tertiary amine cation radicals with $\text{p}K_{\text{a}}$'s of ca. 8–10 for $\text{DCB}^{\bullet+}$ ($\text{p}K_{\text{a}} < 0.1$, ref 20) should be slow.

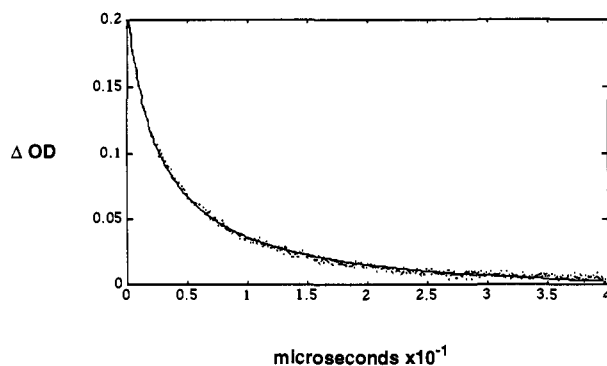


Figure 19. Decay of $7^{+\bullet}$ at 645 nm after excitation of a solution of 0.5 mM **7** and 0.1 M DCB in 25:75 $\text{CH}_3\text{OH}:\text{CH}_3\text{CN}$. Points are experimental data, and the solid curve represents kinetics calculated upon the basis of second-order decay.

Table 4. Rate Constants for $n\text{Bu}_4\text{NOAc}$ -Promoted Decay of α -Substituted N,N -Diphenyl- N -methylamine Cation Radicals in 25:75 $\text{MeOH}:\text{MeCN}$

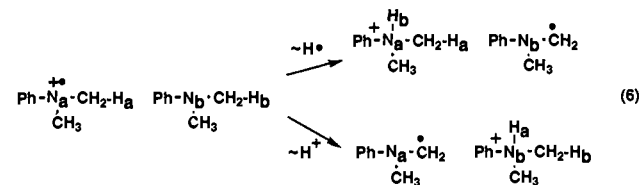
α -substituents in $\text{Ph}_2\text{NCHR}_1\text{R}_2$		k ($\text{M}^{-1} \text{s}^{-1}$) at 25 °C	λ_{max} (nm)
R_1	R_2		
H	H	9.5×10^5	645
CH_3	H	2.3×10^5	650
CH_3	CH_3	1.7×10^5	660
Ph	H	3.2×10^6	680
$\text{CH}=\text{CH}_2$	H	2.6×10^6	670
$\text{C}=\text{CH}$	H	7.0×10^7	675

and $\text{DCB}^{\bullet-}$ decay by BSET were probed. As the data displayed in Figures 4 and 5 demonstrate, the lifetimes of the ion radical transients increase upon the addition of increasing concentrations of tetra-*n*-butylammonium salts. In general, the effects observed are (1) small (for [salt] = 1–0.06 M, the decay rates decrease *ca.* 5-fold), (2) dependent on the nature of the counter anion ($\text{ClO}_4^- > \text{Cl}^-$, BF_4^- , $\text{CF}_3\text{SO}_3^- > \text{F}^-$), and (3) saturating at salt concentrations exceeding *ca.* 0.06 M. It should be noted that a related effect by $\text{Mg}(\text{ClO}_4)_2$ on BSET-promoted decay between 1,4-dicyanonaphthalene anion radical ($\text{DCN}^{\bullet-}$) and *trans*-stilbene cation radicals has been noted earlier by Goodson and Schuster³⁰ and interpreted in terms of Mg^{2+} complexation of $\text{DCN}^{\bullet-}$. Our results show that anions can have a similar stabilizing influence on amine cation radicals. Moreover, the results suggest that attention must be paid to total salt concentration in designing experiments to accurately assess the effects of basic salts on amine cation radical decay.

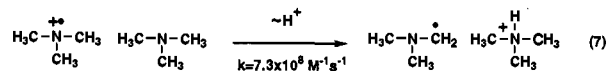
Tertiary Amine Cation Radical α -CH Kinetic Acidities. Perhaps the most significant observations made in the current study are those which relate to the α -CH kinetic acidities of tertiary amine cation radicals. As mentioned briefly in the Introduction, this issue has been of central interest to a number of earlier efforts probing SET-photochemical and anodic oxidation reactions of amines. In order to place our results in proper context, an overview of the early observations will be given first followed then by an interpretation and discussion of the data we have accumulated.

