CH_2Cl_2 as eluent, to give recovered **1** (17 mg) and the alcohol **2** (white solid, 45 mg, 57% isolated yield). The NMR spectrum of the alcohol was identical with that reported.[47]

Photolysis of 3β-Hydroxy-5α-androstan-17-one/TEA in Ethyl Ether. A solution of TEA (0.42 mL, ca. 300 mM) and **1** (85 mg, 32.7 mM) in 10 mL of anhydrous ether was irradiated with 16 254-nm lamps at room temperature for 55 min. The colorless photolysate was shown by GLC to contain four major components, the ketone **1**, the alcohol **2**, the epimer **3**, and the aldehyde **4**, with a peak area ratio of **1**:**2**:**3**:**4** = 3.6:1.0:6.8:1.9 at 67% loss of the ketone **1**. The solvent was removed under reduced pressure and the residue chromatographed on silica gel (230–400 mesh) with 5% $EtOAc/CH_2Cl_2$ as eluent, to give recovered **1** (28 mg) and a mixture of the ketones and the aldehyde (solid, 13 mg). The mixture was shown by GLC to consist of the epimer **3** (60%), aldehyde **4** (19%), and the ketone **1** (17%). Compound **3** (3β-hydroxy-$5\alpha,13\alpha$-androstan-17-one) was purified by further column chromatography to provide an enriched sample (ca. 80%) for spectral analysis: ^1H NMR ($CDCl_3$; 300 MHz) δ 3.56 (m, 3C-αH), 2.4–1.0 (m, steroidal skeletal hydrogen), 0.96 (s, 18-CH_3), 0.62 (s, 19-CH_3). The assignment of structure rests on the characteristic upfield shift of the 19-CH_3 group relative to the starting material (δ 0.62 and 0.83, respectively)[48] and the extensive studies on photoepimerization of 17-keto steroids.[26] The aldehyde, 3β-hydroxy-13,17-seco-5α-androst-13-en-17-aldehyde (**4**), could only be obtained as a 60% pure mixture with the epimer. The proton NMR data match well with those reported[49] for aldehydes formed from analogous 17-keto steroids: ^1H NMR ($CDCl_3$; 300 MHz) δ 9.76 (s, HC=O), 3.52 (m, 3C-αH), 1.62 (s, 18-CH_3), 0.76 (s, 19-CH_3).

Photolysis of 3β-Hydroxy-5α-androstan-17-one/TEA in Ethyl Ether, THF, and CH_3CN with 300-nm Light. Photolysis of 3β-hydroxy-5α-androstan-17-one (**1**, 55 mM) in the presence and absence of TEA (360 mM) was carried in a 2-mL anhydrous solvent (ethyl ether, THF, or CH_3CN). Each run was done in the Rayonet photochemical reactor equipped with 15 300-nm lamps through Pyrex at room temperature for 25 min. Analysis was performed with GLC on column A at 200 °C with an internal standard.

Photolysis of 3β-Methoxy-5α-androstan-17-one/TEA (5) in CH_3CN and CD_3CN. Two quartz tubes, one containing **5** (14 mM) and TEA (143 mM) in CH_3CN (2 mL) and the other containing **5** and TEA at the same concentrations but in CD_3CN (1 mL), were irradiated with 16 254-nm lamps at room temperature for 22 min. GLC analyses on column A showed two product peaks for each solution, with identical retention times for CH_3CN and CD_3CN: 9.31 and 11.73 min. These peaks are assigned to an epimer and the alcohol (**6**) by analogy with the photochemistry of **1**. GLC/mass spectral analyses of the alcohol showed a molecular ion at m/e 306 and $(M + 1)/M$ ratios of 15.9% and 20.3% for CH_3CN and CD_3CN, respectively.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9007569) for support of the research done at Purdue University. Part of the work described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy, and this paper is Document No. NDRL-3382 from the Notre Dame Radiation Laboratory. We thank Professor A. M. Halpern for valuable discussions.

Registry No. 1, 481-29-8; **2**, 571-20-0; **3**, 6247-88-7; **4**, 138313-21-0; **5**, 7680-12-8; **6**, 86679-11-0; TEA, 121-44-8; 3β-methoxy-$5\alpha,13\alpha$,-androstan-17-one, 138382-00-0.

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Reactivities of Diarylmethyl and Triarylmethyl Cations with Primary Amines in Aqueous Acetonitrile Solutions. The Importance of Amine Hydration

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Abstract: By use of the technique of laser flash photolysis, rate constants $k(RNH_2)$ have been directly measured for the reactions of primary amines RCH_2NH_2 ($R = CH_3CH_2$, CH_3OCH_2, $NCCH_2$, CF_3) with diarylmethyl cations (D^+) in acetonitrile/water solutions. In 100% acetonitrile the reactions approach the diffusion limit, 5×10^9 M^{-1} s^{-1}, although they are slower, $k(RNH_2)$ for a given cation increasing with increasing amine basicity and for a given amine increasing with decreased electron donation from substituents in D^+. In the mixed solvents the rate constants decrease in a regular fashion with increasing water content. The changes can be large, being on the order of 10–100 proceeding from 100% acetonitrile to 100% water. Moreover, the rate-retarding effect of water is more pronounced with more basic amines, with the consequence that in water-rich solutions the reactivity order no longer parallels amine basicity. Plots of log $k(RNH_2)$ versus $pK_a(RNH_3^+)$ not only are curved but also show a change in the sign of their slope on progressing from weakly basic amines (positive β_{nuc}) to strongly basic ones (negative β_{nuc}). This behavior is explained by a mechanism in which a hydrated amine $RNH_2 \cdots HOH$ is unreactive and an equilibrium desolvation to form the unhydrated amine precedes reaction with the cation. Quantitative treatment is carried out, using the rate constants in 100% acetonitrile to model the reaction of the free amine. This approach reproduces the experimental data within an average of ±0.04 log unit and results in equilibrium constants for the desolvation with the expected $\beta = -0.2$ dependency on amine basicity. Rate constants have also been measured in 33% acetonitrile/water for a series of triarylmethyl cations ranging from $4,4'\text{-}(Me_2N)_2T^+$ to $4,4'\text{-}(CF_3)_2T^+$. The β_{nuc} values for these are all positive, with a clear trend for β_{nuc} to decrease with increasing cation reactivity, this being true even for the relatively stable cations $4,4'\text{-}(Me_2N)_2T^+$, $4\text{-}Me_2NT^+$, and $4,4',4''\text{-}(MeO)_3T^+$. Thus, amine nucleophiles do not adhere to the N_+ constant selectivity relation, even for stable cations.

The technique of laser flash photolysis is proving highly valuable for the direct study of carbocations generated under conditions where they are commonly found as reactive intermediates. We have described for example experiments where a number of triaryl- and diarylmethyl cations were generated in aqueous acetonitrile solutions[3,4] and rate constants directly measured for their decay

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[1] University of Toronto.

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in the solvent[4] and for their reaction with added azide ion.[5] Previously, only highly stabilized examples of such cations had been examined through direct measurements,[6] data for less stable cations being obtained as ratios of rate constants obtained through competition kinetics or common ion inhibition.[7] This paper considers the reactions of Ar_3C^+ and Ar_2CH^+ with four primary amines—*n*-propylamine, 2-methoxyethylamine, 2-cyanoethylamine, and 2,2,2-trifluoroethylamine, neutral nucleophiles with varying basicity but constant steric requirements. One of the principal objectives was to investigate how selectivity changes as the cation progresses from a relatively stable one to an unstable one. Highly stabilized cations have been found to exhibit an interesting constant selectivity with changing reactivity, their rate constants being reasonably well satisfied by the simple equation $\log k = \log k_0 + N_+$, where k and k_0 are rate constants for combinations with the nucleophile in question and a reference nucleophile and N_+ is a parameter dependent only on the nucleophile and solvent system.[6] This equation has been criticized, with the proposal that a parameter for the electrophile be included.[8] It also seems from flash photolysis studies that less stable cations deviate significantly.[9,10] A further feature of amines is the possibility of an inversion in reactivity, a less basic amine being more reactive. Such a situation has been demonstrated with a short-lived cation in experiments involving competition kinetics[11] and has also been encountered with a phosphoryl electrophile.[12,13] The rate constants reported in this paper do in fact show that on progressing from highly stable cations to unstable ones there is a gradual decrease in selectivity, while short-lived diarylmethyl cations do exhibit inversions. This study also reveals that the amount of water present is an important determinant of both the absolute reactivity and the reactivity order.

