(Na_2SO_4), filtration, and concentration under reduced pressure gave *p*-[*carbonyl*-^{18}O](methoxycarbonyl)benzaldehyde (**15**, 70 mg, 85.4%) as a white solid: mp 59.0–60.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.95 (s, 3 H), 7.89 (d, J = 8.0 Hz, 2 H), 8.15 (d, J = 8.0 Hz, 2 H), 10.00 (bs, 1 H); MS *m/e* (rel intensity) 168 (49.5), 166 (31.3), 164 (4.3), 137 (100), 135 (59.3), 133 (8.1), 107 (37.2), 105 (21.6); IR (neat, NaCl) 1722, 1690, 1655, 1575 cm^{-1}. From the MS data, the product was shown to be a 5.0/12.0/24.6/58.4 mixture of 4-$OHCC_6H_4CO_2Me$/4-$^{18}OHCC_6H_4CO_2Me$/4-$OHCC_6H_4C(^{18}O)OMe$/4-$^{18}OHCC_6H_4C(^{18}O)$-OMe, and the % ^{18}O incorporation at the carbonyl oxygen was calculated to be 83.0%.

The labeled benzaldehyde (70 mg, 0.42 mmol) was treated with tosylhydrazine (78 mg, 0.42 mmol) followed by NaH to give the sodium tosylhydrazonate (140 mg, 98.2%), which was heated at 120 °C under reduced pressure (10^{-5} Torr) to give the desired diazomethane [^{18}O]-**1c** (70.2%) as an orange solid: mp 40.5–43.0 °C; ^{1}H NMR (CCl_4) δ 3.83 (s, 3 H), 4.93 (s, 1 H), 6.86 (d, J = 8.0 Hz, 2 H), 7.85 (d, J = 8.0 Hz, 2 H); IR (KBr) 2060, 1685 cm^{-1} (unlabeled 1719 cm^{-1}).

FVP of [*p*-[*carbonyl*-^{18}O]-(Methoxycarbonyl)phenyl]diazomethane. FVP was carried out as described above, and the following products were isolated by preparative TLC.

3-Methyl[*carbonyl*-^{18}O]phthalide ([^{18}O]-2): ^{1}H NMR (CCl_4) δ 1.57 (d, J = 8.0 Hz, 3 H), 5.50 (q, J = 8.0 Hz, 1 H), 7.31–7.93 (m, 4 H); IR (neat, NaCl) 1759, 1738 cm^{-1} (unlabeled 1762 cm^{-1}); MS, see Table V.

3-Methoxy-1(2*H*)-[*carbonyl*-^{18}O]benzocyclobutenone ([^{18}O]-3): ^{1}H NMR (CCl_4) δ 3.45 (s, 3 H), 5.21 (s, 1 H), 7.31–7.76 (m, 4 H); IR (neat, NaCl) 1735 cm^{-1} (unlabeled 1768 cm^{-1}); MS, see Table IV.

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Facile Proton Transfer Reactions of *N*,*N*-Dimethylaniline Cation Radicals

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Abstract: Ring-substituted *N*,*N*-dimethylaniline (DMA) cation radicals undergo rapid proton transfer reactions with acetate ion or pyridine in acetonitrile. The difference in pK_a of the parent DMA and $DMA^{\cdot+}$ was estimated to equal 27 using electrode potentials in a thermochemical cycle. Second-order rate constants for the reaction with acetate ion at 298 K ranged from 3.2×10^6 for the *p*-methoxy-substituted cation radical to 3×10^9 M^{-1} s^{-1} for the corresponding *p*-nitro derivative. Rate constants for the reactions of the cation radicals with pyridine were observed to be as much as 10^6 lower than with acetate ion. Activation parameters for the two series of reactions differed markedly. Enthalpies of activation ($\Delta H^{\ddagger}$) on the order of 20 kcal/mol and large positive activation entropies ($\Delta S^{\ddagger}$), 35–53 eu, were characteristic of the acetate ion reactions, while for pyridine, $\Delta H^{\ddagger}$ ranged from 2 to 13 kcal/mol and $\Delta S^{\ddagger}$ values were large and negative, −15 to −29 eu. Large k_H/k_D values for reactions of $ArN(CD_3)_2{}^{\cdot+}$ implicate proton transfer as the rate-determining step in both reaction series. The differences in activation parameters for the two sets of reactions were attributed to differences in the position of the preequilibrium between base and cation radicals. A large equilibrium constant is expected for the reversible ion combination between acetate ion and the cation radicals.

