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## Electrophilicity versus Electrofugality of Tritylium Ions in Aqueous Acetonitrile

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Dedicated to Prof. Rudolf Knorr on the occasion of his 75th birthday

**Abstract:** First-order rate constants  $k_w$ for the reactions of a series of donorsubstituted triphenylmethylium (tritylium) ions with water in aqueous acetonitrile have been determined photometrically at 20°C using stopped-flow and laser-flash techniques. The rate constants follow the linear free energy relationship  $\log k(20^{\circ}\text{C}) = s(N+E)$ . The reactivities  $k_w$  of the methyl- and methoxy-substituted tritylium ions towards water correlate linearly with the corresponding  $pK_{R+}$  values with a Leffler-Hammond coefficient  $\alpha = \delta \Delta G^{\dagger} / \delta \Delta G^{0}$ of 0.62. The amino-substituted compounds react more slowly than expected from the correlation of the less stabilized systems. Quantum chemical calculations of tritylium ions and the corresponding triarylmethanols and 1,1,1triarylethanes have been performed at the MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p) level. The calculated gasphase hydroxide and methyl anion affinities of the tritylium ions correlate linearly with a slope of unity, indicating that the relative anion affinities do not depend on the nature of the anion. The  $pK_{R+}$  values of the methyl- and methoxy-substituted tritylium ions correlate

**Keywords:** free-energy profiles • intrinsic barriers • kinetics • linear free-energy relationships • tritylium ions linearly with the calculated gas-phase hydroxide affinities, and the slope of this correlation shows that the differences in carbocation stabilities in the gas phase are attenuated to 66% in solution. Mono- and bis(dimethylamino)substituted derivatives deviate from this correlation; their  $pK_{R^+}$  values are higher than expected from their calculated gas-phase hydroxide affinities, which is explained by the extraordinary solvation of unsymmetrically aminosubstituted tritylium ions. Complete free-energy profiles for the solvolyses of substituted trityl benzoates in 90:10 (v/v) acetonitrile/water have been constructed.

### Introduction

Stabilities (more precisely, Lewis acidities) of carbocations<sup>[1]</sup> are commonly associated with the rates of their formation in solvolysis reactions and the rates of their reactions with nucleophiles. In the preceding article we have reported that the tris(*p*-methoxy)tritylium ion and the *p*-(dimethylamino)-tritylium ion are formed with almost equal rates from the corresponding trityl acetates and benzoates, despite the  $10^3$ -fold higher stability (p $K_{R+}$ ) of the latter carbocation.

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In order to elucidate the origin of this unique breakdown of a rate–equilibrium relationship, we have now investigated the electrophilic reactivities of differently substituted tritylium ions in aqueous acetonitrile, that is, the same solvent as used for the solvolysis studies in the preceding article.<sup>[2]</sup> These investigations were accompanied by quantum chemical calculations.

Early studies on the electrophilic reactivities of tritylium ions focused on stabilized amino- and methoxy-substituted species.<sup>[3-10]</sup> In particular, malachite green,  $(Me_2N)_2Tr^+$ , and derivatives thereof, were subjects of many investigations.<sup>[3]</sup> Rate constants for the reactions of  $(Me_2N)_2Tr^+$ , *p*-nitromalachite green, and crystal violet,  $(Me_2N)_3Tr^+$ , with water, hydroxide, and cyanide in aqueous solution<sup>[4]</sup> were the foundation of Ritchie's well-known constant selectivity relationship:  $\log (k/k_0) = N_+$ .<sup>[5]</sup> Bunton and Hill studied the kinetics of the reactions of the tris(*p*-methoxy)tritylium cation with water and hydroxide in aqueous solution. While Bunton's work concentrated on the salt effects for these reactions,<sup>[6]</sup>



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Hill's studies of kinetic isotope effects showed that the first step, the addition of water to the carbocation, rather than the subsequent proton transfer, is the rate-determining step.<sup>[7]</sup> Taft reported that the rates of the reactions of methoxy- and dimethylamino-substituted tritylium ions with water are not closely correlated with their thermodynamic stabilities,<sup>[8]</sup> and suggested separation into families. Later investigations confirmed Taft's experimental results, but demonstrated that the deviations from the linear  $\log k_w/pK_{R+}$  correlation are marginal when an extended series of compounds is considered.<sup>[5c,9]</sup> Reactivities of less stabilized systems were studied by McClelland, who used laser-flash techniques for the in situ generation of the carbocations.<sup>[9,10]</sup>

### **Results and Discussion**

**Kinetics**: Rate constants  $k_w$  for the reactions of water with the tritylium ions (Scheme 1) listed in Table 1 were determined at 20 °C in aqueous acetonitrile by photometric monitoring of the decays of the tritylium ions, which have absorption maxima between 420 and 504 nm. Different techniques have been utilized for this purpose.



Scheme 1. Reactions of tritylium ions with water.

Table 1. Tritylium ions with corresponding  $pK_{R^+}$  values and electrophilicity parameters *E*.

