Flash-Photolysis Generation and Reactivities of Triarylmethyl and Diarylmethyl Cations in Aqueous Solutions

Robert A. McClelland,[*,1] **V. M. Kanagasabapathy,**[1] **Narinder S. Banait,**[1] **and Steen Steenken**[*,2]

Contribution from the Department of Chemistry and Scarborough Campus, University of Toronto, Toronto, Ontario, Canada, M5S 1A1, and Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim, West Germany. Received November 8, 1988

Abstract: A series of 18 triarylmethyl cations and 10 diarylmethyl cations have been generated by nanosecond laser flash photolysis of cyanide, 4-cyanophenyl ether, and acetate precursors in acetonitrile/water (AN/W) solutions and first-order rate constants for their reaction with the solvent (k_s) have been directly measured following the decay in their optical density. In the standard solvent employed, 1:2 AN/W, the triarylmethyl cations which were studied had k_s values at 20 °C ranging from 10^1 s^{-1} (for the 4,4',4''-(MeO)$_3$-substituted ion) to 9×10^6 s^{-1} (4,4'-(CF$_3$)$_2$)), while diarylmethyl cations had k_s values ranging from 10^5 s^{-1} (4,4'-(MeO)$_2$) to 3×10^7 s^{-1} (4,4'-Me$_2$). The parent diphenylmethyl cation and its derivative with one 4-methyl substituent were too short-lived (<15 ns half-life) to be studied with our equipment in 1:2 AN/W, but they were observed in 100% acetonitrile and in this solvent containing small amounts of water. The effects on k_s of varying the amounts of acetonitrile were investigated for several cations. As water is added to 100% acetonitrile, k_s increases significantly, but at around 15% by volume water, there is a leveling and from that point to 100% water, k_s is almost unchanged, decreasing by about 20%. A plot of log k_s versus σ^+ constructed for the triarylmethyl cations shows significant deviations from linearity for the points for the π donors, in the direction which indicates that σ^+ is underestimating the stabilizing effect of these substituents for a fully formed cation. A plot versus σ^{C+}, a parameter obtained from the analysis of NMR spectra of solutions of carbocations, is reasonably linear. A two-parameter correlation indicates that polar and resonance interactions of substituents do not proceed in parallel along the reaction coordinate, the addition of water to cation resulting at the transition state in the loss of 73% of the equilibrium resonance effect but only a 33% loss of the polar effect. A rate-equilibrium plot (log k_s versus pK_R) was constructed which covers 23 pK_R units. A single line of slope 0.64 can be drawn to include the entire set of data for both triarylmethyl and diarylmethyl cations. From a small extrapolation the k_s value for the *tert*-butyl cation in water is obtained as $10^{10.5}$ s^{-1}.

There have been a number of direct kinetic investigations of the reactions in aqueous solutions of nucleophiles with carbocations.[3,4] These studies however have invariably involved highly stabilized cations, usually with half-lives in water alone greater than 100 ms. The reactivities of less stable cations of the type more commonly encountered as reactive intermediates have been examined with pulse radiolysis, but this has involved their generation in nonnucleophilic chlorocarbon solvents.[5] In solvolytic media, the common practice has been to measure reactivity ratios, as obtained from common-ion rate depressions,[6] or from product analyses of solvolyses carried out under conditions of competition with other nucleophiles.[7,8] Absolute reactivities have been estimated from these ratios, with the assumption that one of the nucleophiles reacts at the diffusion limit (the "azide-clock" approach).[8]

We have embarked upon a study of reactive carbocations generated under solvolytic conditions by pulse radiolysis[9,10] and flash photolysis.[11-13] The latter technique has been previously applied to some triarylmethyl cations[14-16] and vinyl cations[17] and would appear to be more generally applicable. We have described with the use of this approach a study of the reactivities of the parent triphenylmethyl cation, where the half-life in an aqueous acetonitrile solvent was 4 μs.[11] Conditions have now been found for the generation in the same solvent of a number of triarylmethyl and diarylmethyl cations, with half-lives ranging from 100 ms to 20 ns, the limit of our present laser equipment. In this paper we focus on the generation of these cations and consider the effects of cation structure and substituents on reactivities in aqueous acetonitrile solutions. Present research is examining other solvent mixtures, the reactions with various nucleophiles, as well as details of the photochemistry. A preliminary account of some experiments with diarylmethyl cations has been reported.[12]

Results and Discussion

Flash Photolysis. Photolysis experiments were carried out with a KrF excimer laser flash apparatus, which emits at 248 nm with an approximately 20-ns flash width, and with optical and conductivity detection systems to monitor transients. Table I provides a list of the cations and their precursors. As a shorthand notation we define T = triarylmethyl, D = diarylmethyl and OArCN = 4-cyanophenoxy. The standard solvent contained 1 volume of