Perhaps the first detailed discussion of trialkylamine cation radical α -CH acidity is found in Nelsen and Ippoliti's^{15a} 1986 paper in which the Nicholas–Arnold method³¹ was used to estimate thermodynamic acidities of these species. On the basis of the large $\text{p}K_a$ value of *ca.* 15 (in MeCN) these workers calculated for an *N*-adamantyl-9-azaadamantane cation radical, they suggested that α -CH deprotonation of tertiary aminium radicals by the corresponding neutral amines should be slow relative to a

possibly more facile H-atom-transfer (*i.e.* Hoffman–Loeffer–Freytag like) route for α -amino radical production (eq 6).



The pulse radiolysis experiments of Das and von Sonntag¹⁶ represent an early approach to gaining information about tertiary amine cation radical kinetic α -CH acidity. Steady-state radiolysis conditions were used to generate mixtures of the trimethylamine cation radical, its α -amino radical counterpart, and its *N*-protonated α -amino radical analog. Analysis of the equilibrium product ratios and the time-dependent changes in approaching equilibrium provided a value of 8 for the $\text{p}K_a$ of the tertiary cation radical and a rate constant of $7.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for proton transfer to trimethylamine (eq 7). Although interpreted in this way, these results are also consistent with an H-atom-transfer pathway for α -amino radical and ammonium cation production.



More recently, Dinnocenzo and Banach¹⁷ described an interesting technique for directly assessing the kinetics of α -CH proton removal from stable tertiary aminium radicals. Deprotonation reactions of the stable salt (*p*- $\text{CH}_3\text{OC}_6\text{H}_4$)₂ $\text{NCH}_3^{\oplus}\text{AsF}_6^-$ ($\text{p}K_a$ (MeCN) = *ca.* 10) by quinuclidine bases were analyzed by stopped-flow methods. While limited to studies with stable cation radicals,³² these experiments provided detailed information about the α -CH deprotonation reactions including $k_{(\text{CH}_3)}/k_{(\text{CD}_3)} = 7.7$ (15 °C), $\Delta H^\ddagger = 3.7 \text{ kcal/mol}$, $\Delta S^\ddagger = -22.3 \text{ ea}$, and Bronstead $\beta = 0.63$.

The most recent investigation in which tertiary amine cation radical α -CH kinetic acidity was probed used a derivative cyclic voltammetry methodology.¹⁸ Parker and Tilset employed this technique to measure the rates of both acetate ion- and pyridine-induced α -CH deprotonation reactions of para-substituted *N,N*-dimethylaniline cation radicals in MeCN. The most pertinent finding of this study is that a relationship exists between the thermodynamic and kinetic acidities of these cation radicals. Specifically, the rate constants for acetate-induced α -CH deprotonation of the anilinium radicals are inversely related to the estimated $\text{p}K_a$ values which vary with para-substituents in the manner expected.³¹ Para-electron-withdrawing groups, for example, lower the $\text{p}K_a$ values and enhance the rate constants for α -CH deprotonation *via* their influence on amine oxidation potentials (see below) and, as a result, on cation radical stability. Several less clear aspects of the Parker–Tilset results include the abnormally high *d*-isotope effects (*ca.* 5–22) associated with the pyridine-induced α -CH deprotonation processes and the large differences in the enthalpies (20 *vs* 2–13 kcal/mol) and entropies (35–53 *vs* –15 to –29 eu) of activation for the respective acetate ion- and pyridine-promoted α -CH deprotonations.

In contrast to the methods employed previously for kinetic analysis of tertiary aminium radical α -CH deprotonation reactions, the laser spectroscopic technique has many obvious advantages. First, the ion radical species are generated under isotropic conditions. Thus, no questions exist about the degree of their association with other charged radicals or electrode surfaces. In addition, a large variety of aminium radicals can be probed in this way without limitations associated with their

(30) Goodson, B.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 3123. See also: Loupy, A.; Tchoubar, B.; Astruc, D. *Chem. Rev.* **1992**, *92*, 1141.