Experimental Section

The substrates employed as precursors have been described.[4] Photolysis experiments were carried out with a KrF-excimer laser with 20-ns pulse width and with 248-nm excitation. The apparatus and methods of data handling have been described.[9] Solvents were prepared with water from a Millipore-Q system and spectroscopic grade acetonitrile. Concentrations given in the text and figures represent the percent by volume. Solutions for the kinetic measurements were prepared with $\sim 10^{-4}$ M precursor and with five to seven concentrations of amine ranging from 10^{-3} to 4×10^{-2} M (in addition to the solution with no amine). The individual kinetic runs obeyed excellent first-order kinetics, with rate constants from replicate measurements agreeing within ±3%. Plots of the first-order rate constants versus $[RNH_2]$ were linear, and second-order rate constants $k(RNH_2)$ were obtained as the slopes. In general, these rate constants had one standard deviation of 5% or better. To check whether rate accelerations were associated with hydroxide ion formed by the ionization of the amine, control experiments were carried out with *n*-propylamine in which the solution was buffered by the addition of the conjugate acid as the perchlorate salt. These experiments gave rate constants for the amine that were within experimental error identical to those obtained in the unbuffered solutions.

Analysis of the products of photolysis of (4-methoxyphenyl)diphenylacetonitrile was carried out with a Varian VISTA 5500 liquid chromatograph, using a Millipore Waters NOVA PAK C_{18} reversed-phase column with 3:1 (v/v) methanol/water as the eluting solvent pumped at a rate of 1.2 mL/min. The precursor (10 μM), dissolved in aqueous acetonitrile containing 2,2,2-trifluoroethylamine, was photolyzed with one pulse of a conventional flash apparatus. The HPLC analysis showed three compounds accounting for >90% of the initial amount of starting material, with retention times corresponding to starting material, (4-methoxyphenyl)diphenylmethyl alcohol, and (4-methoxyphenyl)(diphenylmethyl)-2,2,2-trifluoroethylamine. Approximately 50% conversion to products occurred in a single flash. Concentrations of the species present were calculated by constructing the appropriate standard curves. Product analyses were performed at several concentrations of amine in the range 0.03–0.1 M amine to calculate the ratio of rate constants.

The authentic sample of (4-methoxyphenyl)(diphenylmethyl)-2,2,2-trifluoroethylamine was prepared by adding silver chloride (3.5 mmol) and 2,2,2-trifluoroethylamine (3.0 mmol) to (4-methoxyphenyl)diphenylmethyl chloride (3.2 mmol) in 50 mL of anhydrous tetrahydrofuran. The mixture was stirred for 5 h at room temperature. A black precipitate was filtered and the solvent removed with a rotary evaporator to give a yellow liquid that crystallized on standing: mp 104–105 °C; ^1H NMR ($CDCl_3$) δ 2.00 (s, 1 H), 2.66 (q, 2 H), 3.77 (s, 3 H), 6.7–7.6 (m, 14 H). Anal. Calcd for $C_{22}H_{20}F_3NO$: C, 71.15; H, 5.43; N, 3.77. Found: C, 70.81; H, 5.15; N, 3.72.

Results

A list of cations and second-order rate constants for their reactions with the four amines are provided in Table I. The triarylmethyl cations were studied in one solvent mixture, while data for four of the diarylmethyl cations were obtained as a function of solvent composition. The three most reactive examples in this class, $4,4'\text{-}Me_2D^+$, $4\text{-}MeD^+$, and D^+, were only studied in 100% acetonitrile, since the addition of small amounts of water places the rate for decay in the solvent alone at or beyond the limit of the nanosecond apparatus.[3,4] The two 4-dimethylamino-substituted cations, $4,4'\text{-}(Me_2N)_2T^+$ and $4\text{-}Me_2NT^+$, were studied so as to provide as wide a range of reactivities as possible. The kinetic experiments with these cations were carried by conventional spectroscopy, by adding an acetonitrile solution of the cation to a solution containing the amine in a UV cuvette.

As has been argued previously,[3,4] these rate constants represent the reaction of the amine with a free cation in the ground state. There is also a question as to whether they represent cation–nucleophile combinations or contain a component for general-base catalysis of the addition of water.[14] For one system, $4\text{-}MeOT^+$ reacting with 2,2,2-trifluoroethylamine, this has been shown not to be the case through the analysis of products. In 33% acetonitrile, the rate constants directly measured are $k(CF_3CH_2NH_2) = 5.0 \times 10^4\ M^{-1}\ s^{-1}$, and for the solvent, $k_s = 1.6 \times 10^3\ s^{-1}$; the ratio is 31.3 M^{-1}. HPLC analysis following photolysis of the precursor acetonitrile shows the presence of the alcohol and the appropriate amine as the only products. The rate constant ratio calculated from these $([4\text{-}MeOTNHCH_2CF_3]/[4\text{-}MeOTOH])(1/[CF_3CH_2NH_2])$ is $33.7 \pm 3.7\ M^{-1}$, in good agreement.

Arguments against the other amines acting as general bases take several forms. Tertiary amines, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) have been demonstrated to react with cations as general bases.[14] However, with the cations under study here, DABCO only gives small rate accelerations and a primary amine of similar basicity is 10–20 times more reactive, indicating that the primary amine principally follows a different mechanism. Moreover, parallelism is expected between rate constants for general-base catalysis and amine basicity, since both involve proton transfer. Thus, the inverted Bronsted-like plots (see later) are inconsistent with a general-base mechanism. In fact, the trends in the rate constants for the reactive diarylmethyl cations are similar to that obtained through product analysis for a phenylethyl derivative.[11] Finally both Bunton and Huang[15] for 4,4′,4″-

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[7] (a) In some cases these ratios can be converted into absolute rate constants with the assumption that one of the nucleophiles reacts at the diffusion limit.[7b,c] Flash photolysis has shown that this assumption is valid for azide ion,[5] the nucleophile most commonly used in these "clock" experiments. (b) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248. (c) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *Ibid.* **1984**, *106*, 1361–1372.

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Table I. Rate Constants for the Reactions of Triarylmethyl (T^+) Cations and Diarylmethyl Cations (D^+) with Primary Amines in Aqueous Acetonitrile at 20 °C