Introduction

Although the thermodynamics of proton transfer reactions of cation radicals has recently received a great deal of attention,[2-4] much less is known about the kinetic acidities of these reactive intermediates.[5-8] Cation radicals of methylbenzenes undergo highly exergonic proton transfer reactions to pyridine bases in acetonitrile at moderate rates.[5] The kinetics of aryl proton transfer from 9-phenylanthracene cation radical, which undergoes facile nucleophilic attack by acetate ion[9] or pyridine,[10] to 2,6-di-*tert*-butylpyridine has recently been reported.[6] Proton transfer from the nitrogen of 9-amino-10-phenylanthracene cation radical is the exclusive reaction with pyridine in acetonitrile at 298 K, with a second-order rate constant of about 10^7 M^{-1} s^{-1}.[7]

Proton transfer from *N*,*N*-dimethylaniline (DMA) cation radicals is implicated in anodic nucleophilic substitution at the α-position to nitrogen by cyanide ion in acetonitrile[11] or methoxide ion in methanol.[12] In the absence of base, dimerization of *N*,*N*-dimethylaniline cation radicals in acetonitrile takes place even when the 4-positions are substituted with a halogen.[13] The observation that strongly nucleophilic cyanide ion attacked an α-proton[11] rather than a ring position of $DMA^{\cdot+}$ suggested suitably 4-substituted *N*,*N*-dimethylaniline cation radicals as substrates for cation radical deprotonation studies. Since the charge on $DMA^{\cdot+}$ is expected to be strongly localized on nitrogen, the

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(2) Nicholas, A. M.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165–2179.

(3) (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473–2474. (b) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792–1795.

(4) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1988**, *110*, 1649–1650.

(5) (a) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472–7482. (b) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263–2276.

(6) Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4968–4969.

(7) Parker, V. D.; Chao, Y.; Reitstöen, B. *J. Am. Chem. Soc.* **1991**, *113*, 2336–2338.

(8) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8646–8653.

(9) Reitstöen, B.; Norrsell, F.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 8463–8465.

(10) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521–2523.

(11) Andreades, S.; Zahnow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 4181–4190.

(12) Weinberg, N. L.; Reddy, T. B. *J. Am. Chem. Soc.* **1968**, *90*, 91–94.

(13) Ahlberg, E.; Helgee, B.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 187–193.

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Table I. Oxidation Potentials and Estimated Cation Radical pK_as of *para*-Substituted *N*,*N*-Dimethylanilines in Acetonitrile

substituent	peak potential[a]	σ^{+} [b]	pK_a(CR)[c]
CH_3O	0.141	−0.78	13
CH_3	0.306	−0.31	12
(H)	(0.460)[d]	0.00	9[e]
Cl	0.482	0.11	9
CN	0.742	0.66	6
NO_2	0.837	0.79	3

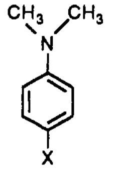
[a] Peak potentials measured by derivative linear sweep voltammetry at 0.5 V/s and 293 K, referenced to Fc/Fc$^{\bullet+}$. [b] Hammett substituent constant from ref 15. [c] Estimated from $\Delta pK_a(CR) = -16.9\Delta E^p$ as described in the text. [d] Value estimated from the Hammett plot of the reversible peak potentials. [e] Value estimated in ref 14.

proximity of the charge to the α-protons was expected to contribute to low reaction barriers.[7]

Deprotonation of tertiary amine cation radicals has previously been discussed in terms of both thermodynamic[8,14] and kinetic acidities.[8] Both studies resulted in the conclusion that the α-protons of *N*-alkylamine cation radicals are weakly acidic. It was pointed out that the observation of reversible oxidation during cyclic voltammetry studies is indicative that R_3N is usually not a strong enough base to lead to extremely rapid deprotonation of its cation radical.[14] The kinetic acidity of *N*-methyldianisylamine (p-An_2NCH_3) cation radical with quinuclidine derivatives in acetonitrile at 15.1 °C was studied in detail, and second-order rate constants for proton transfer of 1.5×10^2 to 6.15×10^4 M^{-1} s^{-1} were observed.[8] It was established that the proton-transfer step is rate-determining.