$R^1, R^2, R^{3[a]}$	Abbreviation	$pK_{R+}^{[b]}$	$E^{[c]}$
H, H, H	Tr+	-6.63	0.51
Me, H, H	MeTr+	-5.41	-0.13
Me, Me, H	Me <sub>2</sub> Tr <sup>+</sup>	-4.71	-0.70
Me, Me, Me	Me <sub>3</sub> Tr <sup>+</sup>	-3.56	-1.21
MeO, H, H	(MeO)Tr+	-3.40	-1.87
MeO, MeO, H	(MeO) <sub>2</sub> Tr <sup>+</sup>	-1.24	-3.04
MeO, MeO, MeO	(MeO) <sub>3</sub> Tr+	0.82	-4.35
$Me_2N$ , H, H	$(Me_2N)Tr^+$	3.88 <sup>[d]</sup>	-7.93
Me <sub>2</sub> N, MeO, H	(Me <sub>2</sub> N)(MeO)Tr <sup>+</sup>	4.86 <sup>[e]</sup>	-7.98
$Me_2N$ , $Me_2N$ , H	$(Me_2N)_2Tr^+$	6.94 <sup>[e]</sup>	-10.29
$Me_2N$ , $Me_2N$ , $Me_2N$	$(Me_2N)_3Tr^+$	9.39 <sup>[e]</sup>	-11.26

[a] For the location of the substituents see Scheme 1. [b] From reference [9]. [c] Empirical electrophilicity parameters from reference [24].[d] From reference [8]. [e] From reference [5c].

The more reactive ions, Tr<sup>+</sup>, MeTr<sup>+</sup>, Me<sub>2</sub>Tr<sup>+</sup>, Me<sub>3</sub>Tr<sup>+</sup>, and (MeO)Tr<sup>+</sup>, were generated in situ by laser-flash photolysis of the corresponding trityl acetates in aqueous acetonitrile. The other tritylium ions were introduced as tetrafluoroborate salts, and their reactions were followed by stopped-flow or conventional photospectrometry. Because in all

cases water was used in large excess, pseudo-first-order rate laws were obeyed, as illustrated in Figure 1. The obtained curves were fitted to the mono-exponential function  $A_t = A_0 e^{-kt} + C$  by the method of least squares.



Figure 1. Absorbance decay of (MeO)Tr<sup>+</sup> at 472 nm. The carbocation was generated from the corresponding acetate ( $c_0 = 1.00 \times 10^{-4} \text{ mol L}^{-1}$ ) using a laser pulse (7 ns, 266 nm, 60 mJ) in 50:50 (v/v) acetonitrile/water, 20°C.

Aqueous solutions of the amino-substituted systems  $(Me_2N)Tr^+BF_4^-$  and  $(Me_2N)(MeO)Tr^+BF_4^-$  in acetonitrile did not decolorize completely. When small amounts of tetra*n*-butylammonium acetate or benzoate were added to trap the generated protons, complete consumption of these carbocations was achieved. The tritylium ions  $(Me_2N)_2Tr^+$  and  $(Me_2N)_3Tr^+$  are so stable in aqueous solution that even the addition of large amounts of carboxylates did not lead to noticeable changes in the carbocation concentrations. For this reason we constrained our studies to systems with  $pK_{R^+} < 5$ .

Are the rate constants for the reactions of tritylium ions with water  $(k_w)$  affected by the presence of carboxylate ions? It has been reported that tertiary amines, such as 1,4diazabicyclo[2.2.2]octane (DABCO), triethylamine, or quinuclidine, act as general base catalysts for the addition of water to tritylium ions in pure water,<sup>[11]</sup> whereas general base catalysis by acetate has not been detected.<sup>[6,7]</sup> To investigate the influence of carboxylate ions on the reaction kinetics in aqueous acetonitrile, the consumption rates of  $(MeO)_{3}Tr^{+}BF_{4}^{-}$  in 90:10 (v/v) acetonitrile/water have been studied in the presence of variable amounts of (nBu)<sub>4</sub>N<sup>+</sup> AcO<sup>-</sup> and  $(nBu)_4N^+BzO^-$  at 25 °C. Figure 2 shows that an increase of the concentration of AcO- or BzO- accelerated the mono-exponential decay of (MeO)<sub>3</sub>Tr<sup>+</sup> linearly. Similar experiments were performed with (Me<sub>2</sub>N)Tr<sup>+</sup>BF<sub>4</sub><sup>-</sup>, and Table 2 gives an overview of all parameters obtained from regression lines as depicted in Figure 2.

The small slopes for the reactions of  $(Me_2N)Tr^+$  with AcO<sup>-</sup> and BzO<sup>-</sup> (entries 7–9) indicate that only high concentrations of carboxylate ions have a significant effect on the rate of consumption of  $(Me_2N)Tr^+$ . As only 4.6 to 8.7 equivalents of carboxylate (c=0.15 to 4.9 mmolL<sup>-1</sup>) were



Figure 2. Plot of  $k_{obs}$  for the decay of the absorbance of (MeO)<sub>3</sub>Tr<sup>+</sup>BF<sub>4</sub><sup>-</sup> ( $c_0 = 3 \times 10^{-5} \text{ mol L}^{-1}$ ) in 90:10 (v/v) acetonitrile/water versus the concentration of added tetra-*n*-butylammonium carboxylate,  $\lambda = 484$  nm, 25 °C.