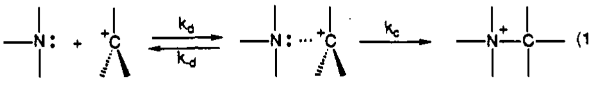
		$k(RCH_2NH_2)$, $M^{-1}\ s^{-1}$			
cation	% AN	CH_3CH_2–	CH_3OCH_2–	$NCCH_2$–	CF_3–
4,4′-$(Me_2N)_2T^+$	33	1.3×10^{1}	3.6×10^{0}	8.8×10^{-1}	5.5×10^{-2}
4-Me_2NT^+	33	1.5×10^{2}	4.9×10^{1}	1.4×10^{1}	1.4×10^{0}
4,4′,4″-$(MeO)_3T^+$	33	4.8×10^{4}	2.5×10^{4}	8.1×10^{3}	9.7×10^{2}
4,4′-$(MeO)_2T^+$	33	2.2×10^{5}	1.4×10^{5}	6.9×10^{4}	6.2×10^{3}
4-Me-4′-$MeOT^+$	33	7.6×10^{5}	4.0×10^{5}	2.5×10^{5}	2.7×10^{4}
3-Me-4′-$MeOT^+$	33	1.0×10^{6}	5.8×10^{5}	2.9×10^{5}	4.5×10^{4}
4-$MeOT^+$	33	1.0×10^{6}	6.2×10^{5}	2.9×10^{5}	5.0×10^{4}
3,4′-$(MeO)_2T^+$	33	1.2×10^{6}	6.6×10^{5}	3.1×10^{5}	5.1×10^{4}
4,4′,4″-Me_3T^+	33	2.6×10^{6}	1.4×10^{6}	6.7×10^{5}	1.0×10^{5}
4,4′-Me_2T^+	33	4.3×10^{6}	2.6×10^{6}	1.4×10^{6}	3.8×10^{5}
4-MeT^+	33	8.0×10^{6}	4.9×10^{6}	2.9×10^{6}	6.3×10^{5}
T^+	33	1.4×10^{7}	9.6×10^{6}	6.7×10^{6}	1.7×10^{6}
3-ClT^+	33	2.5×10^{7}	1.7×10^{7}	1.3×10^{7}	3.5×10^{6}
3-CF_3T^+	33	2.6×10^{7}	2.2×10^{7}	1.4×10^{7}	5.0×10^{6}
4-CF_3T^+	33	2.4×10^{7}	2.5×10^{7}	1.5×10^{7}	6.1×10^{6}
3,3′,3″-Cl_3T^+	33	4.7×10^{7}	4.4×10^{7}	3.3×10^{7}	1.1×10^{7}
4,4′-$(CF_3)_2T^+$	33	6.1×10^{7}	5.7×10^{7}	4.3×10^{7}	1.9×10^{7}
4,4′-$(MeO)_2D^+$	20	1.5×10^{7}	1.7×10^{7}	1.5×10^{7}	7.1×10^{6}
	33	2.2×10^{7}	2.0×10^{7}	1.8×10^{7}	9.3×10^{6}
	67	5.5×10^{7}	4.3×10^{7}	3.6×10^{7}	1.3×10^{7}
	91	2.2×10^{8}	1.4×10^{8}	9.9×10^{7}	2.7×10^{7}
	100	1.0×10^{9}	7.4×10^{8}	2.7×10^{8}	3.5×10^{7}
4-Me-4′-$MeOD^+$	20	3.2×10^{7}	3.5×10^{7}	3.6×10^{7}	2.3×10^{7}
	33	4.0×10^{7}	4.1×10^{7}	4.3×10^{7}	2.8×10^{7}
	67	1.0×10^{8}	9.3×10^{7}	9.0×10^{7}	4.5×10^{7}
	91	3.6×10^{8}	3.0×10^{8}	2.2×10^{8}	1.1×10^{8}
	100	2.3×10^{9}	1.5×10^{9}	7.2×10^{8}	1.5×10^{8}
4-F-4′-$MeOD^+$	20	3.1×10^{7}	3.3×10^{7}	3.6×10^{7}	2.3×10^{7}
4-$MeOD^+$	20	3.3×10^{7}	3.5×10^{7}	4.8×10^{7}	2.7×10^{7}
3,4′-$(MeO)_2D^+$	0	2.7×10^{7}	3.7×10^{7}	3.8×10^{7}	2.7×10^{7}
	20	4.1×10^{7}	4.5×10^{7}	4.7×10^{7}	3.6×10^{7}
	33	5.8×10^{7}	5.5×10^{7}	5.8×10^{7}	4.7×10^{7}
	67	1.3×10^{8}	1.2×10^{8}	1.2×10^{8}	8.1×10^{7}
	91	5.6×10^{8}	4.1×10^{8}	3.2×10^{8}	1.6×10^{8}
	100	2.9×10^{9}	1.9×10^{9}	1.1×10^{9}	2.9×10^{8}
3-Cl-4′-$MeOD^+$	33	6.1×10^{7}	5.9×10^{7}	6.3×10^{7}	4.4×10^{7}
3-CF_3-4′-$MeOD^+$	33	6.4×10^{7}	6.5×10^{7}	6.9×10^{7}	5.2×10^{7}
4-CF_3-4′-$MeOD^+$	20	5.8×10^{7}	7.0×10^{7}	8.0×10^{7}	5.6×10^{7}
	33	7.9×10^{7}	8.1×10^{7}	8.1×10^{7}	6.8×10^{7}
	67	1.6×10^{8}	1.6×10^{8}	1.5×10^{8}	1.1×10^{8}
	91	7.6×10^{8}	5.6×10^{8}	5.3×10^{8}	2.9×10^{8}
	100	3.4×10^{9}	2.6×10^{9}	1.7×10^{9}	4.6×10^{8}
4,4′-Me_2D^+	100	4.1×10^{9}	3.5×10^{9}	2.1×10^{9}	8.5×10^{8}
4-MeD^+	100	4.4×10^{9}	3.7×10^{9}	2.8×10^{9}	1.7×10^{9}
D^+	100	4.5×10^{9}	4.0×10^{9}	3.1×10^{9}	2.0×10^{9}

$(MeO)_3T^+$ and Dixon and Bruice[16] for 4,4′-$(Me_2N)_2T^+$ have previously argued that primary amines react as nucleophiles.

Discussion

Diarylmethyl Cations in 100% Acetonitrile. With diarylmethyl cations in 100% acetonitrile, anionic nucleophiles such as azide[5] and the halides[17] react with diffusional encounter as the rate-limiting step. This is seen experimentally through a common rate constant, $(2 \pm 0.2) \times 10^{10}\ M^{-1}\ s^{-1}$ that is independent of both nucleophile and cation (with only 4,4′-$(MeO)_2D^+$ somewhat slower). With the primary amines in this solvent many of the rate constants are also large, in the 10^{9}–$10^{10}\ M^{-1}\ s^{-1}$ range. The reactions, however, are not entirely diffusion-controlled since, for a given amine, the rate constants increase with decreased electron donation from the substituents on the rings (see Figure 1).[18] In a similar manner, rate constants for a given cation increase with increasing amine basicity, although, as will be discussed later, plots of log $k(RNH_2)$ versus $pK_a(RNH_3^+)$ are curved.

The diffusion limit, however, is being approached, since the rate constants are clearly approaching a plateau value for the more reactive combinations. This situation can be considered in terms of the simple scheme



(1)

in which the amine and cation diffuse together with a rate constant k_d to form a reactant pair, which separates or collapses to product with rate constants k_{-d} and k_c, respectively. For this kinetic system

$$k(RNH_2) = k_d/(1 + k_{-d}/k_c) \qquad (2)$$

and the question as to whether the diffusion step or the combination step is rate-limiting revolves around the relative magnitudes of k_{-d} and k_c. The observed rate constant becomes equal to k_d and diffusion becomes rate-limiting when $k_c \gg k_{-d}$. A situation where these two rate constants are similar in magnitude produces observed rate constants that approach k_d but do not quite reach it. From a simple inspection of the curves in Figure 1, we estimate that k_d for this system is $\sim 5 \times 10^{9}\ M^{-1}\ s^{-1}$. Analysis using an empirical approach[5] developed to treat data for azide ion and Ar_3C^+ gives a similar number, $4.6 \times 10^{9}\ M^{-1}\ s^{-1}$.[19] Thus, pairs

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(18) The use of log k_s for the correlation in Figure 1 is simply to provide a measure of the reactivity of these cations under conditions where the reactions are far from being diffusion controlled. Similar curves are generated if substituent constants σ^+ or σ^{C^+} are employed, although there is considerably more scatter because of nonadditivity[4] on multiple substitution.