Results and Discussion

Cyclic voltammetry studies of para-substituted *N*,*N*-dimethylanilines (**1**) in acetonitrile–Bu_4NPF_6 (0.1 M) at voltage sweep rates in some cases as low as 0.1 V/s indicate that the oxidation processes are reversible and the resulting cation radicals are stable under the conditions of the experiments.



1a, X = CH_3O
b, X = CH_3
c, X = Cl
d, X = CN
e, X = NO_2

Reversible Oxidation Potentials of Para-Substituted *N*,*N*-Dimethylanilines. Peak potentials for the oxidation of **1a**–**1e** in acetonitrile–Bu_4NPF_6 (0.1 M) at 293 K measured at a voltage sweep rate of 0.5 V/s and referred to the ferrocene/ferrocenium ion (Fc/Fc$^{\bullet+}$) reference are summarized in Table I. A plot of $(F/2.303RT)E^p$ vs Hammett[15] σ^+ values resulted in a linear correlation with a slope equal to 7.45 (r = 0.996). It was not possible to measure the reversible potential for parent DMA under the experimental conditions due to rapid followup reactions of DMA$^{\bullet+}$ (the irreversible E^p at 100 V/s was observed to be equal to 0.40 V vs Fc/Fc$^{\bullet+}$). Since an excellent Hammett correlation was observed, the value obtained from the correlation line, 0.460 vs Fc/Fc$^{\bullet+}$, is expected to be reliable.

Table II. Rate Constants, Activation Parameters, and Deuterium Kinetic Isotope Effects for the Reactions of Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals with Pyridine

substituent	$k/M^{-1}\ s^{-1}$ [a]	$\Delta H^{\ddagger}$/kcal mol^{-1} [b]	$\Delta S^{\ddagger}$/eu[c]	k_H/k_D [d]
CH_3O	0.94	12.5	−15	22
Cl	1.0×10^3	6.3	−24	12
NO_2	1.4×10^5	2.7	−28	6.3
CN	2.5×10^5	2.1	−29	4.9

[a] Second-order rate constant in acetonitrile–Bu_4NPF_6 (1.0 M) at 298 K measured by derivative cyclic voltammetry. [b] Enthalpy of activation from the correlation of rate constants measured from 273 to 303 K. [c] Entropy of activation at 298 K. [d] For reactions of cation radicals of $ArN(CH_3)_2$ and $ArN(CD_3)_2$.

Thermodynamic Acidities of Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals. The pK_a of DMA$^{\bullet+}$ in acetonitrile was estimated to be equal to 9, assuming an α-CH bond dissociation energy (BDE) of 80 kcal/mol[8] using the thermochemical cycle presented earlier.[2] Allowing for an uncertainty as great as ±4 kcal/mol in this BDE leads to a ±3 units of error in the pK_a of the DMA$^{\bullet+}$. The difference in pK_a of two different cation radicals (ΔpK_a(CR)) can be estimated using eq 1, in which ΔBDE(α-CH) and $\Delta E°$ refer to changes in BDE and $E°$ of the neutral molecules. There are no α-CH BDE data available for

$$\Delta pK_a(\mathrm{CR}) = \Delta \mathrm{BDE}(\alpha\text{-CH}) - 16.9\Delta E° \qquad (1)$$

this series of DMA. However, it is likely that the remote para substituents will not greatly affect the α-CH BDE, and to a first approximation, the ΔBDE term on the right hand side of eq 1 can be equated to zero.[16] With these uncertainties in mind, the differences in peak potentials (E^p) for the oxidation of **1a**–**1e** were used to obtain a rough estimate of the pK_as of the cation radicals, which are given in the last column of Table I. The pK_a(CR) values allow the equilibrium constants for the reactions in acetonitrile at 293 K of $\mathbf{1}^{\bullet+}$ with acetate ion and pyridine (pK_as of the conjugate acids equal to 22 and 12, respectively) to be estimated.[18]