Table 2. Kinetics of the consumption of tritylium ions in aqueous acetonitrile with different additives in excess at 25 °C.

Entry	Electrophile	Additive	Solvent <sup>[a]</sup>	Slope $[M^{-1}s^{-1}]$	Intercept [s <sup>-1</sup> ]
1	$(MeO)_3Tr^{+[b]}$	$AcO^{-[c]}$	90AN10W	$8.14 \times 10^{3}$	4.82
2	(MeO) <sub>3</sub> Tr <sup>+[b]</sup>	$AcO^{-[c]}$	50AN50W	$1.31 \times 10^{2}$	6.85
3	$(MeO)_3Tr^{+[b]}$	BzO <sup>-[c]</sup>	90AN10W	$2.32 \times 10^4$	4.96
4	$(MeO)_3Tr^{+[b]}$	DABCO	90AN10W	$4.78 \times 10^{2}$	4.34
5	(MeO) <sub>3</sub> Tr <sup>+[b]</sup>	DABCO	50AN50W	$9.82 \times 10^{1}$	7.32
6	$(MeO)_3Tr^{+[b]}$	$OH^{-[c]}$	90AN10W	$2.62 \times 10^{5}$	_[d]
7	$(Me_2N)Tr^{+[b]}$	$AcO^{-[c]}$	90AN10W	$1.94 \times 10^{-1}$	$3.55 \times 10^{-3}$
8	$(Me_2N)Tr^{+[b]}$	$AcO^{-[c]}$	50AN50W	$1.94 \times 10^{-2[e]}$	$3.66 \times 10^{-3[e]}$
9	$(Me_2N)Tr^{+[b]}$	BzO <sup>-[c]</sup>	90AN10W	$3.52 \times 10^{-1}$	$3.48 \times 10^{-3}$
10	$(Me_2N)Tr^{+[b]}$	DABCO	90AN10W	$1.35 \times 10^{-1}$	$3.55\times10^{-3}$

[a] The solvent is given in vol%, AN=acetonitrile, W=water. 90AN10W=90:10 (v/v) acetonitrile/water, etc. [b] The counterion was BF<sub>4</sub><sup>-</sup>. [c] The counterion was  $(nBu)_4N^+$ . [d] Not reliable, because intercept  $\ll k_{obs}$  [e] At 20 °C.

employed to achieve complete consumption of  $(Me_2N)Tr^+$ and  $(Me_2N)(MeO)Tr^+$  in the kinetic experiments at 20°C, we neglected their influence on the rate constants  $k_w$ , which are summarized in Table 3. An interpretation of the slopes of Figure 2 and Table 2 is given in the section "Common ion return of carboxylate anions?".

The presence of dications like  $[(HMe_2N)Tr]^{2+}$ , i.e., *N*-protonated dimethylamino-substituted tritylium ions, has been excluded in neutral aqueous solutions.<sup>[11c]</sup> Because in this work dimethylamino-substituted systems have been studied in the presence of carboxylate ions, i.e., under slightly basic conditions, the contribution of dicationic species could be neglected.

Quantum chemical calculations: A calculated geometry for the parent tritylium cation has previously been reported.<sup>[12a]</sup> Aizman, Contreras, and Pérez have performed DFT calculations of substituted tritylium ions at the B3LYP/6-31G(d) level in order to determine their Parr electrophilicity parameters.<sup>[12b]</sup> Because neither geometries nor energies have been reported, we have now optimized the geometries of tritylium ions, trityl alcohols, and 1,1,1-triarylethanes at the B3LYP/6-31G(d,p) level. Thermochemical corrections for 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at the same level, and combined with single-point energies on the MP2(FC)/6-31+G-(2d,p) level to yield enthalpies  $H_{298}$  and free energies  $G_{298}$ . For tritylium ions carrying two or three p-methoxy groups, and alcohols or ethanes carrying at least one p-methoxy group, different conformations have been considered (see Supporting Information). The structural parameters of the energetically best conformers of the carbocations are summarized in Table 4.<sup>[13]</sup>

When an ion contains three equal *para*-substituents (H, Me, MeO, or Me<sub>2</sub>N), the dihedral angle decreases slightly as the electron-donating ability of the substituent increases (33.6, 33.1, 32.9, and 32.4°, respectively) and the bond lengths remain constant (1.45 Å). For tritylium ions with differently substituted rings, the rings are distorted out of the plane to a different extent. The better the electron-donating ability of the *corresponding ring*, and the shorter the dihedral angle of the corresponding ring, and the shorter the distance between the ring and the central carbon. For (Me<sub>2</sub>N)-(MeO)Tr<sup>+</sup>, the smallest dihedral angle is calculated for the ring carrying the dimethylamino group (26.5°), an intermediate angle for the methoxy-substituted ring (32.8°), and the