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(2) Max-Planck-Institut.
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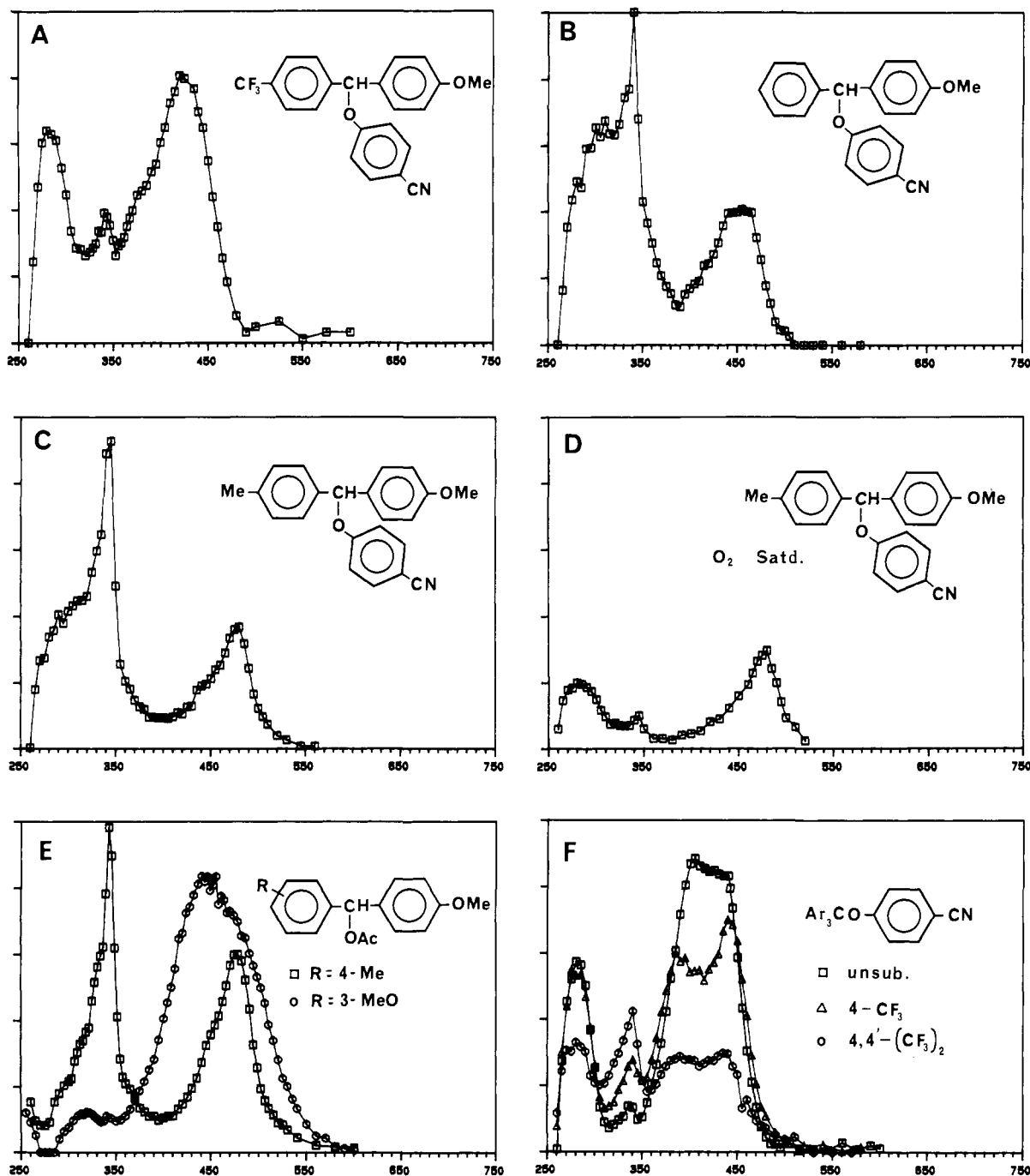
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Figure 1. Transient absorption spectra following 248-nm excitation of 4-cyanophenyl ethers (OAr) and acetates (OAc) in argon-saturated (except D) 1:2 acetonitrile/water containing 10^{-3} M OH⁻ (except E). The ordinate has units of OD/cm and the abscissa has units of nm.

acetonitrile mixed with 2 volumes of water (1:2 AN/W), the acetonitrile being required to dissolve the neutral precursor. Selected cations were studied in solutions of varying acetonitrile content in order to examine the effect of the cosolvent upon reactivity.

The photochemical reaction used to generate the cations was photoheterolysis, whereby electronic excitation results in heterolytic cleavage of a C–X bond. In terms of the final products, this reaction is a photosolvolysis, and in this sense there has been considerable investigation.[18] The standard leaving group was the 4-cyanophenoxide ion, as employed in our previous study[11] and

suggested by an early photosolvolysis investigation.[19] Acetates also undergo efficient photoheterolysis, but as will be discussed, there are some advantages with the 4-cyanophenoxides. Triarylmethyl cations bearing at least one methoxy substituent were generated from triarylacetonitrile precursors. The photochemistry of these systems, including investigations with flash photolysis, has been described in the literature.[15] We also prepared some analogous diarylacetonitriles, the 4,4'-dimethoxy- and 4-methoxy-substituted derivatives, but these failed to give any cation signal upon excitation.

Some representative transient absorption spectra are shown in Figure 1. In general two transients with different kinetic patterns were observed with each precursor, one absorbing in the 400–500-nm region, and a second at 320–350 nm. With the 4-

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Table I. Cations, Leaving Groups, Cation:Radical Ratios Expressed as Relative Optical Densities, and First-Order Rate Constants for Cation Decay at 20 °C[a]

cation[b]	leaving group[c]	OD(R⁺)/ OD(R·)[d]	k_s, s⁻¹	-pK_R
4,4',4'-(MeO)₃T⁺	CN[e]	>10	1.0×10^1	-0.82[f]
4,4'-(MeO)₂T⁺	CN[e]	>10	8.6×10^1	1.24[f]
4-Me, 4'-MeOT⁺	CN	g	5.7×10^2	
3-Me, 4'-MeOT⁺	CN	g	1.1×10^3	
4-MeOT⁺	CN[e]	>10	1.4×10^3	3.40[f]
3,4'-(MeO)₂T⁺	CN	g	1.8×10^3	
4,4',4''-Me₃T⁺	OArCN	h	3.6×10^3	3.56[f]
4,4'-Me₂T⁺	OArCN	h	1.1×10^4	4.71[f]
4-MeT⁺	OArCN	~10	3.7×10^4	5.41[f]
T⁺	OArCN[e]	8.0	1.5×10^5	6.63[f]
3-MeOT⁺	CN	>10	1.7×10^5	
4-ClT⁺	OArCN	g	1.8×10^5	
3-ClT⁺	OArCN	3.6	5.1×10^5	
3-CF₃T⁺	OArCN	g	6.8×10^5	
4-CF₃T⁺	OArCN[e]	3.0	1.1×10^6	
3,3'-Cl₂T⁺	OArCN	2.2	1.6×10^6	
3,3',3''-Cl₃T⁺	OArCN[e]	0.9	4.6×10^6	11.03[f]
4,4'-(CF₃)₂T⁺	OArCN	0.7	8.8×10^6	
4,4'-(Me₂N)₂D⁺	i	i	2.6×10^{-2j}	-5.61[k]
4,4'-(MeO)₂D⁺	OArCN,[e] OAc[e]	0.6,[l] 0.6[m]	1.3×10^5	5.71[f]
4-Me, 4'-MeOD⁺	OArCN, OAc	0.5,[l] 0.6,[m] 0.08[l,n]	9.1×10^5	8.32[o]
4-F, 4'-MeOD⁺	OArCN	0.3	1.7×10^6	
4-MeOD⁺	OArCN,[e] OAc[e]	0.4,[l] 0.6[m]	2.1×10^6	7.90[k]
4-Cl, 4'-MeOD⁺	OArCN	0.3	2.3×10^6	
3,4'-(MeO)₂D⁺	OAc[e]	>10, 0.3[n]	2.4×10^6	
3-Cl, 4'-MeOD⁺	OArCN	0.8	3.6×10^6	
3-CF₃, 4'-MeOD⁺	OArCN	1.3	4.6×10^6	
4-CF₃, 4'-MeOD⁺	OArCN[e]	2.0, 0.2[n]	5.8×10^6	
4,4'-Me₂D⁺	OArCN	~1,[p] 0.15[n]	3.2×10^7	10.4[f]
4-MeD⁺	OArCN	0.12[n]	~1.2×10^{8q}	11.6[k]
D⁺	OArCN	0.10[n]	~9×10^{8q}	13.3[f]