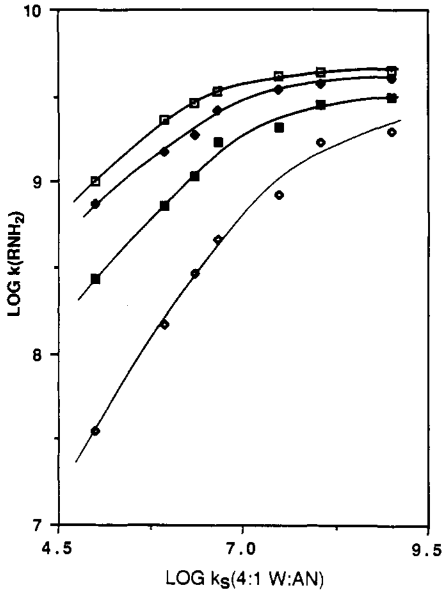

Figure 1. Variation in log $k(RNH_2)$ (M^{-1} s^{-1}) for diarylmethyl cations reacting with primary amines in 100% acetonitrile with log k_s (s^{-1}) for decay of the same cation in 4:1 (v/v) water/acetonitrile: open squares, $CH_3CH_2CH_2NH_2$; closed diamonds, $CH_3OCH_2CH_2NH_2$; closed squares, $NCCH_2CH_2NH_2$; open diamonds, $CF_3CH_2NH_2$. Cations from left to right are 4,4′-$(MeO)_2D^+$, 4-Me-4′-$MeOD^+$, 3,4′-$(MeO)_2D^+$, 4-CF_3-4′-$MeOD^+$, 4,4′-Me_2D^+, 4-MeD^+, and D^+. The k_s values were taken from ref 4; numbers for 4-MeD^+ and D^+ are estimates.

such as D^+ and $PrNH_2$ ($k = 4.5 \times 10^9$), 4-MeD^+ and $PrNH_2$ (4.4×10^9), and D^+ and $MeOCH_2CH_2NH_2$ (4.0×10^9) are reacting close to the diffusion limit, while others move progressively further away as either the amine basicity or the cation reactivity is decreased.

A value of k_d can be calculated through the Smoluchowski equation, $k_d = \alpha_R NR(D_A + D_B)/1000$,[20,21] where N is Avogadro's number, R is the encounter distance normally taken as the sum of ionic or covalent radii, D_A and D_B are diffusion coefficients, and α_R is the solid angle of encounter that leads to reaction. For a diarylmethyl cation in acetonitrile the diffusion coefficient and ionic radius have been estimated as 1.9×10^{-5} cm^2 s^{-1} and 1.8 Å, respectively.[5] For the amine partner, we employ literature data for a compound structurally very similar to the four employed in this study, $HSCH_2CH_2NH_2$—radius 2.1 Å and diffusion coefficient 1.1×10^{-5} cm^2 s^{-1} in water at 25 °C.[22] Assuming the Stokes–Einstein equation[20] is followed, the latter leads to a value in acetonitrile of 2.8×10^{-5} at 25 °C, which can be corrected to 2.5×10^{-5} at 20 °C based on the known temperature dependence of diffusion coefficients. Some confidence that this is reasonable is provided by a report that diffusion coefficients for a variety of organic compounds in acetonitrile at 22 °C lie between 2.12×10^{-5} and 2.46×10^{-5} cm^2 s^{-1}.[23]

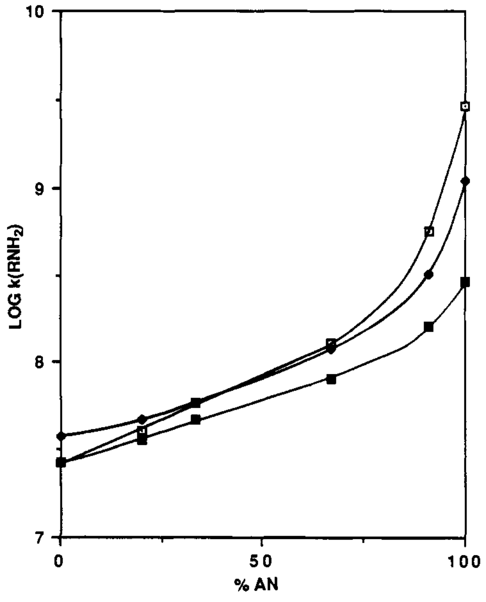

Figure 2. Dependence of $k(RNH_2)$ (M^{-1} s^{-1}) for the diarylmethyl cation 3,4′-$(MeO)_2D^+$ on solvent composition in water/acetonitrile mixtures. % AN is volume percent (v/v) acetonitrile. Amines: $CH_3CH_2CH_2NH_2$, open squares; $NCCH_2CH_2NH_2$, diamonds; $CF_3CH_2NH_2$, closed squares.

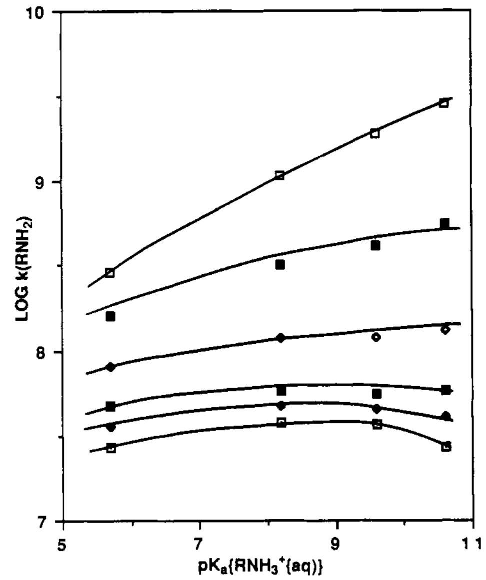

Figure 3. Dependence of log $k(RNH_2)$ on $pK_a(RNH_3^+)$ for the reactions of amines with the diarylmethyl cation 3,4′-$(MeO)_2D^+$ in aqueous acetonitrile solutions. Percent volumes (v/v) of acetonitrile from the top of the figure are 100% (open squares), 91% (closed squares), 67% (open diamonds), 33% (closed squares), 20% (closed diaminds), and 0% (open squares). The curves drawn for the data in the four mixed solvents are calculated from the empirical model (see text).

With these numbers in hand, k_d for the diffusional encounter of an amine and Ar_2CH^+ is calculated as 1.26×10^{10} M^{-1} s^{-1} for the situation $\alpha_R = 4\pi$, where every encounter leads to reaction. This number is 4 times smaller than the k_d values calculated in a similar manner for azide (4.7×10^{10}) and bromide (5.0×10^{10}),[5] a reflection of the increased "effective" R for the encounter of

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(19) In this approach, k_d and k_{-d} are assumed to be independent of substituent, while k_c follows a linear free energy relation in k_s (log $k_c = \alpha$ log k_s + log k_c^0). Substitution into eq 2 then gives an equation, $k(RNH_2) = k_d/\{1 + (k_{-d}/k_c^0)(1/k_s^\alpha)\}$, relating the observed rate constants $k(RNH_2)$ and k_s with three parameters, k_d, α, and the ratio k_{-d}/k_c^0. To treat the amine data where there is more than one nucleophile, the assumption was made that since the four amines should have similar diffusion coefficients, k_d is independent of amine. Calculations were then performed for k_d values ranging from 4×10^9 to 8×10^9, in which the values of the other two parameters were determined for each amine that gave the best fit to the experimental data for that particular k_d. The difference $\{k_{obs}(RNH_2) - k_{calc}(RNH_2)\}^2$ was then determined, with the latter term the rate constant calculated from the above equation using k_d and the other parameters. The overall best fit was then taken as that value of k_d that gave the minimum deviation summing over all 28 rate constants measured in 100% acetonitrile. That occurred with $k_d = 4.6 \times 10^9$ M^{-1} s^{-1} (and $\alpha = 0.57, 0.40, 0.36, 0.48$ and $k_{-d}/k_c^0 = 2.3 \times 10^3, 4.5 \times 10^2, 1.6 \times 10^4, 1.4 \times 10^3$ for propyl-, methoxyethyl-, cyanoethyl-, and trifluoroethylamine, respectively). With these parameters, the average deviation between the observed and calculated k(amine) is 5%.

(20) Rice, S. A. In Diffusion-Limited Reactions. *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Compton, R. G., Eds.; Elsevier: Amsterdam, 1985; Vol. 25.

(21) With the units of R as cm and D as cm^2 s^{-1}, the factor 1000 in the denominator provides k_d in units of M^{-1} s^{-1}.

(22) Hart, E. J.; Anbar, M. *The Hydrated Electron*; Wiley Interscience: New York, 1970. Calculated from data on p 187 using an ionic radius and diffusion coefficient for the electron of 2.5 Å and 4.9×10^{-5} cm^2 s^{-1}, respectively.

(23) Sharma, L. R.; Sharma, A.; Singh, G.; Verma, R. S. *Ind. J. Chem., Sect. A* **1985**, *24A*, 683–684.