Table 3. First-order rate constants  $k_w$  for the reactions of tritylium ions with water in aqueous acetonitrile<sup>[a]</sup> at 20 °C.<sup>[b]</sup>

	90AN10W	80AN20W	$k_{\rm w} \left[ { m s}^{-1}  ight]$ 60AN40W	50AN50W	33AN66W <sup>[c]</sup>	
Tr+	$1.19 \times 10^{5}$	$1.58 \times 10^{5}$	$1.69 \times 10^{5}$	$1.62 \times 10^{5}$	$1.6 \times 10^{5}$	
MeTr+	$2.44 \times 10^{4}$	$3.60 \times 10^{4}$	$4.29 \times 10^{4}$	$4.08 \times 10^{4}$	$3.7 \times 10^{4}$	
Me <sub>2</sub> Tr <sup>+</sup>	$7.85 \times 10^{3}$	$9.35 \times 10^{3}$	$9.84 \times 10^{3}$	$9.89 \times 10^{3}$	$1.1 \times 10^{4}$	
Me <sub>3</sub> Tr <sup>+</sup>	$2.77 \times 10^{3}$	$3.01 \times 10^{3}$	$3.17 \times 10^{3}$	$2.83 \times 10^{3}$	$3.6 \times 10^{3}$	
(MeO)Tr+	$1.17 \times 10^{3}$	$1.43 \times 10^{3}$	$1.75 \times 10^{3}$	$1.73 \times 10^{3}$	$1.4 \times 10^{3}$	
(MeO) <sub>2</sub> Tr <sup>+</sup>	$4.16 \times 10^{1}$	$5.61 \times 10^{1}$	$5.47 \times 10^{1}$	$5.81 \times 10^{1}$	$8.6 \times 10^{1}$	
(MeO) <sub>3</sub> Tr <sup>+</sup>	3.73	4.78	4.93	4.88	$1.0 \times 10^{1}$	
$(Me_2N)Tr^+$	$2.57 \times 10^{-3}$	$3.43 \times 10^{-3}$	$3.77 \times 10^{-3}$	$3.77 \times 10^{-3}$	-	
(Me <sub>2</sub> N)(MeO)Tr <sup>+</sup>	$1.53 \times 10^{-3}$	$1.97 \times 10^{-3}$	$2.16 \times 10^{-3}$	$2.14 \times 10^{-3}$	-	

[a] Solvents are given in vol%, AN=acetonitrile, W=water. [b] Note that the rate constants in this table refer to a different temperature than those in Table 2. [c] From ref. [10a].

unsubstituted ring (clib), and the unsubstituted ring is twisted by 40.0°. The decreasing resonance contribution from the dimethylamino- over the methoxy-substituted to the unsubstituted ring is also indicated by the corresponding bond lengths  $C_2$ - $C_3$ , which increase from 1.43 to 1.45 to 1.47 Å, respectively.

Though these calculations refer to the gas phase, spectroscopic investigations in solution confirm these structural assignments. The extraordinarily high resonance contribution of the

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### Table 4. Structural parameters<sup>[a]</sup> of tritylium ions, B3LYP/6-31G(d,p).

		x—(	2 3 Ar 1 4			
	Dihedral angl	$e C_1 C_2 C_3 C_4 [^{\circ}]$		Bond length	C <sub>2</sub> -C <sub>3</sub> [Å]	
Tr+	33.6 (H) <sup>[b]</sup>			1.45 (H)		
MeTr+	34.4 (H)	31.2 (Me)		1.45 (H)	1.44 (Me)	
Me <sub>2</sub> Tr <sup>+</sup>	35.3 (H)	32.2 (Me)		1.45 (H)	1.45 (Me)	
Me <sub>3</sub> Tr+	33.1 (Me)	. ,		1.45 (Me)		
(MeO)Tr <sup>+</sup>	36.1 (H)	28.0 (MeO)		1.46 (H)	1.43 (MeO)	
$(MeO)_2Tr^+$	38.4 (H)	30.5 (MeO)		1.46 (H)	1.44 (MeO)	
(MeO) <sub>3</sub> Tr <sup>+</sup>	32.9 (MeO)			1.45 (MeO)		
$(Me_2N)Tr^+$	38.3 (H)	$24.0 (Me_2N)$		1.46 (H)	$1.42 (Me_2N)$	
(Me <sub>2</sub> N)(MeO)Tr <sup>+</sup>	40.0 (H)	32.8 (MeO)	26.5 (Me <sub>2</sub> N)	1.47 (H)	1.45 (MeO)	$1.43 (Me_2N)$
$(Me_2N)_2Tr^+$	41.9 (H)	28.7 (Me <sub>2</sub> N)		1.47 (H)	1.43 (Me <sub>2</sub> N)	
$(Me_2N)_3Tr^+$	32.4 (Me <sub>2</sub> N)	. 2 /		1.45 (Me <sub>2</sub> N)	. 2 /	

→ ⊕ Ar

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Gas-phase hydroxide and methyl anion affinities (Table 5) have been calculated according to Equations (1) and (2), and are shown to correlate linearly (Figure 4).

