

Electrophilic Reactivity of the Triphenylmethyl Carbocation in Aqueous Solutions

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Abstract: The triphenylmethyl (trityl) carbocation has been generated as a transient intermediate by laser flash photolysis of 1:2 (v/v) acetonitrile:water solutions of trityl acetate and trityl 4-cyanophenyl ether. Identification of the transient as the free carbocation in the ground state was based on its characteristic absorption spectrum and upon conductivity changes. Rate constants have been measured for the reaction of the cation in this solvent with a series of ionic and neutral nucleophiles. The solvent rate constant at 20 °C is $1.5 \times 10^5 \text{ s}^{-1}$. Azide ion reacts at $4.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; the directly measured azide:water ratio is compared to literature values determined by product analysis. Chloride ion reacts at $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; with bromide the equilibrium addition can be observed with $k(\text{comb}) = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{ion})$ for $\text{Ph}_3\text{CBr} = 8 \times 10^5 \text{ s}^{-1}$. Rate constants do not adhere to the N_+ relationship. This predicts a slope of unity in a plot of $\log k(\text{Ph}_3\text{C}^+) \text{ vs. } N_+$, with the better nucleophiles reacting at the 10^{10} encounter-controlled limit. Azide is the only nucleophile of those studied to approach this. Sulfite and thiolate ions, which are better N_+ nucleophiles, react at $2\text{--}3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, while amines react in the $10^6\text{--}10^7 \text{ M}^{-1} \text{ s}^{-1}$ range. The plot vs. N_+ has a slope of 0.3–0.4. One explanation is that rate constants for the better nucleophiles do level, but this occurs considerably below the 10^{10} limit. Alternatively, the less than unit slope is real and this more reactive cation, in contrast to more stable analogues, is exhibiting selectivity.

There is now a considerable body of data of rate constants directly measured under solvolytic conditions for the reactions of nucleophiles with relatively stable organic cations. Ritchie has proposed a general adherence to eq 1,³ where k is the second-order

$$\log(k/k_0) = N_+ \quad (1)$$

rate constant for the nucleophile–cation combination, k_0 is the rate constant for a reference nucleophile, and N_+ is a nucleophilicity parameter dependent only upon the nature of the nucleophile and reaction conditions. Equation 1 implies that relative nucleophilic reactivity is independent of the structure of the electrophile or, in other words, that selectivity does not correlate with reactivity as required by the reactivity–selectivity principle. To account for this, explanations have been advanced invoking the importance of ion desolvation.^{4,5} The equation has also been applied to reactions of carbonyl and arene electrophiles,^{6,7} although this has been questioned.^{8,9} Proposals have also been put forward that an electrophile parameter should be included,^{9–11} as in the Swain–Scott equation.¹² Ritchie, however, has argued that this is unnecessary, at least for cation electrophiles.¹³

The Ritchie relationship has been established with a number of cations of varying reactivity and structure, principally triarylmethyl carbocations, tropylium ions, and aryl diazonium ions.¹⁴ In general, however, studies have been limited to cations whose rate constant for reaction with solvent is less than $10\text{--}100 \text{ s}^{-1}$. Thus, for example, triarylmethyl carbocations studied have ranged from the tris(*p*-dimethylamino)phenyl)methyl cation (Crystal Violet) with $k(\text{H}_2\text{O})^{10,15,16} \approx 10^{-5} \text{ s}^{-1}$ to the tris(*p*-methoxy-

phenyl)methyl cation (An_3C^+) with $k(\text{H}_2\text{O})^{10,17-19} \approx 10^1 \text{ s}^{-1}$. Solvent rate constants are available for more reactive cations,²⁰ but these are based upon measurements in strong acids where rates with other nucleophiles cannot be obtained. For the more reactive systems relative reactivities are available, determined from the common ion rate depression observed on rates of RX solvolysis in the presence of X^- ,²¹ and, perhaps more commonly, from the analysis of products of $\text{S}_{\text{N}}1$ reactions of RX in the presence of two nucleophiles (the competition method). Azide:water ratios have been the most extensively investigated in this regard^{22–24} (eq 2, where both rate constants are in $\text{M}^{-1} \text{ s}^{-1}$ units). By using the

$$k(\text{N}_3^-)/k(\text{H}_2\text{O}) = (\% \text{RN}_3)/[\text{H}_2\text{O}]/((\% \text{ROH})[\text{N}_3^-]) \quad (2)$$

solvolysis rate as a measure of R^+ reactivity, apparent adherence to the reactivity–selectivity principle has been observed by these authors.^{22–24} It is now believed, however, that this arises because the reaction with azide has become diffusion limited with the R^+ involved, so that changes in selectivity merely reflect changes in $k(\text{H}_2\text{O})$.^{24–26} Richard and Jencks have in fact taken $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as the azide rate constant and through eq 2 calculated $k(\text{H}_2\text{O})$ (and other rate constants) for a series of phenylethyl cations.^{26,27}