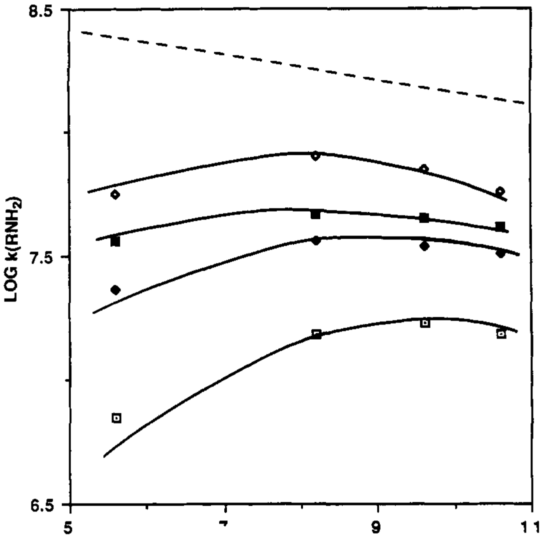


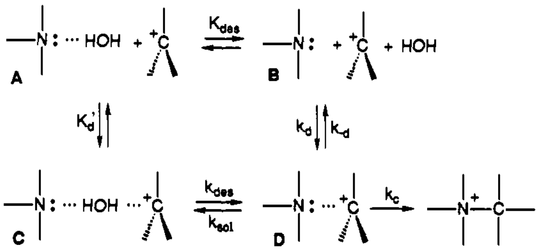
Figure 4. Dependence of log $k(RNH_2)$ on $pK_a(RNH_3^+)$ for the reactions of amines and diarylmethyl cations in 4:1 (v/v) water/acetonitrile. Cations: 4,4′-$(MeO)_2D^+$, open squares; 4-Me-4′-$MeOD^+$, closed diamonds; 3,4′-$(MeO)_2D^+$, closed squares; 4-CF_3-4′-$MeOD^+$, open diamonds. The points are experimental; the curves are calculated from the empirical model (see text). The dashed line represents the Bronsted-like plot for 4-$CH_3OC_6H_4CH^+CF_3$ in 4:1 W/MeOH.[11] Data for this cation were obtained through the competition method; the rate constant for propylamine was calculated from a ratio $k(N_3^-)/k(PrNH_2)$ of 8×10^1, using $k(N_3^-)$ as 7×10^9 M^{-1} s^{-1} [5] and a line then drawn through this point with a slope of −0.08.

two ions of opposite charge.[24] This same difference of a factor of 4 is also seen in the experimental k_d, the latter being 40% of the calculated value for both the anionic and neutral nucleophiles. For the cation–anion combinations, this was explained through a model where only 40% of the collisions produce a reactant pair capable of collapsing to product ($\alpha_R = 0.4 \times 4\pi$).[5] The present calculation shows that the identical situation also applies with a neutral nucleophile.

Diarylmethyl Cations in Aqueous Acetonitrile. As illustrated in Figure 2 for data for one cation, rate constants decrease with the addition of water. This decrease occurs in a monotonic fashion with increasing water content, with the effect being larger in the acetonitrile-rich region. In addition, the more basic the amine, the greater the effect of water, with the consequence that in water-rich solutions the parallelism between amine basicity and nucleophilicity disappears and, in some cases, a less basic amine has a larger rate constant than a more basic one. For example, for 3,4′-$(MeO)_2D^+$ in 100% water, $CH_3CH_2CH_2NH_2$, and $CF_3CH_2NH_2$ have the same rate constant, while the two amines of intermediate basicity, $CH_3OCH_2CH_2NH_2$ and $NCCH_2CH_2NH_2$, actually react faster.

The latter is dramatically illustrated in the Bronsted-like plots of log $k(RNH_2)$ versus $pK_a(RNH_3^+)$. Figures 3 and 4 provide representative examples, the former showing data for one cation as the solvent composition is varied and the latter showing data in one solvent, a water-rich one, for the series of four diarylmethyl cations. In 100% acetonitrile and the acetonitrile-rich solutions, these plots have small positive slopes β_{nuc}. They may be slightly curved, although this is difficult to determine with only four points and a reference pK_a in a different solvent. The value of β_{nuc} decreases as water is added, with the propylamine end of the curve being dragged down more than the trifluoroethylamine end. The result of this is that, in water-rich solutions, the plots are definitely curved, with β_{nuc} being positive for the weakly basic amines and negative for the more basic ones. As shown in Figure 4, this is observed for each cation in water-rich solutions. There is also a general trend that rate constants for the most basic amine are the least affected by the aromatic substituents, a behavior particularly evident if literature data are included for a phenethyl cation derivative.[11] This cation is more reactive than the four diarylmethyl derivatives and has a reasonably linear Bronsted-like plot for primary amines ranging from $CH_3CH_2CH_2NH_2$ to $CF_3CH_2NH_2$, but with a negative slope of −0.08; the plot does break downward if data for amines that are very weakly basic are considered.[11] As will be shown later, Bronsted-like plots for unreactive cations such as 4-Me_2NT^+ have substantially positive β_{nuc}. Thus, there are two extremes of cation reactivity with β_{nuc} values of opposite sign and an intermediate region exhibiting both types of behavior.

Scheme I



The behavior with water present is associated with hydration tying up the amine lone pair.[11-13] As shown in Scheme I, two related mechanisms can be considered, one where a water molecule that is hydrogen-bonded to the amine must be separated from an initial encounter complex C with the cation prior to N–C bond formation and a second where the water molecule is separated in a preequilibrium step before encounter with the cation. Both possibilities accommodate negative β_{nuc} values for highly reactive cations. With the former this is associated with the desolvation step k_{des} becoming rate-limiting in the overall reaction, so that more basic amines become less reactive since they hold this water molecule more tightly. With the latter, observed β_{nuc} values are a sum of the true β_{nuc} for the reaction starting with the free amine and the β value for K_{des}, the equilibrium desolvation. The latter was suggested to be −0.2, the hydrogen-bonded form being more favored for more basic amines.[12,13] Thus, reactions with an intrinsically low dependence on amine basicity would have negative β_{nuc}(obs) if β_{nuc}(free amine) were less than 0.2.

The distinction between the two revolves around the question as to whether the amine nucleophile undergoes desolvation before or after the formation of the reactant cation–amine complex D. This is best examined from the point of view of this complex, in terms of whether the hydration process k_{sol} or the diffusional separation to free amine and cation k_{-d} is of lower energy. By the principle of microscopic reversibility, the reverse of the lower energy pathway is rate-determining in the formation of D. In 100% acetonitrile where there is no water and in acetonitrile-rich solutions where the water concentration is low ($k_{sol}[H_2O] < k_{-d}$), the complex D must form from the free amine, so that the observed rate constants are given by

$$k(RNH_2) = \left(\frac{k_d}{1 + (k_{-d}/k_c)}\right)\left(\frac{K_{des}}{[H_2O] + K_{des}}\right) \quad (3)$$

where the first term on the right side is the rate constant for the reaction of the free amine and cation and, defining K_{des} as $[RNH_2][H_2O]/[RNH_2\cdots HOH]$, the second term is the fraction of amine in the free amine form $\{[RNH_2]/([RNH_2\cdots HOH] + [RNH_2])\}$. In 100% acetonitrile the latter is obviously unity, and as water is added, this decreases as the relative amount of the unreactive hydrogen-bonded amine increases. With the term in $[H_2O]$ in the denominator of this expression, $k(RNH_2)$ is expected to decrease in a regular fashion with increasing $[H_2O]$. Moreover, the observed β_{nuc} also decreases, as the contribution to the overall rate constant from the equilibrium desolvation step increases. Adding water to acetonitrile also results in an increase in the dielectric constant. The effects of this are difficult to establish, and they may operate in opposite directions. For example, the

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[24] For the cation–anion combination, R_{eff} = 15.3 Å, due to the dominating Coulombic attraction term.[5]

Table II. Equilibrium Constants for the Desolvation of Hydrogen-Bonded Amines in 91% Acetonitrile As Calculated from the Decrease Relative to 100% Acetonitrile in the Rate Constants for the Reactions with Diarylmethyl Cations