[a] Solvent is 1:2 acetonitrile/water by volume, unless otherwise noted. [b] T⁺ = triarylmethyl. D⁺ = diarylmethyl. [c] OArCN = 4-cyanophenoxide. OAc = acetate. [d] 5-15 ns after completion of flash. [e] Examined with both optical and conductivity detection. [f] Bethell, D.; Gold, V. *Carbonium Ions. An Introduction*; Academic Press: London, 1967; pp 76-77. [g] Not measured. [h] Not measured because of ground-state solvolysis. [i] Conventional spectroscopy, starting with an acid solution containing cation—see text. [j] In 100% water. [k] Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044-3051. Deno, N. C.; Schriesheim, A. *Ibid.* **1955**, *77*, 3051-3054. [l] For p-cyanophenyl ether. [m] For acetate. [n] In pure acetonitrile. [o] White, W. N.; Stout, C. A. *J. Org. Chem.* **1962**, *27*, 2915-2917. [p] Approximate since cation decays during time required to record optical density. [q] Estimated in 1:2 AN/W. See text.

cyanophenyl ethers, absorptions with maxima below 300 nm were also present (see in particular Figure 1, parts A and F). This absorption, which was permanent in basic solutions but was quenched by H⁺, can be assigned to the 4-cyanophenolate ion. The precursors absorb below 270 nm, and in this region negative signals were observed.

The transients with λ(max) at 400-500 nm were identified as the cations. This was verified by the close match of this portion of the spectrum with that of authentic cation, the latter being obtained by ionization of the alcohol in 40-95% H_2SO_4. The decay of the cation transient was first-order, with the rate constant unaffected by oxygen, but increased by added nucleophiles, particularly by azide which is an excellent scavenger of cations.[12] The transients which absorbed at the lower wavelength decayed with second-order kinetics in solutions which were saturated with argon and were unaffected by nucleophiles but quenched by oxygen (compare Figure 1, parts C and D). These observations suggest that this transient is a radical, and indeed these absorbances match closely the spectra of triarylmethyl and diarylmethyl radicals.[20,21]

The observation of radicals is not surprising since products derived from homolysis are frequently encountered in photosolvolysis studies.[18] Table I summarizes the relative amounts of

cation and radical formed with our precursors, expressing these as ratios of optical densities. A discussion of trends will not be attempted in this paper, since experiments are currently under way to convert the optical densities to quantum yields, which are more meaningful. Where both have been determined, the extinction coefficients of the cation and radical are within a factor of 2,[21] so that the OD ratios are approximately equal to the relative concentrations of the two transients. From the point of view of performing kinetic studies of the decay of the cation, the radical signal was well separated and thus did not interfere.

Corroboration was provided by the use of time-resolved conductivity detection. The observations characteristic of the presence of cations are a conductivity decrease in weakly basic solution and an increase in acid associated with the reaction of the cation with the solvent, neutralizing OH⁻ and releasing H⁺, respectively.[11,13] Several precursors were examined with this detection system, as indicated in Table I, and in all cases such changes were observed. Moreover, the conductivity traces were exponential with rate constants identical with those obtained optically at the λ(max) of the cation.

Formation of the cation was, with one exception, complete after the 20-ns laser pulse. Arguments have been presented that the species observed at that time is in the ground state.[12] With the diarylmethyl precursors, a fraction of the radical absorbance was formed in a delayed process after the flash, with the concentration increasing by as much as 40%; a small amount of delayed formation also occurred with one cation, 4,4'-(MeO)₂D⁺. The nature of these delayed processes is currently being investigated.[21] Delayed formation of transients was not observed in oxygen-saturated solutions nor, under any conditions, with the triarylmethyl precursors.

In addition to their relatively efficient photoheterolysis, the cyanophenyl ethers have three features which make them useful for these laser experiments: (i) a strong absorbance at the 248-nm excitation wavelength (extinction coefficient ~2×10^4 M⁻¹ cm⁻¹), so that dilute solutions of the precursors can be employed, (ii) a relatively slow ground-state solvolysis,[22] and (iii) a low tendency to undergo two-photon ionization. The sequential absorption of two photons is possible with the laser pulses employed in these experiments, and can give rise to electron ejection forming a radical cation. This did appear to occur with the diarylmethyl acetates with methoxy substituents, being particularly notable with higher laser doses where two-photon processes become more probable. The indicator that this was occurring was another transient absorbing in the region of the cation and interfering with its kinetics of decay. Anisole radical cations have been generated by independent routes and do absorb at 400-500 nm.[23] Radical cation formation was less of a problem with the cyanophenyl ethers, even those where methoxyphenyl groups were present. One feature of these ethers is that the cyanophenyl ring is the principal group absorbing at 248 nm, and the electron-withdrawing cyano group should decrease the tendency for electron loss.