It is of interest to calculate the pK_a of DMA on the basis of the BDE used in the estimate[8] of the pK_a of DMA$^{\bullet+}$. This can be done using eq 2[19]

$$\mathrm{BDE} = 1.37pK_a(\mathrm{HA}) + 23.06E_{ox}(\mathrm{A}^-) + C \qquad (2)$$

where $E_{ox}(A^-)$ refers to the oxidation potential of the anion vs the normal hydrogen electrode (NHE) and pK_a(HA) to the neutral molecule. The constant (C) in this equation is equal to 47.2 in acetonitrile.[20] The oxidation potential in acetonitrile[21] is available, and rearranging the equation and using a value of 80 kcal/mol for BDE of the α-CH results in a pK_a equal to 34.

The pK_a of toluene in acetonitrile has been estimated to be 51 (±4),[21] which suggests that a value of 34 may be low for DMA. The difference in pK_a between DMA and DMA$^{\bullet+}$ can be calculated independent of the α-CH BDE estimate using the thermochemical cycle illustrated in Scheme I where the free energy differences for the reactions above and below the double line are equal.[22] In Scheme I, RH is DMA and R^- is the corresponding anion derived by removal of an α-proton. The $\Delta E°$ below the

Scheme I

$$\begin{array}{lr} \mathrm{RH}^{\bullet+} + \mathrm{R}^- \rightleftharpoons \mathrm{R}^{\bullet} + \mathrm{RH} \qquad \Delta G° = 2.303RT\Delta pK_a & \\ \hline\hline \mathrm{RH}^{\bullet+} + \mathrm{R}^- \rightleftharpoons \mathrm{RH} + \mathrm{R}^{\bullet} \qquad -\Delta G° = F\Delta E° & (3) \end{array}$$

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(14) Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879–4881.

(15) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: Tokyo, 1970; 355–361.

(16) The relative insensitivity of C–H BDE to structure is indicated for a series of hydrocarbons of widely different structure.[17] BDEs ranging from 77 to 87 kcal/mol (10 kcal/mol corresponds to 7 pK_a units) were observed for a series of compounds with pK_as ranging from 18 to 44.

(17) Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105.

(18) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23–28.

(19) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.

(20) The value of C depends upon both the solvent and the reference electrode to which $E_{ox}(A^-)$ is referred. When the potentials are referenced to the NHE, C is equal to 47.2. For a description of the parameters that make up C, see: Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6716. Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

(21) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132–137. The reduction potential of the radical reported vs SCE was adjusted to the NHE scale by adding 0.24 V.

(22) The notation used in Scheme I is a general one for reactions involving the interchange of atoms, ions, and electrons between two species: Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.*, in press.

Table III. Rate Constants, Activation Parameters, and Deuterium Kinetic Isotope Effects for the Reactions of Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals with Acetate Ion

substituent	k/M^{-1} s$^{-1\,a}$	$\Delta H^{\ddagger}$/kcal mol$^{-1\,b}$	$\Delta S^{\ddagger}$/eu^{c}	$k_H/k_D{}^{d}$
CH_3O	3.5×10^6	19.2	38	5.3^{e}
CH_3	1.1×10^8	20.4	47	
Cl	6.2×10^8	15.9	35	3.6
CN	1.0×10^9	21.0	53	
O_2N	3.0×10^9			

[a] Second-order rate constant in acetonitrile–Bu_4NPF_6 (0.1 M) at 298 K measured by derivative linear sweep voltammetry. [b] Enthalpy of activation from the correlation of rate constants measured from 263 to 303 K. [c] Entropy of activation at 298 K. [d] For reactions of cation radicals of $ArN(CH_3)_2$ and $ArN(CD_3)_2$. [e] Rate constant for $ArN(CD_3)_2^{\bullet +}$ measured by derivative cyclic voltammetry.

double line is the difference in the reduction potentials of $RH^{\bullet +}$ and $R^{\bullet}$. This procedure results in ΔpK_a equal to 27. The pK_a of $DMA^{\bullet +}$ could be adjusted using this difference, provided a more reliable value of the pK_a of DMA becomes available.