		$K_{des}(RCH_2NH_2)$,[a] M				
% AN	cation	CH_3CH_2–	CH_3OCH_2–	$NCCH_2$–	CF_3–	β[d]
91[b]	4,4′-$(MeO)_2D^+$	1.21	1.41	2.9	12.9	
91	4-Me-4′-$MeOD^+$	0.92	1.25	2.2	11.8	
91	3,4′-$(MeO)_2D^+$	1.20	1.37	2.1	7.2	
91	4-CF_3-4′-$MeOD^+$	1.44	1.37	2.3	8.5	
91	average[c]	1.19 ± 0.20	1.35 ± 0.07	2.4 ± 0.3	10.1 ± 2.3	−0.19
67[e]	average[c]	0.69 ± 0.11	1.10 ± 0.05	2.2 ± 0.2	7.9 ± 1.4	−0.21
33[f]	average[c]	0.76 ± 0.07	1.10 ± 0.04	2.2 ± 0.2	8.9 ± 1.8	−0.22
20[g]	average[c]	0.91 ± 0.06	1.19 ± 0.03	2.4 ± 0.3	7.9 ± 1.2	−0.19
0[h]	3,4′-$(MeO)_2D^+$	0.65	1.4	2.6	8.5	−0.22

[a] Calculated as $[H_2O]R/(1-R)$, where $R = k(RNH_2 \text{ in solvent in question})/k(RNH_2 \text{ in 100\% acetonitrile})$. [b] $[H_2O] = 5.0$. [c] Average value for the four cations. [d] Slope of plot of log K_{des} versus $pK_a(RNH_3^+(aq))$. [e] $[H_2O] = 18$. [f] $[H_2O] = 37$. [g] $[H_2O] = 44$. [h] $[H_2O] = 55.5$.

more polar solvent should stabilize the free cation somewhat relative to D, decreasing k_d/k_{-d}, but k_c may increase slightly as the transition state forming the ammonium ion becomes better solvated. Particularly in comparing 100% and 91% acetonitrile, this dielectric change should have a relatively minor effect and is certainly not sufficient to account for the large decreases in the observed $k(RNH_2)$. The data in 91% acetonitrile can in fact be fit reasonably satisfactorily by a treatment based upon eq 3, assuming that the first term in this equation is unchanged between this solvent and 100% acetonitrile. This means that there is only one parameter that is unknown, and values can be calculated based upon the rate decrease in going from 100% to 91% acetonitrile (Table II). This operation can be performed for each of the four diarylmethyl cations, and for a given amine, reasonable agreement is found in the values of K_{des} so calculated. More importantly, a plot of log K_{des} versus $pK_a(RNH_3^+)$ has a slope of close to −0.2, precisely the value predicted for this type of equilibrium constant.[12] The actual numerical values of K_{des} are also consistent with some recent measurements of Berg and Jencks.[25] These workers obtained rate constants for the breaking of the hydrogen bond between tertiary amines and water, finding values ranging from 1.9×10^9 to 1.2×10^{10} s^{-1} for amines with $pK_a(R_3NH^+)$ ranging from 11.3 to 7.9; the Bronsted β is −0.25. If the assumption is made that the reverse process, $R_3N + HOH \rightarrow R_3N\cdots HOH$, occurs at the diffusion limit with a rate constant of 5×10^9 M^{-1} s^{-1}, then equilibrium constants K_{des} for the desolvation of $R_3N\cdots HOH$ can be calculated, producing values that are in good agreement with ones in Table II. A tertiary amine of the same basicity as propylamine, for example, is estimated to have $K_{des} = 0.6$ M, while an amine of the basicity of 2-cyanoethylamine has $K_{des} = 2.4$ M.

This treatment continues to produce reasonably consistent values of K_{des} even in the more aqueous solvents, with the trend of β around −0.2 continuing in each case (Table II). Overall, the approach reproduces the 64 rate constants (four cations, four amines, four solvents) with an average deviation of the calculated log $k(RNH_2)$ values from the observed ones of ±0.04. The values of K_{des} do vary somewhat with solvent, but this is undoubtedly a result of the neglect of solvent effects, plus the possibility that some of the reaction may be occurring by the alternate route (see below). A treatment in which only one value of K_{des} is allowed for each amine independent of water content provides K_{des} that are the average of those in Table II. The overall fit to the experimental data is however poorer, with an average deviation between calculated and observed $k(RNH_2)$ of ±0.10 log unit.

This model also reproduces the curved Bronsted-like plots observed in the water-rich solvents, as illustrated in Figures 3 and 4 where the lines have been drawn based on calculated $k(RNH_2)$. This is further exemplified in Figure 5, which provides a breakdown of the rate constants for one system. From eq 3, log $k(RNH_2)$ is determined by three log terms.

$$\log k(RNH_2) = \log k_d - \log (1 + k_{-d}/k_c) + \log \{K_{des}/([H_2O] + K_{des})\} \quad (4)$$

The last term is reasonably linear in $pK_a(RNH_3^+)$, with a slope

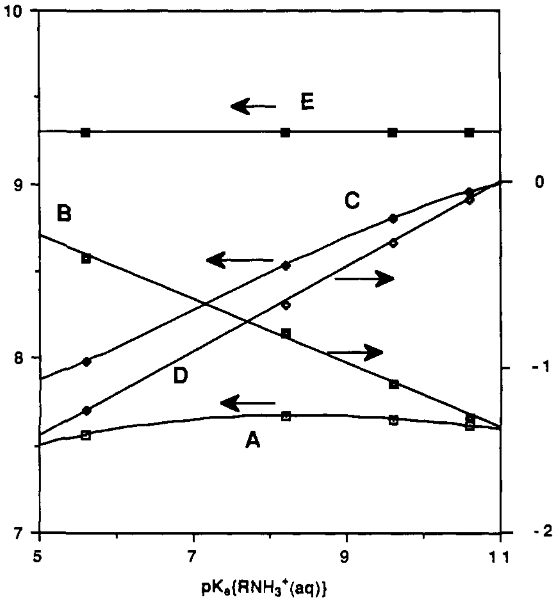

Figure 5. Breakdown of the rate constants for 3,4-$(MeO)_2D^+$ in 4:1 (v/v) water/acetonitrile: A, observed log $k(RNH_2)$; B, log $(K_{des}/([H_2O] + K_{des}))$, slope −0.18; C, log $k(\text{free amine}) = \log (k_d/(1 + k_{-d}/k_c)) = \log \{k(RNH_2)([H_2O] + K_{des})/K_{des}\}$; D, log (k_c/k_{-d}), slope +0.24; E, log k_d, slope 0. Note that the *y* axis for A, C, and E is given on the left and for B and D on the right.

of −0.18 in 20% acetonitrile. The desolvation preequilibrium, in other words, does not account for any significant curvature in the Bronsted-like plot; it simply has the effect of decreasing d log $k(RNH_2)/dpK_a(RNH_3^+)$ by −0.18. As shown by C, converting to the rate constant for the reaction of the free amine produces a plot with a significant β_{nuc}. This is probably still curved, but this is masked now by the positive slope. Curve D shows the behavior of the partitioning ratio, log (k_c/k_{-d});[26] this quantity is linear in $pK_a(RNH_3^+)$, with a slope of +0.24.[27] log k_d is obviously constant (E), since this represents diffusional encounter of the free amine and cation. The quantity that determines log $k(RNH_2)$ however is not log (k_c/k_{-d}) but log $(1 + k_{-d}/k_c)$, and it is this that is curved in a plot versus $pK_a(RNH_3^+)$. The reason for this is apparent from the observation that curve C, the rate constant for the reaction starting with the free amine, is approaching E, the diffusion limit. An equivalent observation is that the ratio k_c/k_{-d} is approaching unity. Thus, although $k_{-d} > k_c$, the numbers are sufficiently close that log $(1 + k_{-d}/k_c)$ does not equal log (k_{-d}/k_c).

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(25) Berg, U.; Jencks, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 6997–7002.

(26) These values were calculated by first correcting the observed rate constant to the rate constant for the free amine by multiplying by $([H_2O] + K_{des})/K_{des}$. This gives values of $k_d/(1 + k_{-d}/k_c)$, and the ratio k_c/k_{-d} was then calculated using $k_d = 2 \times 10^9$ M^{-1} s^{-1}.