(31) Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2166. Nicholas, A. M. P.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 3011.

(32) Application of the Dinnocenzo–Banach method (ref 17) appears limited to stable cation radicals with deprotonation rates that are less than *ca.* $10^3 \text{ M}^{-1} \text{ s}^{-1}$.

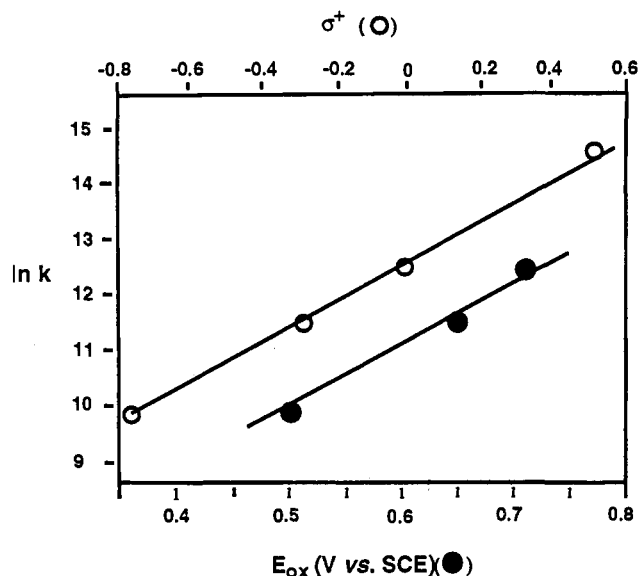


Figure 20. Plots of $\ln k$ (MeCN, 25 °C) for acetate-promoted deprotonation of para-substituted *N,N*-dimethylanilinium radicals vs the corresponding aniline oxidation potentials (E°) (filled circles) and the σ^+ constants of the respective para-substituents (empty circles).

synthesis and stability. Finally, when low concentrations of precursor amines and high concentrations of added bases are used, it is possible to rule out the H-atom abstraction pathway as being responsible for ion radical decay. Indeed, the dependencies of DMA^{•+} decay on base strength and concentration in conjunction with the reasonable primary d-isotope effects all point to α -CH deprotonation as the kinetically significant process involved in tertiary aminium radical decay in the presence of carboxylate anion bases.

One of the main goals of this effort was to delineate how substituents govern the kinetic α -CH acidities of tertiary amine cation radicals. If these reactive intermediates behave as "normal" acids, one might anticipate that kinetic acidity would parallel thermodynamic acidity and, consequently, that kinetic acidity would be influenced by substituents in a predictable fashion. Indeed, as Nicholas and Arnold³¹ have clearly summarized, the pK_a values of cation radicals are related to the oxidation potential (E°) of the neutral precursor and the bond dissociation energy (BDE) of the C-H bond undergoing cleavage (eq 8).

$$pK_a = \frac{-E^\circ}{0.059} + \frac{BDE - 37.5}{1.36} \quad (8)$$

In accord with these considerations, para-ring substituents in dimethylanilinium radicals should alter pK_a values by their influence on E° , *i.e.* the pK_a should decrease as the electron-donating ability of the substituent decreases. This can be viewed as a substituent effect on the stability of the cation radical. Indeed, the rate constants for acetate-promoted deprotonation of the anilinium radicals respond to para-substitution in the same fashion as do the pK_a values. The linear correlations seen between $\ln k$ and both the aniline oxidation potentials and σ^+ constants of the para-substituents (Figure 20) demonstrate clearly that a close relationship exists between kinetic and thermodynamic acidities of the tertiary amine cation radicals.³³

Likewise, α -substitution should govern the α -CH pK_a values of tertiary amine cation radicals principally through a control of α -CH bond dissociation energies. Thus, substituents which stabilize the resulting α -amino radical (*i.e.* lower BDE) should

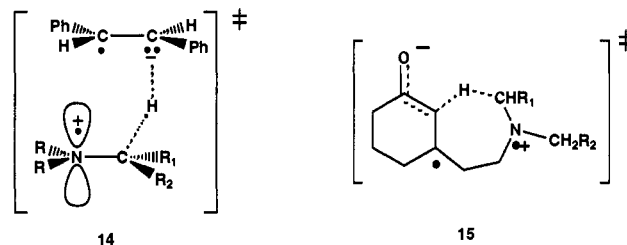
(33) (a) This same parallel exists for toluene and related ring methyl substituted cation radicals (ref 33b). (b) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567, 7472. Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263. Sehested, K.; Holcman, J. *J. Phys. Chem.* **1978**, *82*, 651.