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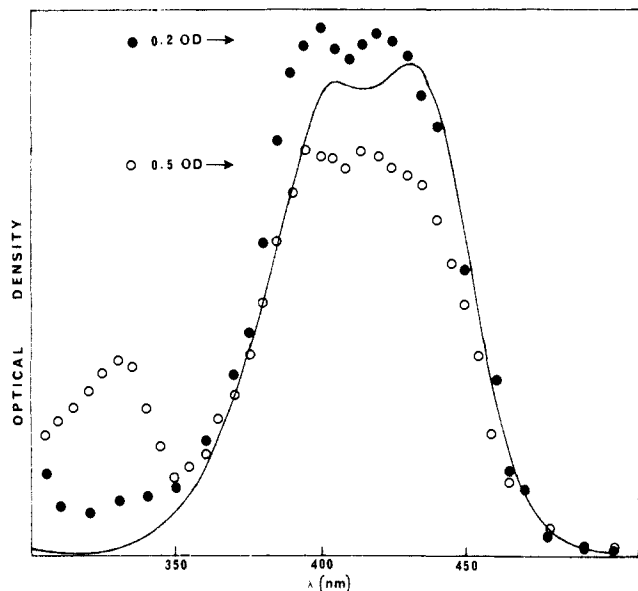


Figure 1. Transient absorption spectra from photolysis of 2×10^{-5} M trityl 4-cyanophenyl ether (●) and 1×10^{-4} M trityl acetate (○) in 1:2 AN:H₂O. Each point is the average optical density in the window 0.5–1.0 μs following the flash. The solid line is the spectrum of the trityl cation in 80% H₂SO₄. The extinction coefficient at 430 nm is 3.9×10^4 M⁻¹ cm⁻¹.

The previously mentioned rate limit has been imposed by the necessity of mixing two solutions. We feel that it is important to measure directly rate constants for more reactive cations, and we believe that this can be accomplished through the technique of flash photolysis.²⁸ Photosolvolyses and photohydrations are quite common and appear to proceed by way of carbocation intermediates.²⁹ With flash photolysis, transient vinyl cations³⁰ and triarylmethyl cations^{31–34} have now been observed from appropriate precursors, demonstrating that the technique can work to generate reactive electrophiles.³⁵ One cation which has been observed in this way is the parent triphenylmethyl (trityl, Ph₃C⁺) cation.³³ This is an important ion since it has been extensively studied by the conventional solvolyses methods, and direct measurements would bridge the gap to the more stable cations such as An₃C⁺.²⁴ The previous flash photolysis investigation of Ph₃C⁺ had used 3.5 M NaClO₄ in the solvent (1:1 EtOH:H₂O),³³ the salt presumably being necessary to slow the hydration sufficiently to permit observation of the cation. In this work we have used nanosecond laser photolysis which allows study in salt-free aqueous

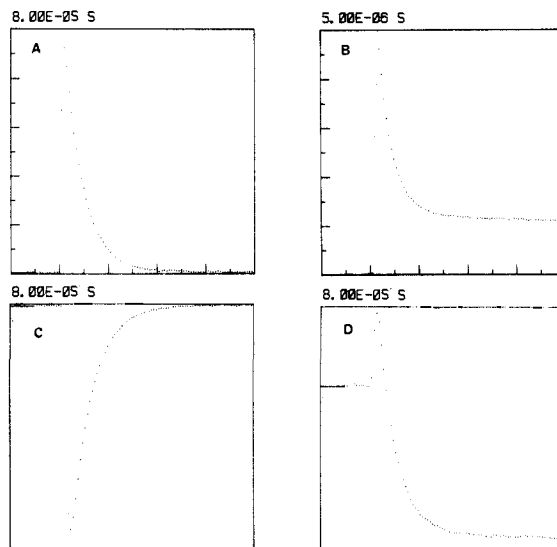


Figure 2. 420-nm absorbance changes (A, B) and conductivity changes (C, D) following 248-nm irradiation of 2×10^{-5} M trityl 4-cyanophenyl ether in 1:2 acetonitrile:water containing 10^{-4} M HCl (A, C), 10^{-4} M NaOH (D), and 0.5 M KBr (B). The time indicated at the top left is that for the entire trace including the preflash portion. In experiment B a slower decrease follows that shown, returning the signal to the base line.