One precursor which proved exceptional was (3,4'-dimethoxydiphenyl)methyl acetate, which gave a large cation signal with little radical (see the comparison with the 4-methyl-4'-methoxy analogue in Figure 1E). A *m*-methoxy substituent frequently, although not always, leads to higher yields of benzylic cations than a *p*-methoxy substituent upon photochemical generation.[24] We examined this system anticipating that the meta substituent would assist photoheterolysis, while the para substituent would kinetically stabilize the ground-state cation. One important observation is that the observed lifetime of the cation transient is that expected

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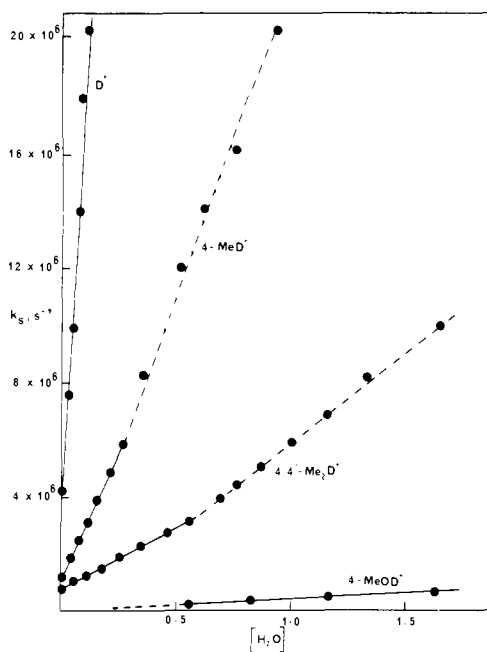(21) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* To be submitted.

(22) This became a problem with tris(4-methylphenyl)methyl 4-cyanophenyl ether and with bis(4-methylphenyl)phenylmethyl 4-cyanophenyl ether, which had half-lives in 1:2 AN/W of approximately 2 and 15 min, respectively.

(23) O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773-2779.

(24) (a) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 913-922. (b) Turro, N. J.; Wan, P. *J. Photochem.* **1985**, *28*, 93-102. (c) Cristol, S. J.; Aeling, E. O.; Heng, R. *J. Am. Chem. Soc.* **1987**, *109*, 830-838. (d) Foster, B.; Gaillard, B.; Mathur, N.; Pincock, A. L.; Pincock, J. A.; Sehmbey, C. *Can. J. Chem.* **1987**, *65*, 1599-1607.

Figure 2. First-order rate constants (s^{-1}, 20 °C) for the decay of diarylmethyl cations as a function of water concentration in acetonitrile.

for the ground state, this cation being slightly more reactive than 4-MeOD$^+$ due to the weak electron-withdrawing effect of a 3-MeO substituent. This acetate proved important since a cation signal and the kinetics of decay could be observed in water (for a 2 μM solution of the precursor). This experiment thus furnishes one measurement of a rate constant in the pure solvent H_2O.

Diarylmethyl cations, not surprisingly, were significantly more reactive than triarylmethyl cations. The bis(4-methylphenyl)-methyl cation proved to be the least stable example of this class which could be observed in 1:2 AN/W. This cation had a half-life of only 22 ns, so that a significant fraction decayed during the laser flash. The parent diphenylmethyl cation and the derivative with one 4-Me substituent were not detected, although, the appearance of the p-cyanophenolate peak upon photolysis was indicative that heterolysis had occurred. These two cations could, however, be seen in pure acetonitrile and in this solvent with small amounts of water present. Acetonitrile is apparently sufficiently polar to allow some photoheterolysis, although, as shown by the examples given in Table I, the relative amount of cation is small, particularly when compared to the amount which is formed in the more polar 1:2 AN/W. Dichloromethane as a solvent was examined with two systems, triphenylmethyl 4-cyanophenyl ether and bis(4-methoxyphenyl)methyl 4-cyanophenyl ether, but there was no cation signal in either case.

Rate Constants. The decay of the cation in general followed good exponential kinetics and the symbol k_s is defined for the first-order rate constant in a particular solvent. Values of k_s obtained for the entire set of cations in 1:2 AN/W are listed in Table I. Rate constants from replicate measurements, including those that were made with conductivity detection, agreed within ±3%.

Table I also lists pK_R values, where these are available from the literature. These constants refer to the equilibrium addition of water to cation. Where both k_s and K_R are known, the rate

$$R^+ + H_2O \underset{k_H}{\overset{k_s}{\rightleftharpoons}} ROH + H^+ \qquad (1)$$
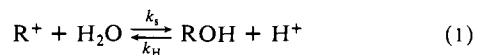
constant k_H can also be calculated as the ratio k_s/K_R. The values of k_s show little dependency on the acetonitrile content in aqueous solutions (next section). Thus there is little error introduced in using the k_s obtained in 1:2 AN/W in conjunction with a K_R for 100% water. For the less stable cations there are uncertainities in the pK_R values, since an extrapolation from moderately concentrated acids is required. In this context, the values that we are using are those based on the acidity-function method, which
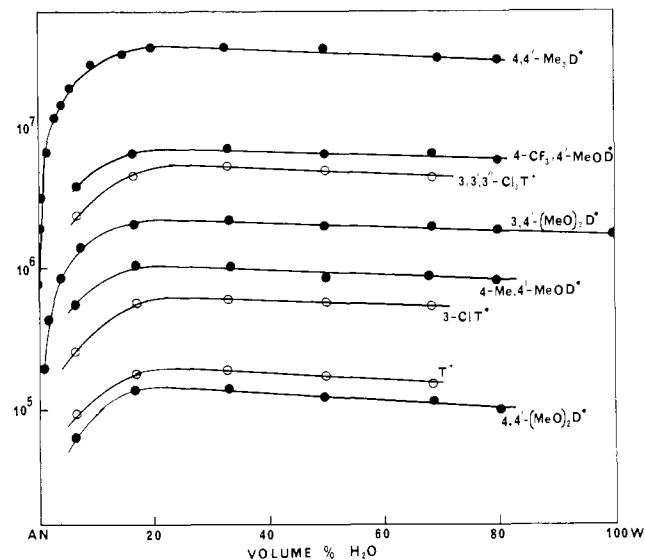

Figure 3. First-order rate constants (s^{-1}, 20 °C) for the decay of cations in aqueous acetonitrile.