Kinetics of the Reactions of Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals with Pyridine. The second-order rate constants measured by derivative cyclic voltammetry[23] at 298 K show a linear Hammett relationship when plotted vs σ^+, with ρ equal 3.5 ($r = 0.99$). The Brönsted plot, log k vs pK_a(CR), gives rise to α equal to 0.51 ($r = 0.95$). The fact that the nitro-substituted cation radical is 3 pK_a units more acidic than **1d**$^{\bullet +}$ and yet reacts more slowly contributes to the relatively poor correlation in this case. A very interesting feature of the data in Table II is that plots of log k vs all of the other quantities in Table II, which includes $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and k_H/k_D (for the reactions of $ArN(CD_3)_2$) are linear with correlation coefficients greater than 0.99. log k increases linearly with decreases in each of the three quantities. While linearity in the log $k/\Delta H^{\ddagger}$ plot requires that log k vs $\Delta S^{\ddagger}$ be linear as well, the linear log $k/(k_H/k_D)$ relationship is not necessarily expected.

The large k_H/k_D for the *p*-methoxy- and *p*-chloro-substituted cation radicals appears to indicate a tunneling effect in these reactions.[24] The theoretical maximum for k_H/k_D is 6.9 at 298 K, although higher values are common. Deuterium kinetic isotope effects greater than 18 are seldom observed.[24a] Although this was not pursued, further evidence for tunneling can be derived from low ratios of the Arrhenius preexponential factors, A_H/A_D. Somewhat lower k_H/k_D were observed for the reactions of *p*-$An_2NCH_3^{\bullet +}$ with quinuclidines and could not be definitively attributed to tunneling.[8] The deuterium kinetic isotope effects for the *p*-cyano and *p*-nitro derivatives are more in the normal range.

The magnitudes of the activation parameters will be discussed below together with those for the corresponding reactions of the cation radicals with acetate ion.

Kinetics of the Reactions of Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals with Acetate Ion. The reactions of the cation radicals with acetate ion (Table III) are as much as 3×10^6 as rapid as those with pyridine (Table II). A reasonably linear Hammett correlation was observed with ρ equal to 1.67 ($r = 0.95$). Correlation of log k vs pK_a(CR) resulted in a Brönsted α equal to 0.24 ($r = 0.88$). Although there is some variation in the magnitude of $\Delta H^{\ddagger}$, the quantity is large and on the order of 20 kcal/mol in all cases. Likewise, $\Delta S^{\ddagger}$ is uniformly large and positive. In the two cases where deuterium kinetic isotope effects were measured, primary effects were observed.

Mechanism of Proton-Transfer Reactions between Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals and Bases. The second-order kinetics and large deuterium kinetic isotope effects are indicative that the rate-determining step in the reactions is the transfer of a proton from the cation radical to the base, either pyridine or acetate ion. The Hammett ρ values (pyridine (3.5), acetate (1.7)) as well as the Brönsted α values (pyridine (0.51), acetate (0.24)) reflect the decreasing substituent effect as the reaction becomes more exergonic. The apparent inconsistency in the rate constants for the reactions of the cyano- and nitro-substituted cation radicals with pyridine has a detrimental effect on the linearity of both the Hammett and Brönsted correlations. The inconsistency is well outside the range of experimental error and is consistent with a mechanism involving more than one step.

The most intriguing differences in the data for the two reaction series are the magnitudes of the activation enthalpies and the signs of the activation entropies. The large $\Delta H^{\ddagger}$ for the reactions of acetate ion are a clear indication that C–H bond breaking makes up the barrier. On the other hand, $\Delta H^{\ddagger}$ for the reactions of the cyano- and nitro-substituted cation radicals with pyridine are less than expected for the diffusion of reactants. The differences in $\Delta S^{\ddagger}$ are equally obvious: those for the pyridine reactions range from −15 to −29 eu while those for the acetate reactions are positive, ranging from 35 to 53 eu. Despite these substantial differences in activation parameters, we believe the same mechanism applies to both reaction series and that the observed differences are a consequence of the position of the initial equilibrium between cation radical and base.