Table 5. Relative Rates of α -CH Deprotonation of α -Substituted Tertiary Amine Cation Radicals from Product Distribution and Laser Spectroscopy Studies

entry	X	Y	relative rates		
			per-H from stilbene-amine SET photo-additions ^a	per-H from amine-enone SET photo-cyclizations ^b	from rate constants for <i>N</i> -alkyl- <i>N,N</i> -diphenylaminium radical decay ^c
a	H	H	1.1	0.1	0.3
b	H	CH ₃	0.5	0.2	0.1
c	CH ₃	CH ₃	<0.05		0.05
d	H	Ph	1	1	1
e	H	CH=CH ₂	0.5	1.9	0.8
f	H	C≡CH	111	3.9	22

^a Taken from ref 13. ^b Taken from ref 11. ^c This work, Table 4.

enhance the thermodynamic acidities of these charged radical intermediates. Bordwell and his co-workers³⁴ have presented a number of examples showing that radical-stabilizing C-9 and benzylic substituents lower the pK_a 's of the respective fluorene^{34a} and toluene^{34b} cation radicals. Stabilization of the transition state for α -CH deprotonation by radical-stabilizing groups should also lead to enhanced kinetic acidity. As pointed out earlier by Lewis and his co-workers,¹³ steric and/or stereoelectronic effects associated with α -substitution could also be important in governing the rates of tertiary amine cation radical α -CH deprotonation. Product distributions from SET-induced stilbene-tertiary amine photoaddition reactions suggest that alkyl substitution slows the rates of α -CH proton transfer from the tertiary aminium radicals to the stilbene anion radicals in contact ion radical pairs (see Table 5). This is a result of steric repulsion which raises the energy of the stereoelectronically preferred transition-state conformation (14) of the aminium radical having half-vacant N_p



and filled σ_{C-H} orbital overlap. As seen by viewing the summary of Lewis' results given in Table 5, this effect is counterbalanced by the pure electronic effects (BDE effects) of α -substituents.

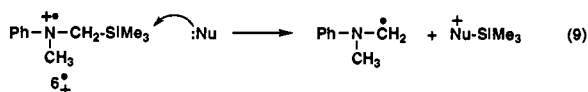
Different conclusions about the effects of α -substituents on tertiary aminium radical α -CH kinetic acidity have come from product distribution determinations in photochemical studies with tethered amino enones.¹¹ SET-promoted photoreactions of these systems follow pathways in which α -CH proton transfer occurs in intermediate zwitterionic diradicals 15. The results of this work, included in Table 5, suggest that steric effects are less pronounced in governing kinetic acidity than in the stilbene-amine system. Moreover, the remarkable effect of the acetylene moiety on the rate of α -CH deprotonation at a propargylic center seen in the latter system was greatly attenuated in tethered enone-amine photoreactions.

(34) (a) Bordwell, F. G.; Cheng, J. P.; Bausch, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 2867. (b) Zhang, X.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163. (c) Arnett, E. M.; Venimadhavan, S. *J. Am. Chem. Soc.* **1991**, *113*, 6967.

The effects of α -substituents on the rates of aminium radical α -CH deprotonation as measured by the earlier product distribution methods and by the current direct laser spectroscopic technique are reflected in the relative rate data given in Table 5. It is remarkable that the same general trends are seen in both of these data sets even though they are obtained by use of different techniques and with systems in which structurally different amine cation radicals are generated by SET to different acceptors and in which deprotonation is induced by different negatively charged bases. However, several noteworthy differences do exist. It appears that the relative α -CH deprotonation rates as judged by the stilbene-amine SET-photoaddition reactions are more sensitive to steric effects of the α -substituents (e.g., compare entries a vs d and e). In contrast, results from the tethered amine-enone photocyclization reactions show a greater dependence of α -CH kinetic acidities on electronic contributions (BDE) of the substituents (e.g. compare entries a vs b and e). In addition, except for magnitude differences, the product distribution results agree with those from the direct laser spectroscopy results in demonstrating that the acetylene substituent has a remarkably large enhancing effect on α -CH kinetic acidities of tertiary amine cation radicals.