$$R_3C^+ + OH^- \rightarrow R_3C - OH$$
 (1)

$$R_3C^+ + Me^- \rightarrow R_3C - Me$$
 (2)

The slope of unity implies that structural variations of the tritylium ions affect their affinities toward  $Me^-$  and  $OH^-$  to the same extent. A similar behavior has previously been re-

[a] The values are assigned to the rings with the substituents in parentheses. [b] In reference [14] a value of 32.4° was determined for tritylium perchlorate by X-ray diffraction.

dimethylamino group can be directly observed in the <sup>13</sup>C NMR spectrum of  $(Me_2N)(MeO)Tr^+BF_4^-$  (Figure 3). The two *ortho*-carbon atoms, as well as the two *meta*-carbon atoms of the dimethylamino-substituted ring, are not iso-chronous due to the high rotational barrier of this ring.

As neither of the two signal pairs coalesces in acetonitrile solution at 70 °C (100 MHz), the interconversion barrier for these carbon atoms must be higher than 75 kJ mol<sup>-1</sup>. The equivalence of the corresponding carbon signals in the other two phenyl rings even at ambient temperature indicates a fast rotation of these rings on the NMR timescale. The details of the dynamic behavior of tritylium cations have previously been investigated by several groups.<sup>[15]</sup>

Table 5. Theoretical gas-phase hydroxide and methyl anion affinities  $\Delta H_{298}$ , MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p).<sup>[a]</sup>

	( <sup>1</sup>	( ·I )
	$\Delta H_{298}$ [Eq. (1)] [kJ mol <sup>-1</sup> ]	$\Delta H_{298}$ [Eq. (2)] [kJ mol <sup>-1</sup> ]
Tr+	-715.54	-883.72
MeTr <sup>+</sup>	-704.42	-871.61
Me <sub>2</sub> +	-694.23	-862.00
Me <sub>3</sub> Tr <sup>+</sup>	-684.90	-852.30
(MeO)Tr <sup>+</sup>	-688.99	-857.22
(MeO) <sub>2</sub> Tr <sup>+</sup>	-667.15	-835.36
(MeO) <sub>3</sub> Tr <sup>+</sup>	-649.64	-817.64
$(Me_2N)Tr^+$	-648.75	-816.71
$(Me_2N)(MeO)Tr^+$	-632.90	-799.91
$(Me_2N)_2^+$	-605.42	-774.20
$(Me_2N)_3Tr^+$	-574.12	-740.66

[a] For total energies and thermochemical corrections needed for the calculations see the Supporting Information.



Figure 3. Part of the  ${}^{13}$ C NMR spectrum (150 MHz) of (Me<sub>2</sub>N)(MeO)Tr<sup>+</sup> BF<sub>4</sub><sup>-</sup> in CDCl<sub>3</sub> at 27 °C.



Figure 4. Correlation of theoretical Me<sup>-</sup> and OH<sup>-</sup> affinities ( $\Delta H_{298}$  in kJ mol<sup>-1</sup>), MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p), slope = 1.00,  $R^2$  = 1.00.

ported for benzhydrylium ions.<sup>[16]</sup> In each of the three subseries  $Me_xTr$ ,  $(MeO)_xTr$ , and  $(Me_2N)_xTr$ , the substituent effect on the anion affinity decreases as one goes from mono- to di- and trisubstituted systems (Figure 5). Here, the common saturation effects in multisubstituted systems are enforced by the propeller-like conformations of the tritylium ions, which allow the first substituent to stabilize the carbo-



Figure 5. Plot of relative OH<sup>-</sup> affinities  $(\Delta H_{298} \text{ in } \text{kJmol}^{-1}, \text{Tr}^+ = 0 \text{ kJmol}^{-1})$  versus the number of identical substituents in  $\text{Ar}_x \text{Ph}_{(3-x)}\text{C}^+$ , MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p).

cation more efficiently by planarizing the donor-substituted ring and squeezing the less electron-donating rings out of plane.

Linear free-energy relationships: The comparison of hydroxide affinities in solution ( $pK_{R+}$ ) with the corresponding gasphase data shows a good correlation for the methyl- and methoxy-substituted systems as well as the tris(dimethylamino)-substituted tritylium ion. However, the unsymmetrical dimethylamino-substituted systems (Me<sub>2</sub>N)Tr<sup>+</sup>, (Me<sub>2</sub>N)<sub>2</sub>Tr<sup>+</sup>, and (Me<sub>2</sub>N)(OMe)Tr<sup>+</sup> (open circles in Figure 6) are more stable in solution than expected on the basis of their gasphase hydroxide affinities. These deviations indicate exceptionally high solvation enthalpies of the mono- and diaminosubstituted tritylium ions, which may account for the high intrinsic barriers for the formation and reactions of these tritylium ions (see below). The slope of the line drawn in Figure 6 (0.66) suggests that the stabilizing effects of the



Figure 6. Correlation of  $\Delta G^0$  (=2.303*RT*pK<sub>R+</sub>) of water attack at tritylium ions versus calculated OH<sup>-</sup> affinities (gas phase,  $\Delta G_{298}$ , MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p)); the open circles have been omitted from the linear regression, slope 0.66.