solutions,³⁶ and we report rate constants for a series of nucleophiles. The Ph₃C⁺ cation turns out to be 10^4 more reactive toward water than An₃C⁺ so that a 10^{10} range of solvent reactivities has now been covered in studies involving triarylmethyl carbocations.

Results and Discussion

Generation of Ph₃C⁺. Experiments involved 248-nm laser excitation and employed two precursors, trityl acetate and trityl 4-cyanophenyl ether. The former was the compound used previously.³³ The latter was suggested by steady state photolysis experiments which showed production of Ph₃COH from this compound with a quantum efficiency of 15%.³⁷ A solvent of 1:2 acetonitrile (AN):H₂O was used, neither precursor being sufficiently soluble in pure water to generate any cation signal.

Large absorbances are produced upon irradiation of both compounds, and spectra for the signal 0.5–1 μs after the flash are shown in Figure 1. Although there is possibly a slight solvent effect, these are in general the same as the spectrum of authentic Ph₃C⁺ obtained in 80% H₂SO₄. Absorbance in the 300–350-nm range not associated with Ph₃C⁺ is also observed in the photolysis, particularly with the acetate. This signal decays at a slower rate than that due to Ph₃C⁺ and appears not to follow exponential kinetics. This possibly corresponds to triphenylmethyl radical, which does absorb in this region.³⁸ Photolyses of RX frequently result in mixtures of heterolysis and homolysis type products,^{29a,c} and in fact a small amount of 9-phenylfluorene is formed from the cyanophenyl ether, possibly arising from a radical route.^{37a}

The trityl signal has formed upon completion of the 20-ns laser flash. Its return to zero optical density (Figure 2A) obeys excellent first-order kinetics. With both precursors the rate constants for the decay are identical, evidence that it is ground state free trityl

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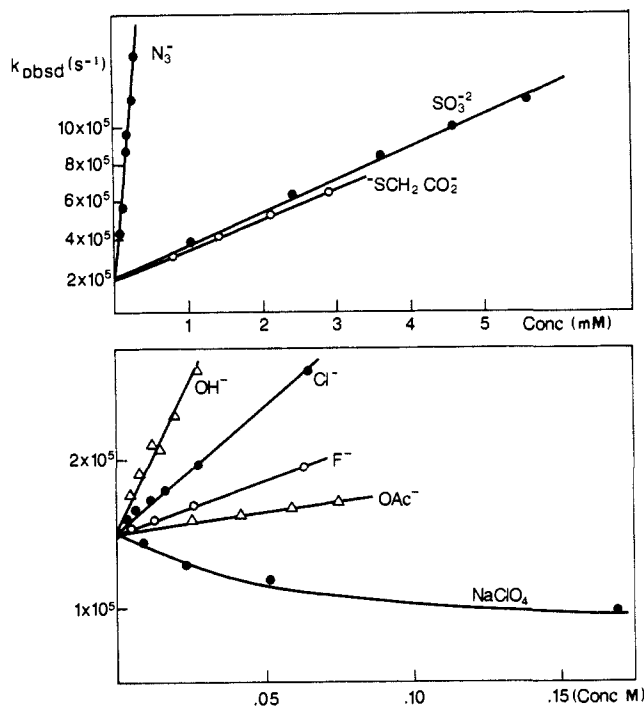


Figure 3. First-order rate constants for Ph_3C^+ decay in the presence of anionic nucleophiles.

cation that is involved and that essentially no recombination with the leaving group is occurring. The cation is presumably formed initially as an ion pair, but judging from rate constants obtained recently for ion pair processes, this will dissociate to free ions (or recombine) within the 20-ns flash time.^{35b}

Experiments with conductivity detection were also performed in order to corroborate the cation formation. These result in signals changing exponentially at rates identical with those with optical detection. Traces for the 4-cyanophenyl ether are shown in Figure 2. In acid solution, irradiation results in a rapid conductivity decrease (Figure 2C), in base, an increase (Figure 2D). The latter is explained by the photolysis releasing the two ions Ph_3C^+ and ArO^- . In acid the phenoxide ion reacts with H^+ (rate constant greater than $10^{10} \text{ M}^{-1} \text{ s}^{-1}$),³⁹ so that irradiation is resulting in the replacement of H^+ by the less mobile Ph_3C^+ . In acid the conductivity then rises, returning to its original level as the cation hydration releases back the proton. In base the signal decays, but now to a level significantly below the original. Neutralization of the cation consumes hydroxide,⁴⁰ so that a net reaction in base has occurred, with OH^- being replaced by the more poorly conducting ArO^- .