The initial step in a variety of cation radical reactions involves the formation of a π-complex between the electrophilic cation radical and another reactant.[25] This is believed to be the case for the reactions of arene cation radicals with both pyridine[9] and acetate ion[26] in acetonitrile. For the proton-transfer reaction between substituted $DMA^{\bullet +}$ and a base, the mechanism is shown in Scheme II. The formation and dissociation of the π-complex is regarded as being rapid and reversible. The rate law under these conditions is given by eq 6 or 7, depending upon the magnitude of K_4.

Scheme II

$$ArN(CH_3)_2^{\bullet +} + B \rightleftarrows ArN(CH_3)_2^{\bullet +}/B \qquad (4)$$

$$ArN(CH_3)_2^{\bullet +}/B \rightarrow ArN(CH_3)CH_2^{\bullet} + BH^+ \qquad (5)$$

$$\text{rate} = k_5K_4[ArN(CH_3)_2^{\bullet +}][B] \qquad (6)$$

$$\text{rate} = k_5[ArN(CH_3)_2^{\bullet +}/B] = k_5[\text{limiting reactant}] \qquad (7)$$

If K_4 is of such magnitude that equilibrium 4 lies on the left, rate law 6 prevails, and the apparent activation parameters are given by eqs 8 and 9. This situation frequently gives rise to much

$$(\Delta H^{\ddagger})_{app} = (\Delta H^{\circ})_4 + (\Delta H^{\ddagger})_5 \qquad (8)$$

$$(\Delta S^{\ddagger})_{app} = (\Delta S^{\circ})_4 + (\Delta S^{\ddagger})_5 \qquad (9)$$

smaller than expected, and sometimes negative, values of $(\Delta H^{\ddagger})_{app}$.[27] The reactions of $ArN(CH_3)_2^{\bullet +}$ with pyridine as the base apparently fit into this category. Both $(\Delta H^{\ddagger})_5$ and $(\Delta S^{\ddagger})_5$ are expected to be positive and the former to be of substantial magnitude since it reflects the heterolytic cleavage of a C–H bond. On the other hand, both $(\Delta H^{\circ})_4$ and $(\Delta S^{\circ})_4$ are most likely negative, as is commonly observed for association reactions. This results in the apparent activation parameters (eqs 8 and 9) being substantially more negative than those for reaction 5. These considerations account for the lower than expected activation enthalpies for the reactions of $ArN(CH_3)_2^{\bullet +}$ with pyridine.

The activation parameters that we observe for the reactions of $ArN(CH_3)_2^{\bullet +}$ with pyridine are comparable to those reported for the reaction of *p*-$An_2NCH_3^{\bullet +}$ with quinuclidine in acetonitrile.[8] Although the preequilibrium mechanism (Scheme II) was not

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(23) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1–110.

(24) (a) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley: New York, 1984; Chapter 5. (b) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; Chapter 5.

(25) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243–250. Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–189.

(26) Parker, V. D.; Reitstöen, B.; Tilset, M. *J. Phys. Org. Chem.* **1989**, *2*, 580–584.

(27) For examples of low or negative activation enthalpies for ion radical reactions, see ref 28.

(28) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1986**, *108*, 6371–6377. Hammerich, O.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 379–392. Svaan, M.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1985**, *B39*, 445–451. Parker, V. D. *Acta Chem. Scand.* **1983**, *A37*, 423–430.