substituents in the gas phase are reduced to 66% in aqueous solution. A value of 72% has been reported for benzhydrylium ions.<sup>[16]</sup>

For the construction of the rate–equilibrium relationship in Figure 7, we have complemented the  $k_w$  values of Table 1 with the rate constants for  $(Me_2N)_2Tr^+$  and  $(Me_2N)_3Tr^+$ ,



Figure 7. Plot of  $\log k_w$  (50% aqueous acetonitrile, 20°C) versus  $pK_{R+}$  (from Table 1);  $\log k_w$  of  $(Me_2N)_2Tr^+$  and  $(Me_2N)_3Tr^+ = -3.97$  and -4.94, respectively (from refs. [3a, 11c], see text); the open circles have been omitted from the linear regression, slope = -0.62,  $R^2 = 0.99$ .

which have previously been reported in the literature. Cigén has determined the rate constant of the reaction of  $(Me_2N)_2Tr^+$  with water in pure water at 20 °C as  $1.08 \times 10^{-4} s^{-1}$ .<sup>[3a]</sup> Ritchie reported a rate constant of  $1.94 \times 10^{-5} s^{-1}$  for  $(Me_2N)_3Tr^+$  at 25 °C.<sup>[11c]</sup> With a value of 73.3 kJ mol<sup>-1</sup> for the enthalpy of activation (calculated with data taken from ref. [11c]), one can calculate a rate constant of  $1.15 \times 10^{-5} s^{-1}$  at 20 °C on the basis of the Eyring equation.

Table 3 shows that the nucleophilic reactivity of water in aqueous acetonitrile remains almost constant as the amount of water exceeds 20 vol %. This observation is in agreement with McClelland's<sup>[9]</sup> and our previous observations<sup>[17]</sup> that carbocations are trapped with almost equal rates in different acetonitrile/water mixtures containing 20 to 100% water. We can, therefore, assume that the  $k_w$  values determined by Cigén and Ritchie in pure water<sup>[3a,11c]</sup> also hold for 50:50 (v/ v) acetonitrile/water, and we included them in the correlation of Figure 7. Like the ionization rate constants of trityl acetates,<sup>[2]</sup> only the electrophilicities of the methyl- and methoxy-substituted tritylium ions  $(\log k_w)$  depend linearly on their Lewis acidities  $(pK_{R+})$ . The unsymmetrical dimethylamino-substituted tritylium ions react more slowly than expected from their thermodynamic stabilities in aqueous solution, indicating higher intrinsic barriers for the reactions of these systems. In line with these findings, highly resonance-stabilized carbocations have previously been reported to show low intrinsic reactivities.[18]

**Hammett analysis:** Hammett–Brown parameters  $\sigma_p^+$  were designed for reactions involving a positively-charged center in conjugation to the substituents under consideration.<sup>[19]</sup>

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Figure 8 shows that the four symmetric systems Tr, Me<sub>3</sub>Tr,  $(MeO)_3$ Tr, and  $(Me_2N)_3$ Tr correlate perfectly linearly with  $\Sigma \sigma_p^+$ . Unsymmetrically substituted systems deviate, and the



Figure 8. Plot of  $\log k_w$  (50% aqueous acetonitrile, 20°C) versus  $\Sigma \sigma_p^+$  ( $\sigma_p^+=0$  (H), -0.31 (Me), -0.78 (OMe), and -1.70 (NMe<sub>2</sub>) from ref. [22]; for  $k_w$  of  $(Me_2N)_2Tr^+$  and  $(Me_2N)_3Tr^+$ : see text); the regression line is drawn through the four symmetrically substituted systems Ar<sub>3</sub>Tr<sup>+</sup>,  $\rho = 1.99$ ,  $R^2 = 1.00$ .

magnitude of the deviations increases with increasing electron-donating ability of the *p*-substituents. A similar behavior has been found for the correlation between the ionization rates of trityl esters and  $\Sigma \sigma_{\rm p}^{+,[2]}$  Many examples have shown that in the case of multiple ring substitution in diand triarylcarbenium ions,  $\sigma^+$  parameters are non-additive,<sup>[9,20]</sup> for reasons which have been discussed previously.<sup>[20]</sup>

Electrophilicity parameters of tritylium ions: Equation (3), in which *E* is an electrophile-specific reactivity parameter, and *s* and *N* are nucleophile-specific parameters, was designed to correlate bimolecular rate constants  $k_2$  for electrophile–nucleophile combinations.<sup>[21]</sup>

$$\log k_2 \ (20\,^{\circ}\mathrm{C}) = s(N+E) \tag{3}$$

A set of benzhydrylium ions and quinone methides were used as reference electrophiles for determining the N and sparameters of a large number of  $\sigma$ -, n-, and  $\pi$ -nucleophiles.<sup>[23]</sup> Because steric effects are not specifically included, Equation (3) only provides reliable predictions of rate constants for reactions of nucleophiles with carbocations and Michael acceptors if bulky systems are excluded. It has been discussed that reactions of tritylium ions can only be treated by Equation (3) if nucleophiles with negligible steric requirements, for example, primary amines and alcohols or hydride donors, are considered.<sup>[24]</sup> Figure 9 shows a good linear correlation of  $\log k_w$  with the electrophilicity parameters Eof tritylium ions (Table 1), which have previously been derived<sup>[24]</sup> from the rate constants for their reactions with water and *n*-PrNH<sub>2</sub> taken from the literature.