The differences seen in these results might be a consequence of the varying nature (e.g., inter- vs intramolecular base pK_a and steric requirements) of the proton-transfer processes and/or the degree of C-H bond cleavage in the corresponding transition states. For example, it is known¹³ that proton transfer in the stilbene-amine photoreaction occurs in a contact ion radical pair whose rigid structure (i.e., relative orientation of negative and positive radical partners) may be governed by the need for maximum charge neutralization.³⁵ This effect could cause kinetic acidities to more greatly weight steric factors than those determined for acetate-promoted deprotonation of free cation radical intermediates. Likewise, the intramolecular nature of proton transfer in the enone-amine zwitterionic diradicals disfavors coplanar alignment of the σ_{CH} and N_p orbitals at the cation radical center. This could very well result in the minimization of steric/stereoelectronic influences on kinetic acidity and lead to the greater importance of electronic effects of α -substituents. Clearly, α -CH deprotonation of free tertiary aminium radicals by acetate ion is not affected by these factors. Consequently, we believe that kinetic acidities of these reactive intermediates determined by the laser spectroscopic technique are more reflective of the intrinsic effects (both steric and electronic) of α -substituents.

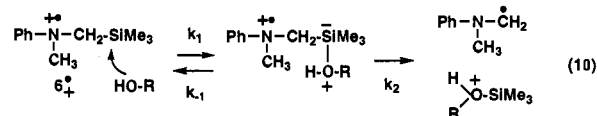
(Silylmethyl)aniline Cation Radical Desilylation. The results described above show that the cation radical derived from the (silylmethyl)aniline **6**, like DMA^{•+}, has a lifetime in MeCN determined only by diffusion-controlled BSET to DCB⁻. Thus, in the absence of a silophile stronger than MeCN, desilylation of **6**^{•+} is slow relative to BSET. However, this cation radical does participate in facile silyl-transfer reactions (eq 9) with oxygen-



containing, nucleophilic solvents such as MeOH and H₂O. The second-order rate constants (8.9×10^5 and $1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (at low [H₂O]), respectively) appear to parallel silophilicity (see below).³⁶ In light of this it is not surprising that fluoride ion is the silophile most potent toward **6**^{•+} with a second-order rate

constant of $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which approaches the diffusion-controlled limit in MeCN ($k_{\text{diff}} = \text{ca. } 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Thus, the high Si-F bond dissociation energy of ca. 200 kcal/mol (vs Si-O of ca. 135 kcal/mol) is reflected in the transition-state energetics of this silyl-transfer process.

While the observations discussed above are understandable in light of silophilicity, the effects of H₂O on **6**^{•+} decay at high [H₂O] (Figure 12) are unexpected. Specifically, the contrasting behavior of **6**^{•+} in MeOH-MeCN solutions (decay rates increase 20-fold in a linear fashion for [MeOH] from 2.5 to 25 M) vs in H₂O-MeCN solutions (decay rates increase ca. 7-fold in the range of [H₂O] from 2 to 5 M and remain nearly invariant with changes in [H₂O] above 5 M) is difficult to rationalize. One view of these phenomena is that two different amine cation radicals are involved in the decay process: a more reactive transient in low H₂O-content solvent systems and a more stable species at high [H₂O]. Following this reasoning, the less reactive and more reactive forms of **6**^{•+} might differ in the degree of solvation by water vs MeCN or MeOH. An alternate explanation for these observations is based on a two-step mechanism for cation radical α -desilylation. Accordingly, this process could follow an addition-elimination route *via* the intermediacy of a reversibly formed, pentavalent silicon species (eq 10) where the degree to which the



second C-Si bond breaking step contributes to the overall rate of the process is dependent on the nature of the silophile. Accordingly, the differences observed between MeOH and H₂O could be a result of the greater rate for return to the cation radical from the water ($k_{-1} > k_2$) vs MeOH ($k_{-1} < k_2$) bound silicate anion intermediate. In this event, the desilylation rate would remain first order in MeOH over the range of concentrations used while the process would be first order in H₂O at low concentrations and pseudo-zeroth order in H₂O at high concentrations. A definitive conclusion concerning which of these explanations best rationalizes the observations cannot be drawn at this time.