Table II. Rate Constants for Cation Decay in Acetonitrile and in Acetonitrile Containing Small Amounts of Water (20 °C)

| cation	$k_s(AN)$,[a] s^{-1}	$k_{H_2O}(AN)$,[b] $M^{-1} s^{-1}$	[H_2O] range
D$^+$	4.0×10^6	1.3×10^7	0.0–0.15
4-MeD$^+$	1.3×10^6	1.7×10^7	0.0–0.30
4,4′-Me$_2$D$^+$	7.8×10^5	4.3×10^6	0.0–0.40

[a] First-order rate constants for decay of cations in 100% acetonitrile. [b] Slope of a plot of first-order rate constants for cation decay versus the molar concentration of water over the range given in fourth column.

gives better substituent correlations than the excess-acidity method.[25]

A "stable" diarylmethyl cation which appears not to have seen kinetic investigation is the bis[p-(dimethylamino)phenyl]methyl cation. A pK_R value of 5.6 has been reported for this cation. We therefore dissolved the corresponding alcohol in a dilute (2 mM) pH 5 acetate buffer, forming a solution containing the cation which is recognizable from its λ(max) of 600 nm. The pH of this solution was then adjusted to eight by the addition of a dilute borate buffer, and the decay of the cation was monitored by conventional spectroscopy to obtain the value of k_s listed in Table I.

Solvent Effects. Figures 2 and 3 summarize the variations which occur in the rate constants k_s as the acetonitrile/water ratio is varied. The three most reactive cations examined in this study, D$^+$, 4-MeD$^+$ and 4,4′-Me$_2$D$^+$, were found to decay with reasonable first-order kinetics in 100% acetonitrile. The reaction here would appear to involve formation of a nitrilium ion. Consistent with

$$CH_3C{\equiv}N + Ar_2\overset{+}{C}H \rightarrow CH_3C{\equiv}\overset{+}{N}CHAr_2 \qquad (2)$$
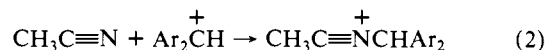
this interpretation, N-(diphenylmethyl)acetamide, the product of the reaction of water with the nitrilium ion, has been detected in photolysis experiments with the parent system in acetonitrile containing trace amounts of water.[21]

With those cations which underwent exponential decay in 100% acetonitrile, the addition of small amounts of water had a marked rate-accelerating effect, with the rate constants reasonably linear in water concentration up to 0.3–0.4 M. Table II summarizes this behavior, listing the first-order rate constants in 100% acetonitrile and the second-order rate constants for water obtained as the slopes of the linear regions. With both the parent cation and the 4-methyl derivative, a water concentration is reached where the decay becomes too fast to be measured with our apparatus. Rate constants for these two cations in 1:2 AN/W have been estimated with the assumption that their reactivity in that solvent relative to 4,4′-dimethyl derivative is the same as that given
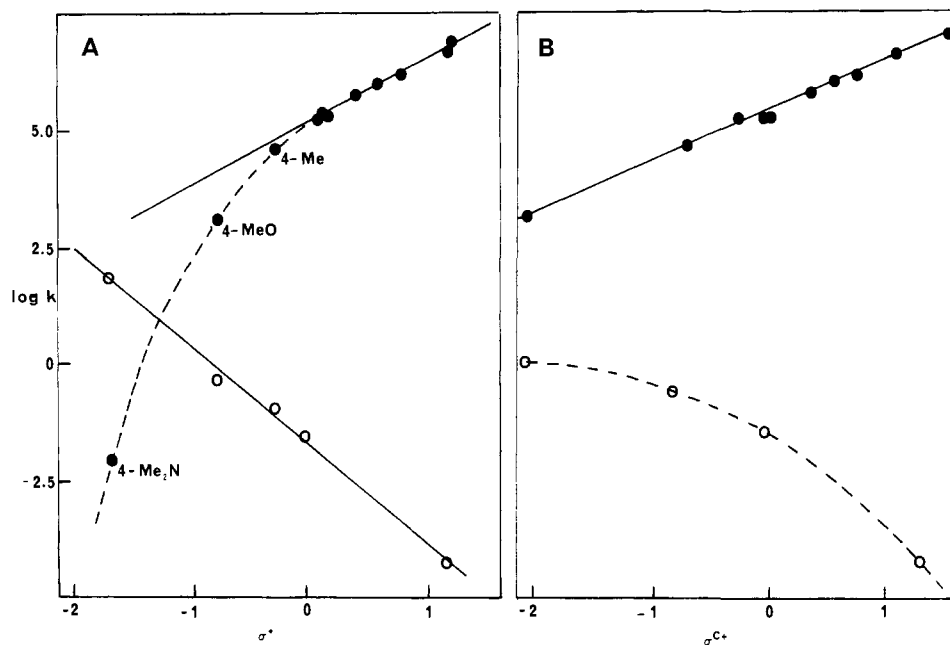
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(25) Johnson, C. D.; Stratton, B. *J. Org. Chem.* **1986**, *51*, 4100–4106.

Figure 4. Correlations with σ^+ and σ^{C+} of the rate constants k_s (●) and k_H (O) for triarylmethyl cations.

by the ratios of the second-order rate constants for water measured in the acetonitrile-rich solutions. This calculation predicts half-lives in the aqueous solvent of 0.8 and 5 ns for the parent and 4-methyl cation, respectively.

The other more stable cations did not decay with first-order kinetics in pure acetonitrile, and appreciable amounts of water had to be added before reasonable exponential behavior was obtained. One interpretation is that these cations do not react with acetonitrile or that the reaction of eq 2 is an equilibrium with cation still present. Cation does eventually disappear, even in 100% acetonitrile. This is likely due to a combination with the anion produced in the heterolysis, a process which is not first-order since the nucleophile is not in excess.