Reactions with Nucleophiles. For detailed kinetic studies the cyanophenyl ether precursor was chosen, since this gives less of the 300–350-nm product upon photolysis. First-order rate constants for Ph_3C^+ decay were measured at 420 nm in the presence of a number of anionic and neutral nucleophiles; in most cases 10^{-3} M NaOH was used in order to suppress protonation. The actual rate constants are available as supplementary material; plots of $k(\text{obsd})$ vs. nucleophile concentration are shown in Figure 3 for some selected anionic nucleophiles. Second-order rate constants were evaluated as the slopes of such plots or from the quantity $(k - k_0)/[\text{nucleophile}]$ where k and k_0 are rate constants in the presence and absence of nucleophile respectively. No attempt was made to keep the ionic strength constant. For the anionic nucleophiles where ionic strength necessarily changes with concentration, there is a slight curvature in the k vs. nucleophile plots. In this case the second-order rate constant has been extrapolated to zero ionic strength. Table I summarizes the nucleophiles studied

Table I. Rate Constants for the Reactions of Nucleophiles with the Trityl Cation (20 °C, $\text{M}^{-1} \text{ s}^{-1}$, 1:2 Acetonitrile:Water, Unless Specified Otherwise)

	nucleophile	k
(sol)	H_2O	$1.50 (\pm 0.05) \times 10^5$ ^e
(a)	OH^-	$5.2 (\pm 0.4) \times 10^6$
(b)	$\text{CF}_3\text{CH}_2\text{O}^-$	$6.5 (\pm 1.0) \times 10^6$
(c)	N_3^-	$4.1 (\pm 0.1) \times 10^9$
(d)	SO_3^{2-}	$2.4 (\pm 0.2) \times 10^8$
(e)	CN^-	$5.5 (\pm 0.5) \times 10^6$
(f)	CH_3CO_2^-	$4 (\pm 1) \times 10^5$
(g)	F^-	$8.6 (\pm 0.6) \times 10^5$
(h)	Cl^-	$2.2 (\pm 0.5) \times 10^6$
(i)	Br^- ^a	5×10^6
(j)	$^- \text{SCH}_2\text{CO}_2^-$	$2.2 (\pm 0.3) \times 10^8$
(k)	$\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-$	$3.0 (\pm 0.2) \times 10^8$
(l)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	$1.3 (\pm 0.1) \times 10^7$
(m)	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{NH}_2$	$9.6 (\pm 0.2) \times 10^6$
(n)	$\text{CF}_3\text{CH}_2\text{NH}_2$ ^b	$2.7 (\pm 0.5) \times 10^6$
(o)	NH_2NH_2 ^c	$2.1 (\pm 0.1) \times 10^7$
(p)	NH_2OH ^b	$1.3 (\pm 0.1) \times 10^7$
(q)	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	$1.9 (\pm 0.1) \times 10^7$
(r)	morpholine	$9.0 (\pm 0.7) \times 10^6$
(s)	piperidine	$1.04 (\pm 0.06) \times 10^7$
(t)	imidazole	$2.8 (\pm 0.2) \times 10^6$
(u)	Dabco ^d	$7.7 (\pm 0.4) \times 10^5$

^a0.1–0.3 M KBr. ^bIn 0.05 M NaCl. ^cIn 0.02 M Na_2SO_4 . ^dDiazabicyclo[2.2.2]octane. ^e s^{-1} units.

and lists their rate constants. The following nucleophiles merit some special comment.