(27) Since k_{-d} should not depend significantly on amine basicity, this slope is the β value for collapse within the encounter complex. The reasonable linearity of this plot indicates that this reaction does quantitatively follow amine basicity, although with a low sensitivity.

In qualitative terms, the Bronsted-like plots are curved for the simple reason that the rate-limiting step is beginning to change from collapse within the reactant complex to rate-limiting formation of this complex, and the extent to which this is true depends on amine basicity. Considering a hypothetical series of amines covering a much wider range of basicity, one can visualize the two extremes. For very weakly basic amines, $k_c/k_{-d} \ll 1$, collapse of the reactant complex would be entirely rate-limiting, and

$$k(\mathrm{RNH_2}) = \left(\frac{k_c k_d}{k_{-d}}\right)\left(\frac{K_{des}}{[\mathrm{H_2O}] + K_{des}}\right) \qquad (5)$$

The Bronsted-like plot would be linear, with a small positive slope, +0.06, equal to the sum of the β values for k_c/k_{-d} and $K_{des}/([\mathrm{H_2O}] + K_{des})$. The other extreme would occur for extremely basic amines and would correspond to the situation where $k_c/k_{-d} \gg 1$, so that the rate-limiting step is diffusion, and

$$k(\mathrm{RNH_2}) = k_d\left(\frac{K_{des}}{[\mathrm{H_2O}] + K_{des}}\right) \qquad (6)$$

Here also, the Bronsted-like plot is linear, but now the slope is −0.18, being determined solely by the desolvation equilibrium. Overall, the rate of change of d log $k(\mathrm{RNH_2})/\mathrm{d}pK_a(\mathrm{RNH_3^+})$ with changing $pK_a(\mathrm{RNH_3^+})$ is small, and for a series of amines with a small ΔpK_a, it is difficult to distinguish curved and linear Bronsted-like plots. The curved nature is however most apparent where the observed β_{nuc} is changing from positive to negative, as just happens to be the case in the water-rich solutions for the diarylmethyl cation–amine combinations that were studied in this work (Figure 4).

Although desolvation occurring after the encounter with the cation cannot be completely ignored in water-rich solutions, this proves to be inconsistent with the trends observed in β_{nuc} with changing water concentration. For this mechanism

$$k(\mathrm{RNH_2}) = K_d'\left(\frac{k_{des}}{k_{sol}[\mathrm{H_2O}]/k_c + 1}\right) \qquad (7)$$

and there are again two extremes representing rate-limiting C–N bond formation and desolvation dependent on the relative magnitudes of $k_{sol}[\mathrm{H_2O}]$ and k_c, with the intermediate situation where these are of similar magnitude accounting for the curved Bronsted-like plots. The explanation here requires that k_c increase with increased basicity, so that for cases where $k_{sol}[\mathrm{H_2O}] \sim k_c$, the slope of a plot of log $k(\mathrm{RNH_2})$ versus $pK_a(\mathrm{RNH_3^+})$ decreases with increased amine basicity since the rate-limiting step is moving away from C–N bond formation with a positive slope to desolvation with a negative one. This argument accounts for the shape of the Bronsted-like plots in a particular solvent. The problem however is that it makes the wrong prediction about the way these plots respond to changing water content. Specifically, this model predicts that as the amount of water in the solution is increased, the changeover from positive to negative β_{nuc} will occur at higher pK_a, since $k_s[\mathrm{H_2O}]$ will increase relative to k_c and a more basic amine will be required to make the latter rate constant larger than the former. Stating this argument in another way, this model predicts that, for a given combination of cation and amine, d log $k(\mathrm{RNH_2})/\mathrm{d}pK_a(\mathrm{RNH_3^+})$ should become more positive as water concentration is increased. As shown in Figure 3, exactly the reverse behavior is observed.

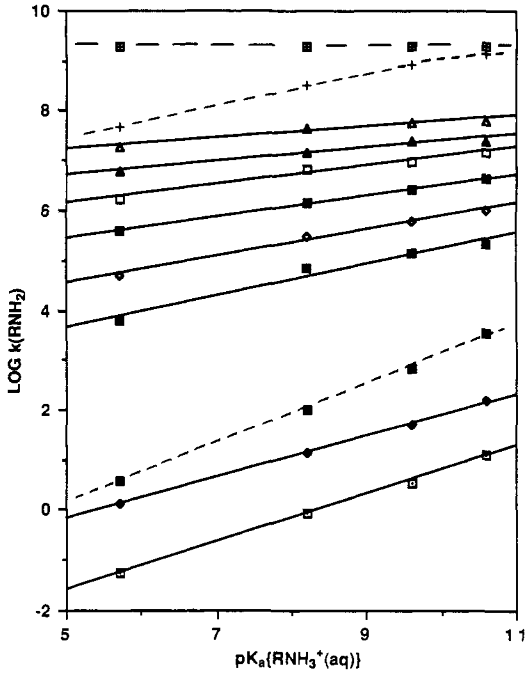

Figure 6. Dependence of log $k(\mathrm{RNH_2})$ on $pK_a(\mathrm{RNH_3^+})$ for the reactions of amines and triarylmethyl cations in 2:1 (v/v) water/acetonitrile. Cations, starting from the bottom: $4,4'\text{-}(\mathrm{Me_2N})_2\mathrm{T^+}$, open squares; $4\text{-}\mathrm{Me_2NT^+}$, closed diamonds; $4,4'\text{-}(\mathrm{MeO})_2\mathrm{T^+}$, closed squares; $4\text{-}\mathrm{MeOT^+}$, open diamonds; $4,4'\text{-}\mathrm{Me_2T^+}$, closed squares; $\mathrm{T^+}$, open squares; $4\text{-}\mathrm{CF_3T^+}$, closed triangles; $4,4'\text{-}(\mathrm{CF_3})_2\mathrm{T^+}$, open triangles. The line at the top of the figure represents log k_d. The dashed lines show plots of rate constants corrected for the desolvation preequilibrium, for $4,4'\text{-}(\mathrm{CF_3})_2\mathrm{T^+}$ (top line) and $4\text{-}\mathrm{Me_2NT^+}$ (bottom line).

Table III. β_{nuc} Values for the Reactions of Triarylmethyl Cations with Primary Amines

cation	$\beta_{nuc}(\mathrm{obs})^a$	$\beta_{nuc}(\mathrm{corr})^b$	$k_{-d}/k_c(\mathrm{PrNH_2})^c$
$4,4'\text{-}(\mathrm{Me_2N})_2\mathrm{T^+}$	0.48	0.67	7×10^6
$4\text{-}\mathrm{Me_2NT^+}$	0.41	0.60	6×10^5
$4,4',4''\text{-}(\mathrm{MeO})_3\mathrm{T^+}$	0.35	0.54	2×10^3
$4,4'\text{-}(\mathrm{MeO})_2\mathrm{T^+}$	0.32	0.51	4×10^2
$4\text{-Me-}4'\text{-}\mathrm{MeOT^+}$	0.29	0.48	2×10^2
$3\text{-Me-}4'\text{-}\mathrm{MeOT^+}$	0.27	0.46	9×10^1
$4\text{-}\mathrm{MeOT^+}$	0.27	0.46	9×10^1
$3,4'\text{-}(\mathrm{MeO})_2\mathrm{T^+}$	0.28	0.47	8×10^1
$4,4',4''\text{-}\mathrm{Me_3T^+}$	0.29	0.48	3×10^1
$4,4'\text{-}\mathrm{Me_2T^+}$	0.21	0.40	2×10^1
$4\text{-}\mathrm{MeT^+}$	0.22	0.41	1×10^1
$\mathrm{T^+}$	0.19	0.38	5×10^0
$3\text{-}\mathrm{ClT^+}$	0.17	0.36	3×10^0
$3\text{-}\mathrm{CF_3T^+}$	0.14	0.33	3×10^0
$4\text{-}\mathrm{CF_3T^+}$	0.13	0.32	3×10^0
$3,3',3''\text{-}\mathrm{ClT^+}$	0.13	0.32	1×10^0
$4,4\text{-}(\mathrm{CF_3})_2\mathrm{T^+}$	0.10	0.29	6×10^{-1}

^{a} Based upon observed $k(\mathrm{RNH_2})$. ^{b} For the reaction of the free amine. ^{c} See note 25 for method of calculation.