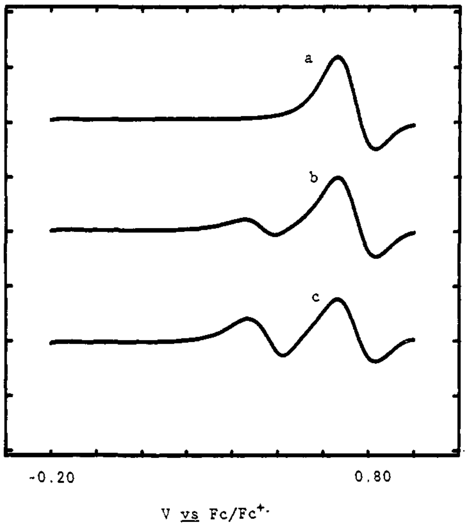

Figure 1. Linear sweep voltammograms for the oxidation of 4-chloro-*N*,*N*-dimethylaniline (**1c**) (1.00 mM) in acetonitrile–Bu_4NPF_6 (0.1 M) at a voltage sweep rate of 0.1 V/s at 293 K. [Bu_4NOAc] = 0 (a), 0.25 mM (b), and 0.50 mM (c).

among the four mechanisms considered,[8] the deprotonation mechanism proposed can be readily modified to account for a kinetically important preequilibrium. All bimolecular reactions in solution involve an encounter complex, and whether or not its existence is manifested as a distinct intermediate is sometimes a subtle question.

When the magnitude of K_4 becomes sufficiently great that the equilibrium lies far to the right (Scheme II), rate law 6 is no longer applicable. Under these conditions the concentration of the π-complex is equal to that of the limiting reactant. This appears to be the case for the reactions of $ArN(CH_3)_2^{\cdot+}$ with acetate ion in acetonitrile. The derivative linear sweep voltammetry prepeak method[10,29] used to study the kinetics of the reactions is not capable of detecting the position of equilibrium 4. Although acetate ion is present in a lower concentration than the substrate, the limiting reactant concentration in eq 7 refers to $[ArN(CH_3)_2^{\cdot+}]$. This is a consequence of the nature of the experiment as illustrated in Figure 1. The position of the prepeak is as much as 200 mV less positive than the reversible potential ($E°$). The electrode surface concentration ratio, $[ArN(CH_3)_2^{\cdot+}]/[ArN(CH_3)_2]$, is unity at $E°$ and decreases by a decade for every 59-mV potential increment in the negative direction.

Products of the Reactions of Proton-Transfer Reactions between Para-Substituted *N*,*N*-Dimethylaniline Cation Radicals and Bases. The products of proton-transfer reaction 5 are $ArN(CH_3)CH_2^{\cdot}$ and BH^+. Since the free radical is expected to be easily oxidized relative to $ArN(CH_3)_2$, electron transfer 10 is one expected followup reaction. The final products are likely to be derived

$$ArN(CH_3)_2^{\cdot+} + ArN(CH_3)CH_2^{\cdot} \rightarrow ArN(CH_3)_2 + ArN(CH_3)CH_2^{+} \quad (10)$$

from both $ArN(CH_3)CH_2^{+}$ and $ArN(CH_3)CH_2^{\cdot}$. Since the rate-determining steps in the reactions involve the initial proton transfer (Scheme II), the product-forming reactions will not affect the kinetics.

Product studies were carried out for the oxidations of **1** in acetonitrile in the presence of acetate ion. The isolated products include "dimeric" **2** and the corresponding monomethylaniline **3**.

$$\underset{\mathbf{2}}{ArN(CH_3)CH_2N(CH_3)Ar} \qquad \underset{\mathbf{3}}{ArNHCH_3}$$

The primary products **2** were not stable in solution, and the formation of **3** could be monitored by ^1H NMR when solutions of **2** were allowed to stand. Similar product mixtures have been observed during chemical oxidation of 4-cyano-*N*,*N*-dimethylaniline.[30]

Experimental Section

The dimethylanilines **1** were prepared by standard procedures. Acetonitrile was purified by distillation from P_2O_5 and stored under argon. Pyridine was distilled under reduced pressure. Tetraalkylammonium salts were obtained from Aldrich and used as received.