Azide. The azide:water rate ratio calculated from Table I is 1.0×10^6 , expressing the water rate constant in $\text{M}^{-1} \text{ s}^{-1}$ (with $[\text{H}_2\text{O}] = 36 \text{ M}$ in the mixed solvent). This number has been determined with the competition method in acetone:water mixtures by several groups with several Ph_3CX precursors.^{41,42} A considerable range of leaving group dependent values (4×10^2 – 3×10^5)²⁴ has been obtained. This variation is somewhat surprising since, as demonstrated by these direct measurements, the trityl cation is sufficiently long lived that free cations should form in the solvolysis and the rates should be independent of leaving group. One experimental problem which has been noted is poor mixing during the rapid Ph_3CX solvolysis, resulting in a local depletion of azide and thus an artificially low experimental number.^{42b} In this regard the directly measured value is not that different, particularly considering that a different solvent mixture is involved, from ratios obtained with Ph_3CSCN (3.1×10^5)⁴¹ and Ph_3CF (2.4×10^5 and 2.8×10^5),⁴¹ trityl derivatives where the mixing problem may be less severe since the solvolysis proceeds at a reasonably slow rate.⁴¹

The azide rate itself, $4.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, is of some interest since this approaches the 5×10^9 value employed by Richard and Jencks in their calculations of phenethyl cation reactivity.²⁶ Whether the directly measured number is indicating that the trityl–azide combination is fully diffusion limited is debatable, but it certainly cannot be far off. Values which have recently been obtained⁴³ by flash photolysis for the 9-phenylxanthylum ion [$k(\text{H}_2\text{O}) = 23 \text{ s}^{-1}$, $k(\text{N}_3^-) = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and the parent xanthylum ion [$k(\text{H}_2\text{O}) = 2.2 \times 10^4 \text{ s}^{-1}$, $k(\text{N}_3^-) = 5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$] attest to the levelling of the azide rate constant around 5×10^9 as the diffusion limit is being reached. It would appear therefore that azide was an excellent choice as a “clock”²⁶ to estimate short-lived cation reactivities. It is particularly interesting in this regard that the sulfite ion and thiol anions, also excellent N_3^- nucleophiles, react with Ph_3C^+ more than an order of magnitude more slowly.

Chloride. With An_3C^+ , the addition to the solution of alkali halides or sodium perchlorate simply retards the rate through a salt effect.¹⁹ As seen in Figure 3, perchlorate has a similar effect

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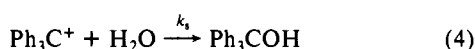
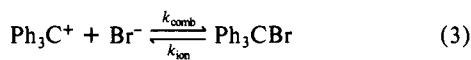
Table II. Rate and Equilibrium Constants for the Addition of Anions to the Trityl Cation (1:2 Acetonitrile:Water)

nuc.	$k_{\text{comb}}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{ion}}, \text{s}^{-1}$	$K_{\text{eq}}, \text{M}^{-1}$
Cl ⁻	2.2×10^6 ^a	3×10^4 ^b	7×10^1
F ⁻	8.6×10^5 ^a	8×10^{-3} ^c	1×10^8
OAc ⁻	4×10^5 ^a	7×10^{-3} ^d	6×10^7
Br ⁻	5×10^6 ^a	8×10^5 ^a	6×10^0

^aThis work. ^b21.9 s⁻¹ in 80% acetone:H₂O, 25 °C, ref 46. ^c7.7 × 10⁻⁴ s⁻¹ in 50% acetone:H₂O, 25 °C, ref 41 and 47. ^d7.2 × 10⁻⁴ s⁻¹ in 50% acetone:H₂O, 25 °C, ref 41 and 47.

on Ph₃C⁺, but with this cation chloride can now act as a nucleophile⁴⁴ and the rate increases. This is a direct observation of "external ion return", the phenomenon believed to be responsible for the rate depression of RX solvolysis in the presence of X⁻.^{21,45} Ph₃CCl solvolysis in 85% acetone at -34.5 °C is slowed 3.5-fold by 0.01 M chloride.⁴¹ This translates into a $k(\text{Cl}^-)/k(\text{H}_2\text{O})$ ratio of $2.5 \times 10^2 \text{M}^{-1}$. The number directly measured in this work is 14 M⁻¹. The difference in the two values is not surprising considering the difference in temperature and the fact that there is more water in the solvent in the present study.