As shown in Figure 3, after the initial steep increase in k_s as water is added to 100% acetonitrile, there is a levelling, and from ~20% water to pure water only a small decrease is observed. Several factors could be behind this behavior, including solvation, changing water structure, and even the formation of water pools.[15] One comment which can be made is that in comparing reactivities of cations in solutions with a different water content it is clearly not valid to divide by the water molarity to obtain a second-order rate constant, as is often done.[26]

Substituent Effects. This section analyzes the effect of the substituents, focusing mainly on the triarylmethyl cations for which there is a considerable body of data including both electron-donating and electron-withdrawing substituents. As concluded previously in examining more limited data,[27] the effects of multiple substitution involving π donors at the para positions are nonadditive. Thus the first 4-methoxy substituent decreases the k_s value of a triarylmethyl cation by a factor of 107 with respect to the parent cation, but with the second 4-MeO, the further decrease is only 16, and with the third it is 8.6. This trend where the effect diminishes with each substitution is consistent with the idea of a "resonance saturation",[28] where, for example, the charge stabilization due to the first substituent results in a weaker interaction when the second is introduced. The three rings in triarylmethyl cations are not planar,[29] and this could also be a contributing

Table III. Parameters Obtained from a Yukawa–Tsuno-Type Treatment of Rate and Equilibrium Constant Data for Triarylmethyl and Arylethyl Cations

	triaryl-methyl	1-aryl-ethyl[a]		triaryl-methyl	1-aryl-ethyl[a]
$\rho_n(K_R)$	+4.0	+7.6	$\rho_n^{norm}(k_s)$	0.33	0.36
$\rho_r(K_R)$	+6.5	+9.3	$\rho_r^{norm}(k_s)$	0.73	0.56
$\rho_n(k_s)$	+1.3	+2.7	$\rho_n(k_H)$	-2.7	-4.9
$\rho_r(k_s)$	+4.7	+5.2	$\rho_r(k_H)$	-1.8	-4.1

[a] Taken from ref 8g.

factor. However, the effects of 4-MeO and 4-Me₂N substituents on diarylmethyl cations closely parallel those on triarylmethyl cations (see later), and the former should be more planar. Moreover, the effects of electron-withdrawing groups on the reactivities of triarylmethyl cations are more additive. Successive 3-Cl substitution for example results in increases in k_s by factors of 3.4, 3.1, and 2.9.

In examining single-parameter correlations, the σ^+ scale would seem most appropriate since that has been defined for reactions involving carbocations. As shown in Figure 4A, the correlation of k_s with this parameter is however poor,[30] even with the limitation of considering only monosubstituted donors. Moreover, the deviations are in the unusual direction of implying cation-stabilizing interactions for the π donors greater than those defined by the σ^+ values. The rate constant k_H on the other hand exhibits a much better correlation. The k_H reaction resembles more closely that employed to obtain σ^+ values, in that both involve an initial state with a saturated carbon and a transition state leading to cation. The k_s process in contrast starts at the ion and proceeds in the reverse direction to the same transition state. The implication is that σ^+ underestimates the stabilizing effect of the π donors for the cation but not for the transition state.

A similar conclusion about substituent effects on fully formed carbocations has been reached in the analysis of ¹³C NMR chemical shifts, for which π donors deviate significantly in plots versus σ^{+}.[31a] To overcome this a substituent constant σ^{C+} was established; this scale has more negative values for π donors so as to place the data for these substituents on the NMR correlations. As shown in Figure 4B this scale does provide a good

(26) See ref 7 and discussion therein.

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(30) (a) There is some uncertainty in the σ^+ value for 4-Me₂N,[30b] but regardless of its exact value the point will deviate widely. (b) Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Org. Chem.* **1978**, *43*, 4720–4745.

(31) (a) Brown, H. C.; Kelley, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956–6960. (b) There appears to be no σ^{C+} for 4-Me₂N. In order to fit 4-Me₂NT⁺ on the T⁺ line in Figure 7, this value must be -6.8.
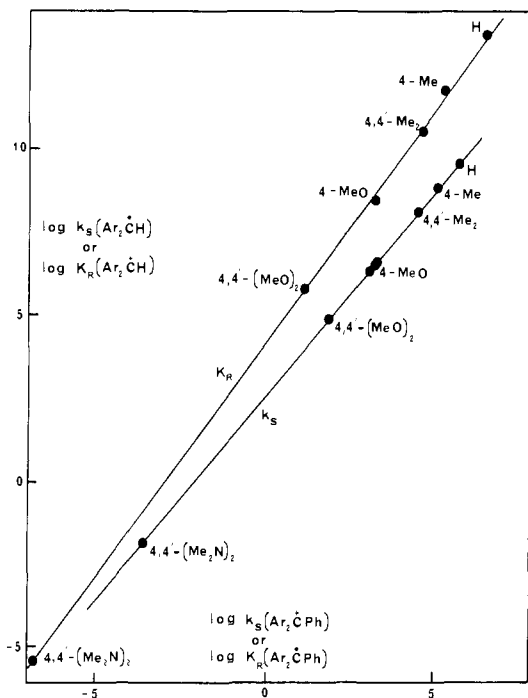
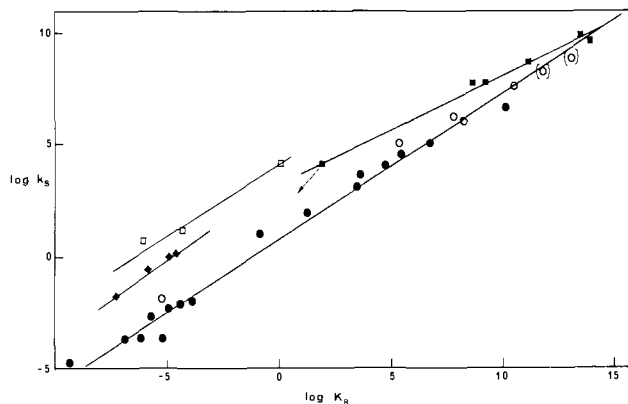**Figure 5.** Linear free energy correlations.

Figure 6. Rate–equilibrium correlations for addition of water to carbocations. Cation types and linear regression slopes of the solid lines are as follows. (●) Triarylmethyl and (○) diarylmethyl, 0.64; (◆) phenyltropylium, 0.58; (□) xanthylium ions unsubstituted at 9-position; (■) 1-arylethyl, 0.48. Values of k_s and K_R for phenyltropylium, xanthylium, and 4-Me$_2$N-substituted triarylmethyl ions are from ref 4, those for 1-arylethyl cations are from ref 8g (see also note 32), and those for other cations are from Table I. The bracketed open circles represent the parent diphenylmethyl ion and its 4-methyl derivative, for which values of k_s are estimated.

correlation for k_s,[31b] and now it is the rate constant k_H with the curved plot.