Instrumentation and Data Acquisition. The potentiostat was a JAS Instruments Systems Model J-1600-B driven by a Hewlett-Packard HP 3314A function generator. Data were recorded using a Nicolet Model 310 digital oscilloscope with 12-bit precision. The oscilloscope and the function generator were controlled by a PC-AT via a GPIB interface. Trigger periods were selected to minimize interference by line noise.[31] The current–voltage curves were passed through a Stanford Research Systems Model SR640 low-pass filter to remove high-frequency noise. Data acquisition, including Fast Fourier Transform filtering, and manipulation were accomplished using FORTRAN programs.[32]

Kinetic Methods. Rate constants for the reactions of $DMA^{\cdot+}$ with pyridine were obtained using derivative cyclic voltammetry (DCV)[23] measurements on solutions containing substrate/base, usually in 1/2 molar ratios and typically with substrate concentrations ranging from 0.5 to 2.0 mM. The rate constants were derived by measuring derivative peak ratios for the oxidation of substrate and reduction of cation radical and comparing these with theoretical data. The fit of experimental to theoretical data was demonstrated by consistent values of the rate constants independent of concentration. Rate constants measured by DCV are generally reproducible to about ±5%.[23]

Most of the reactions of $DMA^{\cdot+}$ with acetate ion were observed to be too fast to measure reliably by derivative cyclic voltammetry. The rate constants for these reactions were measured by the derivative linear sweep voltammetry prepeak method.[10,29] The method is illustrated by the voltammogram shown in Figure 1. The voltammogram labelled "a" is for the reversible oxidation of **1c** in acetonitrile–Bu_4NPF_6 (0.1 M). Addition of acetate ion (0.25 mM) resulted in the observation of a prepeak at less positive potentials than that for the reversible oxidation (b). Increasing the acetate ion concentration (0.5 mM) resulted in the enhancement of the prepeak intensity at the expense of the main peak (c). The rate constant for the reaction of $\mathbf{1c}^{\cdot+}$ with acetate ion was evaluated from the difference in potentials of the prepeak and that of the main oxidation peak.[10,29] Rate constants estimated by the prepeak method were reproducible to about ±10%.

Determination of Activation Parameters. Rate constants were evaluated at ≈10-degree intervals at temperatures ranging from −10 to 40 °C. Correlations of log *k* vs $1/T$ involving a minimum of 4 data points were linear in all cases, with correlation coefficients greater than 0.99.

Preparative Electrooxidation of Dimethylanilines in the Presence of Acetate Ion. The anode compartment of the divided cell was loaded with **1** (0.2 mmol) and dry, crystalline Bu_4NOAc (0.4–0.5 mmol, stored and weighed in a drybox), and then the electrolyte (MeCN/0.05 M Me_4NBF_4) was added, 20 mL to each compartment. Electrolysis was carried out at room temperature while purging with argon, until 2 faradays/mol of charge had passed. The solvent was removed by rotatory evaporation. Aqueous $NaHCO_3$ (5 mL, 5%) was added and the product mixture was extracted with ether. The ether layer was separated, dried ($MgSO_4$), and filtered. The ether was removed, and the residue was dried on the vacuum line. The product mixture was analyzed by ^1H NMR ($CDCl_3$). Although relative amounts of the main components, **2** and **3**, varied from one electrolysis to another, single runs where **2** was the dominant component were observed for the oxidation of **1a**, **1c**, **1d**, and **1e**. Decomposition of **5** was observed in all cases upon attempts to purify by TLC (Al_2O_3, SiO_2).

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Registry No. **1a**, 701-56-4; $\mathbf{1a}^{\cdot+}$, 72835-09-7; **1b**, 99-97-8; $\mathbf{1b}^{\cdot+}$, 77133-47-2; **1c**, 698-69-1; $\mathbf{1c}^{\cdot+}$, 72773-96-7; **1d**, 1197-19-9; $\mathbf{1d}^{\cdot+}$, 65018-31-7; **1e**, 100-23-2; $\mathbf{1e}^{\cdot+}$, 34539-21-4; $DMA^{\cdot+}$, 34529-89-0; D_2, 7782-39-0; pyridine, 110-86-1; acetic acid ion, 71-50-1.

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[29] Jensen, B. S.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 665–676.

[30] Dicken, C. M.; Lu, F.-L.; Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 5776–5789.

[31] Lasson, E.; Parker, V. D. *Anal. Chem.* **1990**, *62*, 412–414.

[32] Lasson, E.; Parker, V. D. Unpublished work.