Bromide. Solutions containing bromide proved particularly interesting since it was possible to observe the equilibrium addition of the nucleophile to the cation. At low bromide concentrations (less than 0.01 M) the Ph₃C⁺ decay was slightly retarded—the salt effect—but above this point the decay became two component. Figure 2B shows the initial faster portion of the change in 0.5 M KBr, a solution where the two kinetic stages are particularly well separated. The behavior can be analyzed in terms of eq 3 and 4, where, in simple terms, the initial Ph₃C⁺ decay corresponds



to the approach to the equilibrium (eq 3) and the subsequent slower decay represents the complete conversion of the equilibrating mixture to Ph₃COH. An equilibrium constant of 5.5 M⁻¹ can be calculated as $(A_0 - A_{\text{int}})/(A_{\text{int}}[\text{Br}^-])$ where A_0 and A_{int} are absorbance readings immediately after the flash and at the intermediate stage, respectively. For the reactions in 0.1–0.5 M bromide, where the two kinetic components are well separated the initial stage can be approximated by

$$k_{\text{obsd}}(\text{fast}) = k_{\text{comb}}[\text{Br}^-] + k_{\text{ion}} \quad (5)$$

A plot of $k_{\text{obsd}}(\text{fast})$ vs. $[\text{Br}^-]$ is reasonably linear, providing $k_{\text{comb}} = 5.1 \times 10^6 \text{M}^{-1} \text{s}^{-1}$, $k_{\text{ion}} = 7.6 \times 10^5 \text{s}^{-1}$, and K_{eq} (as their ratio) = 6.6 M⁻¹, the latter in reasonable agreement with the value based upon absorbances.

It is possible to estimate k_{ion} for chloride, fluoride, and acetate based upon literature solvolysis data.^{41,46,47} The assumption made here is that Ph₃CX solvolysis follows the Grunwald–Winstein mY relationship with $m = 1$.⁴⁸ The most lengthy extrapolation involves Ph₃CCl, but the value obtained seems reasonable since the chloride:bromide solvolysis ratio is about the expected for S_N1 reactions.^{49,50} The data are summarized in Table II. The

(44) (a) Ritchie has recently predicted that chloride combination will only be observed with cations whose $\text{p}K_{\text{R}}$ values are more negative than -5.^{44b} Ph₃C⁺ has $\text{p}K_{\text{R}} = -6.6$. (b) Ritchie, C. D. Nucleophilicity Symposium, Sept. 1985, ACS Meeting, to be published as *Advances in Chemistry*, edited by M. Harris and S. McManus.

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(48) Y parameters in acetonitrile:water from Bunton et al. (Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, *49*, 3637–3639) and in acetone:water from Fainberg and Winstein (Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770–2777).

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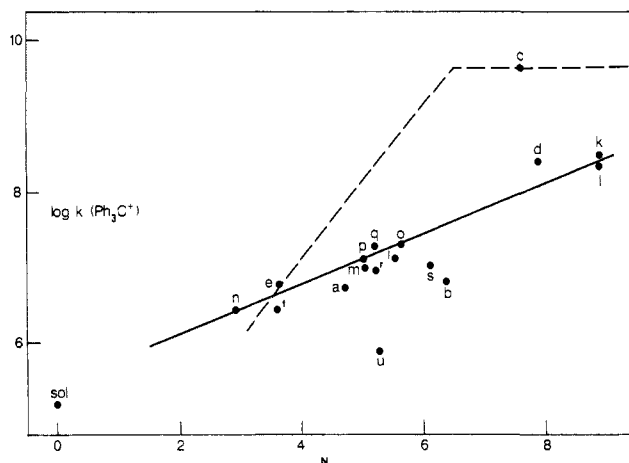


Figure 4. N_+ correlation for reaction of the trityl cation with nucleophiles. Nucleophiles are identified in Table I. N_+ values are taken from ref 6. For RS^- an N_+ of 8.8 was used, based upon data in ref 52. The line drawn has a slope of 0.33 and is the linear regression line excluding points c, u, and sol. For the significance of the dashed line, see text.

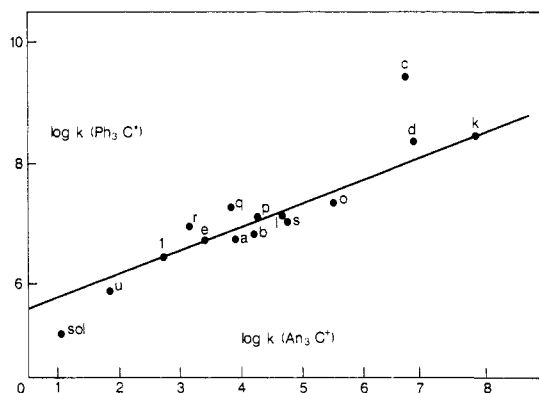


Figure 5. Correlation of trityl cation rate constants (1:2 AN: water, 20 °C) with those for the tris(4-methoxyphenyl)methyl cation (water, 25 °C) (refs 19, 53b, 54; the An_3C^+ point for k is that for $\text{HOCH}_2\text{CH}_2\text{S}^-$). The line drawn has a slope of 0.39 and is the linear regression line excluding points c, u, and sol.