Triarylmethyl Cations. Overall, we conclude that the model where desolvation occurs prior to the encounter with cation is better satisfied by the experimental data, and we will treat the triarylmethyl cations in terms of this mechanism. Here we see the effect of moving away from reactive cations to relatively unreactive ones (Figure 6). At the reactive end of this series, e.g., $4,4'\text{-}(\mathrm{CF_3})_2\mathrm{T^+}$, the values of $k(\mathrm{RNH_2})$ are large and the diffusion limit for the reaction involving the free amine is being approached. This can be seen in the rate constants corrected for the desolvation preequilibrium (compare the dashed line at the top in Figure 6 with the line for log k_d) and is also apparent in calculated values of the partitioning ratio k_{-d}/k_c (see Table III for values for the most basic amine, propylamine). However, for over half the series of $\mathrm{Ar_3C^+}$—all of the cations above the parent $\mathrm{T^+}$ in Table III—k_{-d} is at least 10 times greater than k_c for all four amines.[28] Thus, these systems lie at the extreme described by eq 5 where collapse of the reactant complex D of Scheme I is completely rate-limiting.

In this limit, the observed β_{nuc} is comprised of the ~−0.2 contribution from the desolvation step, since k_d and k_{-d} should be relatively insensitive to amine, a positive contribution due to k_c, the rate constant for the C–N bond-forming process. β_{nuc} values, both based upon the observed $k(\mathrm{RNH_2})$ and those corrected for desolvation by adding 0.19,[29] are given in Table III. The numbers are all positive, especially those for the set ranging

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[28] Note that, for given cation, the values of this ratio for the other amines are larger than that in Table III for $\mathrm{CH_3CH_2CH_2NH_2}$.

[29] The contribution calculated using the K_{des} values in Table II.

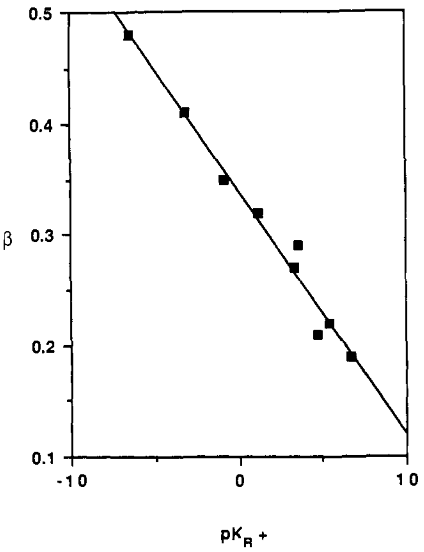
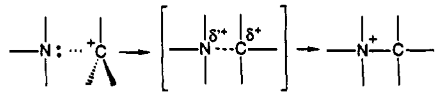


Figure 7. Dependence of β_{nuc} (for the observed $k(RNH_2)$) on pK_{R^+} for cations ranging from 4,4′-$(Me_2N)_2T^+$ to T^+.

from 4,4′-$(Me_2N)_2T^+$ to 4-MeT^+ where k_c is entirely rate-limiting throughout. They become even more positive on correcting for the desolvation step. The conclusion is that there is considerable bond formation in the transition state, with substantial positive charge being placed on the amine nitrogen.



What is also interesting is that β_{nuc} varies with cation, the values showing a clear trend of decreasing with increasing cation reactivity.[30] In fact, as shown in Figure 7, a plot versus the cation's pK_{R^+} value is reasonably linear, with a slope $d\beta_{nuc}/dpK_{R^+}$ of −0.022. The implication is that the position of the transition state varies with cation stability, with less C–N bond formation for more reactive cations. This of course has the consequence of placing less positive charge on the amine nitrogen in the transition state, so that there is a lower sensitivity to amine pK_a.

The dependence of β_{nuc} on cation stability is observed throughout the series, even with the highly stabilized 4′,4′-$(Me_2N)_2T^+$, 4-Me_2NT^+, and 4,4′,4″-$(MeO)_3T^+$ cations previously employed in the development of the simple N_+ relationship. Constant selectivity equates to constant β_{nuc}, and we conclude that none of the triarylmethyl cations follow the simple N_+ equation where primary amines are concerned. Proposals have been made that a parameter for the electrophile be included in this equation,[8] and the amine data are consistent with this idea. It has been argued that the deviations with the highly stabilized cations from the constant selectivity relation are not sufficient to warrant modification.[31] However, on considering the larger range of cation reactivities available with flash photolysis, a change in selectivity is clearly apparent.[32] It can be further noted that although the reactivity–selectivity principle has come under heavy criticism as a general principle,[33] the amine–cation combinations do follow the expected pattern, more reactive cations being less selective.

Summary. Starting with a very stable cation in aqueous solutions, reactions with primary amines are characterized by substantially positive β_{nuc} values reflecting substantial C–N bond formation in the transition state with positive charge being placed on nitrogen. This β_{nuc} is the sum of a −0.2 contribution from a preequilibrium desolvation step and the positive value for the actual reaction of the free amine. As cation stability is decreased, β_{nuc} decreases in a regular fashion. This is a reflection of a reactivity–selectivity relation, more reactive cations requiring less C–N bond formation to reach the transition state. As cation stability is further decreased, plots of log $k(RNH_2)$ versus $pK_a(RNH_3^+)$ become curved, with positive slopes for weakly basic amines and negative slopes for strongly basic ones. This is a reflection of the reaction of the free amine and cation approaching diffusion control, so that the negative β associated with the desolvation step begins to outweigh the β_{nuc} (now small) for the actual C–N bond formation. In the limit of extremely reactive cations, reaction of the free amine and cation occurs with rate-limiting diffusional encounter and the Bronsted-like plots become linear again. Now, however, the slope is negative, around −0.2, this value due solely to the requirement of removing a water of hydration from the amine.

For a given cation–amine combination, starting in an aqueous solution and proceeding to 100% acetonitrile results in a monotonic increase in rate constant and, at the same time, d log $k(RNH_2)/dpK_a(RNH_3^+)$ increases in a regular manner. Both effects are related to the increasing amounts of free, unhydrated, amine that is present with decreasing water content in the solution.

Acknowledgment. R.A.M. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada for support of this work.

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(30) (a) A reviewer has commented that the literature data[30b,c] for Malachite Green obtained in 100% water give an observed β_{nuc} of 0.37 as compared to the value of 0.48 measured in this work. There is a however difference in solvent, and moreover, a different series of amines was employed, including charged amines. The reviewer has also questioned whether Bronsted slopes that are different by 0.1 are meaningful. This is probably a fair comment when there are differences such as exist in the above comparison. The data in Table III and Figure 7 were however obtained for the same series of amines in the same solvent, and for such a comparison differences in β_{nuc} values of better than 0.05 are probably significant. Admittedly, if our comparison had involved only cations of similar reactivity, such as, for example 4,4′-$(Me_2N)_2T^+$ and 4-Me_2NT^+, the change in β_{nuc} could not be considered to be much outside of experimental error. However, for the entire series of triarylmethyl cations β_{nuc} changes by 0.4, well outside experimental uncertainty, and moreover, as shown in Figure 7, it does this in a regular manner. (b) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1973**, *95*, 1882–1889. (c) Ritchie, C. D.; VanVerth, J. E.; Virtanen, P. O. I. *Ibid.* **1982**, *104*, 3491–3497.

(31) Ritchie, C. D.; Minasz, R. J.; Kamego, A. A.; Sawada, M. *J. Am. Chem. Soc.* **1977**, *99*, 3747–3753.

(32) (a) The failure of the simple N_+ relationship has been noted previously in the aforementioned flash photolysis studies,[9,10] in the reaction of alcohols with phenethyl cations,[13c] and in the reaction of chloride with CF_3-substituted cations.[32b] Richard, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 4588–4595.

(33) (a) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461–3480. (b) Buncel, E.; Wilson, H. *J. Chem. Educ.* **1987**, *64*, 475–480.