Conclusion. The investigation described above has demonstrated that laser spectroscopic techniques can be used to generate characterizable ion radical intermediates. In this fashion, a series of tertiary aminium radicals have been prepared by photoinduced SET routes as free ion radicals and solvent and salt effects on the rates of their decay by back electron transfer have been delineated. Moreover, the rates of α -desilylation and α -CH deprotonation of these transients in the presence of respective silophiles and bases can be measured by use of this methodology. Importantly, measurements by this method of the kinetic α -CH acidities of para-substituted *N,N*-dimethylanilinium radicals and α -substituted *N*-methyl-*N,N*-diphenylanilinium radicals have provided insight into the effects of remote substituents, which parallel those on thermodynamic acidity, and of α -substituents, which operate through a combination of electronic and steric effects. Finally, the results of this investigation exemplify the type of information which can be gained through a direct study of the dynamics of ion radical processes which are key in determining chemical and regiochemical selectivities of SET-promoted photochemical reactions.

Experimental Section

General Procedure. *N,N*-Dimethylaniline (**1**) (Aldrich) was distilled prior to use. The 4-methylaniline **2** (Aldrich) was used without purification. *n*Bu₄NOAc (Aldrich) was recrystallized (EtOAc) prior to use. *n*Bu₄NO₂CCF₃ was prepared by the reported procedure, as were

(35) (a) The issue of rigid orientational requirements of contact ion radical pairs has been discussed previously (ref 35b) and used in explaining the regioselectivity of an amine cation radical deprotonation reaction (ref 25b). (b) Wagner, P. J.; Kemppainen, A. E.; Jellinek, T. *J. Am. Chem. Soc.* **1972**, *94*, 7512. Wagner, P. J.; Ersfeld, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4516. (36) Allen, A. D.; Charlton, J. C.; Eaborn, C.; Modena, G. *J. Chem. Soc.* **1957**, 3668. Allen, A. D.; Modena, G. *J. Chem. Soc.* **1957**, 3671. (37) Clark, J. H.; Emsley, J. *J. Chem. Soc., Dalton Trans.* **1974**, 11, 1125.

the anilines 6,³⁸ 3,^{39,40} 4,^{39,40} 5,⁴¹ 12,⁴² 7, 3,^{38,39} 4,^{38,39} 6,⁴⁰ 7,⁴¹ 8,⁴² 9,⁴¹ 10,⁴³, 11,⁴⁴ 12,⁴⁵ and 13.^{25b} The salts LiClO₄ (Aldrich), nBu₄NClO₄ (Fluka), nBu₄NCl (Aldrich), nBu₄NF (Aldrich), nBu₄NBF₄ (Aldrich), and nBu₄NO₃SCF₃ (Aldrich) were commercial materials.

Laser Flash Spectroscopy Experiments. These experiments were performed using a Questek 2120 excimer laser as the excitation source. All of the spectra and kinetic runs reported were done using XeCl reagent gas which provides UV pulses at 308 nm with a duration of 6–10 ns and a pulse energy of 30–50 mJ. Transient UV/vis absorption signals were monitored using a CW 500-W Xe lamp beam which was passed through the sample perpendicular to the excitation beam. Single-wavelength

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transient wave forms were digitized using a LeCroy 9420 350-MHz digital oscilloscope and transferred to a IBM PS/2 286 computer for storage and spectral analysis.

Sample solutions were placed in 10- × 10-mm quartz cuvettes which were then sealed with a rubber serum cap and purged with N₂ for 10–15 min prior to the experiment. Sample concentrations were adjusted such that their optical densities were 1.0–1.5 at the excitation wavelength.

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Supplementary Material Available: Figures showing transient absorption spectra and decay curves for the ion radical intermediates discussed in this paper (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead for ordering information.