nucleophilicity order for the halides is $\text{Br}^- > \text{Cl}^- > \text{F}^-$ following that for S_N2 reactions, with smaller differences.⁵¹ The equilibrium order (or Ph₃C⁺ basicity) is the opposite, $\text{F}^- \approx \text{OAc}^- \gg \text{Cl}^- > \text{Br}^-$.

Reactivity–Selectivity. The correlation of the trityl cation rate constants with the N_+ nucleophilicity parameters is shown in Figure 4. If this cation were to have behaved like its more stable triarylmethyl counterparts, this plot would have resulted in a line of unit slope rising to the encounter-controlled limit, at which point a sharp break would occur. Such a behavior is illustrated by a dashed line in the figure. The unit slope portion has been arbitrarily drawn through the rate constant for cyanide ion, rather than that for the solvent. The mechanism for water is probably different, involving general base catalysis.⁶ (This is likely also true for the reaction with the tertiary amine Dabco.^{16,53}) The simple predicted behavior is clearly not observed. With the exception of azide, all of the nucleophiles react considerably below the 10¹⁰ limit, including sulfite and thiol anions which are excellent

(50) Note also that the simple kinetics observed for Ph₃C⁺ decay in the presence of chloride requires that the chloride stick on the carbon, on the time scale of the experiment. The number $3 \times 10^4 \text{s}^{-1}$ just satisfies this requirement.

(51) Reference 49, pp 331–334.

(52) Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318–7323.

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N_+ nucleophiles. A linear regression line, ignoring the points for azide, water, and Dabco has a slope of only 0.33. A plot of the Ph_3C^+ data vs. rates for An_3C^+ is shown in Figure 5. This has a general similarity to the $\text{Ph}_3\text{C}^+-N_+$ correlation, attesting to the adherence of An_3C^+ to the N_+ scale. The linear regression line, ignoring the same three nucleophiles, has a slope of 0.39.

One explanation for the Ph_3C^+ behavior is that rate constants for the better nucleophiles are levelling and that this is occurring below the 10^{10} limit normally associated with diffusional processes. Some precedence for such a phenomenon has appeared in the literature. Richard and Jencks found that the estimated rate constants for oxyanions such as $\text{CF}_3\text{CH}_2\text{O}^-$ and AcO^- reacting with phenethyl cations levelled at $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ even for very reactive cations such as the 4-methylphenethyl ion.^{26c} Strong solvation of the oxyanion was proposed to be the reason behind this. Thus, although no barrier may exist for the combination of the oxyanion with very reactive cations, a desolvation barrier still slows the reaction. Jencks and co-workers have recently underlined the importance of the desolvation requirement by their observation of negative β_{nuc} values (decreasing nucleophilic reactivity with increasing basicity) for reactions of tertiary amines with some phosphate derivatives.⁵⁵ This was argued to arise through the need to desolvate the amine before nucleophilic attack, the desolvation being more difficult with more basic amines. In studies of carboxyl participation in the hydrolysis of maleamic acids, Kluger and Chin have suggested that diffusional separation of a maleic anhydride:amine encounter complex was rate-limiting.⁵⁶ Rate constants for the aminolysis of the anhydride, the reaction in the reverse direction, are, however, significantly less than $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁵⁷

Some problems with this interpretation do exist. It is, for example, difficult to understand why amines would level at 10^7 or so, well below the limit for the more highly solvated oxyanions (although complete desolvation of the amine is required while this is not true for an oxyanion⁵⁵). Moreover Richard and Jencks with the 4-methoxyphenethyl cation observed a $k(\text{N}_3^-)/k(\text{RS}^-)$ ratio of only 1.8. Azide almost certainly is reacting with this cation at the 10^{10} limit, so that this result suggests that RS^- must also be able to reach this level. One factor which might contribute to a lowering of reactivity with Ph_3C^+ is a steric effect. Comparisons of triarylmethyl cations with planar pyronin cations (dimethylamino-stabilized xanthylium ions) reveal that there are significant differences attributable to steric crowding in the former. One interesting result in this respect involves the parent xanthylium ion,⁴³ which reacts with OH^- six times more rapidly than Ph_3C^+ , and yet reacts with H_2O seven times more slowly.