Jencks and co-workers[8g] analyzed data for 1-arylethyl cations through a two-parameter equation (3a), modified from that of Yukawa–Tsuno (eq 3b).[28b] The results of a similar treatment

$$\log (k/k_0) = \rho_n \sigma^n + \rho_r(\sigma^+ - \sigma^n) \qquad (3a)$$

$$\log (k/k_0) = \rho_n(\sigma^n + r^+(\sigma^+ - \sigma^n)) \qquad (3b)$$

applied to triarylmethyl cations are tabulated in Table III, alongside the arylethyl results. The parameter ρ_r is equivalent to $\rho_n r^+$ of the Yukawa–Tsuno treatment, where r^+ was intended to range from 0 to 1 and thus allow for substituent interactions intermediate between σ^+ and σ^n. The analyses of k_s and K_R values for the triarylmethyl cations however require that the r^+ values be greater than 1 since $\rho_r > \rho_n$. This is the same phenomenon as just discussed, namely that π donors interact more strongly than their π^+ values indicate.

The quantities ρ^{norm} listed in Table III are defined as $\rho(k)/\rho$-(K).[8g] These provide a measure of the fraction of the overall change which has occurred at the transition state. These normalized parameters indicate that on reacting a triarylmethyl cation with water 73% of the resonance interaction between the substituent and the charge has disappeared by the time the transition state has been reached but that only 33% of the polar interaction has disappeared. The reaction in the reverse direction has the opposite behavior, conversion of alcohol to cation developing 67% of the polar interaction at the transition state, but only 27% of the resonance interaction. This failure of the resonance and polar effects to parallel one another as the reaction proceeds is also seen with 1-arylethyl cations,[8g] for which the data were obtained indirectly.[32] A simple model[8g] is that, because of the partial bond to the nucleophile, in the transition state the fractional positive

charge which still resides on Ar$_3$C is localized on the central carbon, attenuating the resonance interaction more than the polar interaction. One consequence of this behavior is that a substituent scale such as σ^+ which is based upon a reaction in which cation is forming must underestimate the full resonance-stabilizing effect of strong π donors such as 4-MeO and 4-Me$_2$N.

Substituent effects for diarylmethyl cations will not be considered in detail, since there are no data for cations containing only electron-withdrawing groups. As shown in Figure 5, the patterns appear very similar to those found with triarylmethyl cations. This figure shows the correlations of log k_s and log K_R, plotting data for one cation-type versus the other. Good linearity is observed even when π donors and multiple substitutions are included. The diarylmethyl cations are somewhat more sensitive to substituent change, as shown by the slopes in Figure 5 being greater than one (1.37 for K_R, 1.25 for k_s). Including the arylethyl cations, the sensitivity order is ArCHCH$_3^+$ > Ar$_2$CH$^+$ > Ar$_3$C$^+$, the effects of substituents decreasing as the number of aromatic rings increases, and there is a greater inherent delocalization of charge.

Rate-Equilibrium Correlation. The relationship between log k_s and pK_R has been considered in the past,[4,27,33] and with kinetic data for more reactive triarylmethyl and diarylmethyl cations now available, a plot covering 23 pK_R units can be constructed (Figure 6). From their original version based upon relatively stable triarylmethyl cations, Taft and co-workers concluded that the data were best accommodated by separation into families—at that time, two families, one for 4-Me$_2$N-substituted ions and a second for 4-MeO-substituted ions.[27] Such families do exist; there are clearly separate correlations for cations of quite different structure, particularly xanthylium and tropylium ions. However, there is a reasonably linear correlation encompassing the entire set of triarylmethyl and diarylmethyl cations, with a small amount of scatter.[34] A single relationship was suggested both by Arnett and Hofelich[33] and by Ritchie.[4] The implication is that despite

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(32) The k_s values were measured through competition between solvent and added nucleophile (mainly azide), with the assumption of a rate constant of 5×10^9 M^{-1} s^{-1} for the nucleophile; k_H values were based upon ROH to ROCH$_2$CF$_3$ exchange in trifluoroethanol:water, and K_R values were calculated as their ratio.[8g] We suspect that the k_s value for the cation 4-NMe$_2$C$_6$H$_4$CHCH$_3^+$ has been overestimated, a possibility admitted by Jencks and co-workers.[8g] This value, 2×10^3 s^{-1}, was based upon competition with a thiolate nucleophile, and in our experience[11-13] cations with this reactivity toward water do not react at the diffusion limit with nucleophiles. The 4-Me$_2$N substituent has a major influence on the two parameter substituent treatment, and if the k_s value for this cation were lower, $\rho_r^{norm}(k_s)$ would be higher. For the log k_s-pK_R correlation, a lower k_s moves the point for 4-NMe$_2$C$_6$H$_4$CHCH$_3^+$ in the direction indicated by the arrow in Figure 6.

(33) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895.

(34) (a) The scatter may mask a gentle downward curve, possibly two curves, one for T$^+$ and a second for D$^+$. A downward curve is consistent with the Hammond postulate[34b,c] and Marcus theory[34d–f], but considering the range of cation stabilities, the overall change in the slope of log k_s versus pK_R is small, and a linear relationship provides as good a fit. (b) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338. (c) Leffler, J. E.; Grunwald, E. In *Rates and Equilibria of Organic Reactions*; Wiley, New York, 1963; p 26. (d) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21–31; *J. Phys. Chem.* **1968**, *72*, 891–899. (e) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87–157. (f) For a criticism of the use of the Marcus equation for cation–nucleophile combinations, see: Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 279–284.
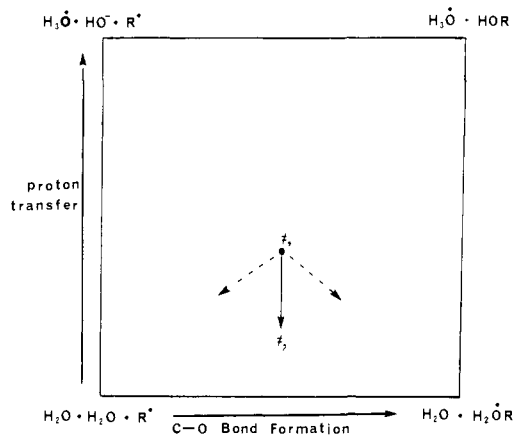
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Figure 7. Reaction-coordinate diagram for the addition of water to carbocations, with catalysis by a second water molecule. The x and y axis represent C–O bond formation and proton transfer, respectively. The point $\ddagger_1$ is a transition state for a relatively stable cation, and the dashed arrows represent the effects parallel to and perpendicular to the reaction coordinate for a change to a less stable cation. The solid arrow is a net change in transition state position to $\ddagger_2$ resulting in no effect on the amount of C–O bond making.

a change in cation stability from Crystal Violet $(4,4',4''\text{-}(Me_2N)_3T^+)$ to diphenylmethyl, there is little change in the apparent position of the transition state, at least as revealed in this rate–equilibrium relationship.