Figure 9. Plot of  $\log k_w$  versus *E*-parameters of tritylium ions; for  $k_w$  of  $(Me_2N)_2Tr^+$  and  $(Me_2N)_3Tr^+$ : see text; 50:50 (v/v) acetonitrile/water, 20 °C,  $R^2 = 0.99$ .

The quality of the correlation shown in Figure 9 corroborates the reliability of the previously reported *E*-parameters.<sup>[24]</sup> Moreover, if Figure 9 had been employed to determine the nucleophilicity parameters of 50AN50W (50:50 (v/ v) acetonitrile/water), values of N=5.32 and s=0.86 would have been obtained, close to the parameters derived from reactions with benzhydrylium ions (N=5.05 and s=0.89).<sup>[17]</sup> The internal consistency of our reactivity parameters is thus demonstrated.

**Comparison of electrofugality and electrophilicity**: It is generally assumed that highly stabilized carbocations are generated rapidly in solvolysis reactions, and react slowly with nucleophiles. Recently, we have reported that the inverse relationship between electrofugality (rate of formation of  $R^+$  in a heterolytic process) and electrophilicity (rate of reactions of  $R^+$  with nucleophiles), which holds for nonstabilized and slightly stabilized benzhydrylium ions.<sup>[25]</sup> A comparably poor correlation between electrophilicity and electrofugality for tritylium ions is shown in Figure 10.

As in the series of benzhydrylium ions, electrophilicity is inversely correlated with electrofugality for methyl- and methoxy-substituted systems, whereas amino-substituted systems ionize much more slowly than expected from the rates of their reactions with nucleophiles. The same argument that has been used to rationalize the deviation of the aminosubstituted tritylium ions from the log  $k_{ion}/pK_{R+}$  correlation (Figure 12 in ref. [2]), that is, late development of the resonance stabilization by the amino group on the reaction coordinate of the ionization process, can be used to explain the correlation in Figure 10. Because these deviations turn up in each of the correlations  $log k_{ion}/pK_{R+}$ ,<sup>[2]</sup>  $log k_w/pK_{R+}$ (Figure 7) and  $log k_{ion}/log k_w$  (Figure 10), they cannot be due to errors in one of the data sets.



Figure 10. Plot of  $\log k_w$  (20°C) versus  $\log k_{\rm ion}$  (acetates, 25°C, from ref. [2]), 90:10 (v/v) acetonitrile/water;  $\log k_w$  for  $(Me_2N)_2Tr^+$  in 90AN10W has been calculated by dividing  $1.08 \times 10^{-4}$  ( $k_w$  in 50AN50W) by 1.36 (average ratio  $k_w$ (50AN50W)/ $k_w$ (90AN10W) for all other tritylium ions in Table 3).

**Common ion return of carboxylate anions?** In order to determine the rate constants  $k_w$  for the reactions of dimethylamino-substituted tritylium ions in aqueous acetonitrile, we had to add AcO<sup>-</sup> and BzO<sup>-</sup> as proton traps to suppress reionization of the generated triarylmethanols. We will now analyze the origin of the rate enhancement by these carboxylate ions, which was described in Figure 2 and Table 2. Four different processes may account for the consumption of tritylium ions in aqueous solvents in the presence of a base B (carboxylate or amine). Apart from the reaction of the carbocation with water [ $k_w$  in Scheme 2 and Eq. (4)], the alco-



Scheme 2.

hol can be produced by attack of hydroxide  $(k_{OH})$ . Furthermore, the base can either act as a nucleophile and directly attack the carbocationic center  $(k_{ion})$ , or catalyze the addition of water by abstracting a proton in a concerted manner  $(k_{cat})$ .

$$-d[\mathbf{R}^{+}]/dt = [\mathbf{R}^{+}](k_{\rm w} + k_{\rm OH}[\mathbf{OH}^{-}] + k_{\rm -ion}[\mathbf{B}] + k_{\rm cat}[\mathbf{B}])$$
(4)

If the reaction with the base is reversible, a fifth term has to be considered, which refers to the ionization of the adduct  $(k_{ion})$ . In this case, Equation (4) transforms into Equation (5).

$$-d[R^{+}]/dt = [R^{+}](k_{w} + k_{OH}[OH^{-}] + k_{-ion}[B] + k_{cat}[B]) - k_{ion}[R-B]$$
(5)

While the intercepts of the lines shown in Figure 2 can be assigned unambiguously to  $k_w$  (4.71 s<sup>-1</sup> in the case of (MeO)<sub>3</sub>Tr<sup>+</sup> in 90AN10W, average of entries 1, 3, 4 of Table 2), the interpretation of the slopes is less straightforward.