The other possibility is that the less than unit slopes in Figures 4 and 5 are real. The inclusion of a slope parameter in the N_+ equation has been proposed,^{9,10} although in the particular cases involved the slopes only ranged from 0.8 to 1.2 and, considering the scatter in the data, may not have been statistically different from one.¹³ The slope in the present case is different from unity, and it is obviously also in the direction expected on the basis of the reactivity-selectivity principle—the more reactive Ph_3C^+ being

less selective than, for example, An_3C^+ (Figure 5). Also consistent with a change in selectivity are the results for the three primary amines, propyl, methoxyethyl, and trifluoroethyl. These still show a correlation of reactivity with basicity, suggesting that they are not reacting at a limit. However, the slope of this correlation, $\beta_{\text{nuc}} = 0.13$, is significantly smaller than that ($\beta_{\text{nuc}} = 0.41$) found for the reaction of primary amines with Malachite Green.⁵⁹ The β_{nuc} difference is also in the direction expected on the basis of the reactivity-selectivity principle.

We are currently conducting further experiments with this cation and other derivatives in an attempt to resolve these questions. The present study does show that it is possible to use flash photolysis to investigate the electrophilic reactions of carbocations of, what might be termed, intermediate stability. The results suggest that the behavior of this type of cation may, in some respects, not be predictable on the basis of behavior observed with very stable cations. Also of interest is the suggestion that the frequently used probe nucleophile azide may be unusual, in being able to approach the diffusion limit earlier than other nucleophiles.

Experimental Section

Triphenylmethyl acetate⁶⁰ and triphenylmethyl 4-cyanophenyl ether^{37a} were prepared by literature procedures. Solutions were prepared by mixing spectroscopic grade acetonitrile and water from a Millipore Milli-Q system in a 1:2 (v/v) ratio. Nucleophiles were added neat or as 0.5–1.0 M solutions in the same solvent, and the solutions were saturated with argon. (Sulfur nucleophiles were added after the removal of oxygen in order to avoid oxidation.) Solutions of the triphenylmethyl compound (0.02 M) in acetonitrile were prepared, and an aliquot was added to the mixed aqueous solution shortly before the irradiation experiments. (Ground-state solvolysis does occur (see Table II), and this is minimized in this way.)

Solutions contained $2-10 \times 10^{-5} \text{ M}$ trityl compound and had OD/cm = 0.3–1.0 at 248 nm. These were photolyzed with ≈ 20 -ns pulses ($\approx 100 \text{ mJ}$) of 248-nm light (KrF) from a Lambda Physik EMG 103 MSC excimer laser. The optical and conductance (from a 10 MHz AC and a DC system) signals were digitized by a Tektronix 7612 transient recorder interfaced with a DEC 11/73 computer which was also used for the analysis and documentation of the data.

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Registry No. DABCO, 280-57-9; Ph_3C^+ , 13948-08-8; H_2O , 7732-18-5; OH^- , 14280-30-9; $\text{CF}_3\text{CH}_2\text{O}^-$, 24265-37-0; N_3^- , 14343-69-2; SO_3^{2-} , 14265-45-3; CN^- , 57-12-5; CH_3CO_2^- , 71-50-1; F^- , 16984-48-8; Cl^- , 16887-00-6; Br^- , 24959-67-9; $\text{SCH}_2\text{CO}_2^-$, 16561-17-4; $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-$, 40055-94-5; $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, 107-10-8; $\text{CH}_3\text{OCH}_2\text{CH}_2\text{NH}_2$, 109-85-3; $\text{CF}_3\text{CH}_2\text{NH}_2$, 753-90-2; NH_2NH_2 , 302-01-2; NH_2OH , 7803-49-8; $\text{NH}_2\text{CH}_2\text{CO}_2^-$, 23297-34-9; morpholine, 110-91-8; piperidine, 110-89-4; imidazole, 288-32-4; trityl 4-cyanophenyl ether, 95953-45-0; trityl acetate, 971-85-7.

Supplementary Material Available: Table of observed first-order rate constants for the disappearance of the triphenylmethyl carbocation in acetonitrile/water (9 pages). Ordering information is given on any current masthead page.

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