The addition of water to carbocations appears to be catalyzed by a second water acting as a base,[4,8h,9,10] and the reaction coordinate diagram is therefore drawn[8h] as in Figure 7 with both C–O bond formation and proton transfer in the transition state. Starting at the point indicated by $\ddagger_1$, a change in substituent which produces a less stable cation results in a tendency for the transition state to move toward the cation corner in the direction along the reaction coordinate and toward the protonated alcohol in the direction perpendicular to the reaction coordinate. If these two effects are of a similar magnitude, the effect will be a net movement toward the bottom edge of Figure 7 (toward the transition state $\ddagger_2$), in a direction parallel to the sides. In such a case there would be little change in the amount of C–O bond formation at the transition state, and the slope of a plot of log k_s versus pK_R would remain relatively constant. The parameter which does change is the amount of proton transfer, the more reactive cation having less proton transfer at the transition state. The Brønsted β values for general-base catalysis of water addition do change precisely in this direction.[8h,35]

***tert*-Butyl Cation.** Arnett and Hofelich estimated a pK_R of -14.7 for this cation from a correlation of heats of reaction with pK_R;[33] a second estimate of -15.5 has recently been reported from electrochemical data.[36] Arnett and Hofelich then considered a plot of log k_s versus pK_R and performed a long extrapolation to estimate k_s for the *tert*-butyl cation. The value thus obtained, 10^{13} s^{-1}, suggested that the free ion is unlikely to exist in water. The more extensive log k_s–pK_R correlation of the present paper has a smaller slope than that used by Arnett and Hofelich, and required a less lengthy extrapolation. The k_s which results from using $pK_R = -15$ is $10^{10.5}$ s^{-1}. This number is more consistent with the value of 10^{10} s^{-1} estimated from a correlation of log k_s values

with σ^+ constants.[37] There is also a third estimate of a similar order of magnitude, based upon a rate constant of 4×10^{-6} M^{-1} s^{-1} at 25 °C for H$^+$-catalyzed oxygen exchange in *tert*-butyl alcohol.[38] With the assumption that this rate constant represents formation of free cation, it can be equated with the constant k_H of eq 1. Then, taking the value of pK_R to be -15, a value of k_s of 4×10^9 s^{-1} is calculated. We conclude therefore that the *tert*-butyl cation reacts in water with $k_s \approx 10^{10}$ s^{-1}, and thus in spite of its high reactivity, it could have a finite lifetime.

Experimental Section

Flash Photolysis. Descriptions of the procedure and equipment have been presented.[11] In summary, solutions contained spectroscopic-grade acetonitrile and water from a Millipore-Q system mixed in the appropriate volume ratios. These were saturated with the appropriate gas, and shortly before the irradiation experiments aliquots of a solution of the precursor in acetonitrile ($\sim$0.1 M) were added to give a concentration of 50–200 μM and OD/cm at 248 nm of $\sim$1. Photolyses were carried out with $\sim$20-ns pulses of 245-nm light (KrF) from a Lambda Physik EMG 103 MSC excimer laser.

Triarylacetonitriles and diarylacetonitriles were prepared by melting mercury(II) cyanide with the corresponding triarylmethyl and diarylmethyl chloride, as described in the literature.[39] Diarylmethyl acetates were prepared from the alcohol, acetic anhydride, and pyridine following a literature method.[40] The procedure (with typical quantities) for the 4-cyanophenyl ethers, modified from the literature,[19] was as follows. Under nitrogen 2.1 g of 35% KH in a mineral oil suspension (18 mmol of KH) was transferred into a dry flask and the mineral oil was removed by washing with dry pentane. The latter was then removed by passing a stream of dry nitrogen through the flask. Tetrahydrofuran (THF, 20 mL), freshly distilled from Na, was added, and at 0 °C, 4-cyanophenol (20 mmol) in 30 mL of dry THF was added with vigorous stirring. After 1 h, the appropriate triarylmethyl or diarylmethyl chloride (18 mmol) dissolved in 35 mL of THF was added and the mixture was gently refluxed for 1–3 days. After cooling, diethyl ether (200 mL) was added; residual solid was removed by filtration, and the solution was washed with cold 5% KOH followed by water. After drying of the solution over anhydrous magnesium sulfate, volatiles were removed with a rotary evaporator. Purification involved recrystallization from hexane/benzene or column chromatography on alumina with progressive elution with diethyl ether or dichloromethane in hexanes. All compounds had ^{1}H NMR spectra, ir spectra, and elemental analyses consistent with their structure.

Triarylmethyl chlorides containing 4-methoxy substituents were prepared from the alcohol and acetyl chloride.[39] Other triarylmethyl chlorides and diarylmethyl chlorides were obtained by refluxing for 1–3 days in dry hexane a mixture of the alcohol and excess thionyl chloride. In the latter synthesis, the material obtained after removal of the solvent and excess thionyl chloride was used directly in the next step. Alcohols were obtained by using standard procedures of LiAlH$_4$ reduction of the appropriate benzophenone or by reaction of an arylmagnesium bromide with a substituted benzaldehyde, benzophenone, methyl benzoate, or diethyl carbonate. Bis[4-(N,N-dimethylamino)phenyl]methanol was prepared by following a literature procedure[41] and purified by progressive elution with ethyl acetate in toluene on alumina.

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