For the reaction of  $(MeO)_3Tr^+$  with hydroxide in pure water, a second-order rate constant of  $k_{OH} = 8200 \text{ M}^{-1} \text{ s}^{-1}$  has been reported,<sup>[6]</sup> which is considerably smaller than the value of  $k_{OH} = 2.62 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in 90AN10W (Table 2, entry 6). This difference can be explained by the better solvation of hydroxide in water than in acetonitrile. However, at the low concentrations of hydroxide present under the conditions of these experiments,  $k_{OH}[OH^-]$  appears to be negligible, because comparison of entries 1, 3, and 4 of Table 2 shows that the acceleration by DABCO is smaller than that by AcO<sup>-</sup> and BzO<sup>-</sup>, in spite of the much higher basicity of DABCO, which must lead to higher OH<sup>-</sup> concentrations.

A similar argument allows the exclusion of the idea that carboxylates act as general base catalysts ( $k_{cat}$ ). DABCO and several quinuclidines have been reported to catalyze the addition of water to tritylium ions in pure water, and it has been shown that the  $\log k_{cat}$  values correlate linearly with the corresponding  $pK_{aH}$  values of the amines.<sup>[11b]</sup> Because AcO<sup>-</sup> is much less basic than DABCO, it should catalyze the addition of water less efficiently than DABCO. The observation that AcO<sup>-</sup> and BzO<sup>-</sup> accelerate the consumption of (MeO)<sub>3</sub>Tr<sup>+</sup> more than DABCO (Table 2, cf. slopes in entries 1, 3, 4 or 2, 5) leads to the conclusion that carboxylate ions attack the carbenium ion directly. These reactions are reversible and do not occur in pure water, for which the consumption rate of (MeO)<sub>3</sub>Tr<sup>+</sup> has been found to be independent of the concentration of AcO-.[6,7] Because the concentrations of AcO<sup>-</sup> in the experiments of Figure 2 are considerably higher than they were during the ionization studies of (MeO)<sub>3</sub>Tr–OAc in the preceding paper,<sup>[2]</sup> the equilibria of Scheme 2 lie almost completely on the side of the covalent ester. For this reason, in the experiments of Figure 2, the absorbances of (MeO)<sub>3</sub>Tr<sup>+</sup> decreased mono-exponentially to zero with  $k_{obs} = k_w + k_{-ion}[B]$ , i.e., the slopes given in entries 1 and 3 of Table 2 reflect  $k_{-ion}$ .

This rationalization of Figure 2 is supported by the following considerations. Nucleophilicity parameters of benzoate in 90AN10W have been determined as  $N_{25}=11.3$  and  $s_{25}=$ 0.72 at 25°C.<sup>[25]</sup> By employing Equation (3), the rate constant for the bimolecular reaction of (MeO)<sub>3</sub>Tr<sup>+</sup> with BzO<sup>-</sup> can be calculated as  $1.01 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . Comparison with the experimental value of  $2.32 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (Table 2, entry 3) reveals agreement within a factor of 4.4, showing that the observed rate constant is in the correct order of magnitude. The deviation is within the range of tolerance of Equation (3), especially when sterically demanding electrophiles like tritylium ions are involved.

An analogous calculation for the reaction of (Me<sub>2</sub>N)Tr<sup>+</sup> with  $BzO^-$  yields a rate constant of  $267 M^{-1} s^{-1}$  [from Eq. (3)], which is much bigger than the slope of  $0.352 \,\mathrm{m}^{-1} \mathrm{s}^{-1}$ given in entry 9 of Table 2, suggesting that this slope cannot reflect the rate constant for the attack of BzO- at (Me<sub>2</sub>N)Tr<sup>+</sup>. Division of the larger of these two numbers  $(k_{-ion} = 267 \text{ M}^{-1} \text{ s}^{-1})$  by  $k_{ion}$  (5.37 s<sup>-1</sup>, from ref. [2]) yields the upper limit for the equilibrium constant of the ester formation  $K = k_{-ion}/k_{ion} = 50 \text{ M}^{-1}$ . Hence, for  $[BzO^{-}] = 10^{-3} \text{ M}$  ( $\approx 20$ fold excess in our experiment), the ratio [(Me<sub>2</sub>N)Tr-OBz]/ [(Me<sub>2</sub>N)Tr<sup>+</sup>] must be smaller than 0.05, which implies that the reaction of (Me<sub>2</sub>N)Tr<sup>+</sup> with BzO<sup>-</sup> in 90AN10W is thermodynamically unfavorable and, therefore, cannot be observed. The small accelerations of the consumption of (Me<sub>2</sub>N)Tr<sup>+</sup> in the presence of carboxylates are concluded to be due to the sum of  $k_{\text{OH}}$  and  $k_{\text{cat}}$ .

On the other hand, a ratio  $[(MeO)_3Tr-OBz]/[(MeO)_3 Tr^+]=6.1$  (with  $k_{-ion}=2.32 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ ,  $k_{ion}=3.79 \text{ s}^{-1}$ ,<sup>[2]</sup> and  $[BzO^-]=10^{-3} \text{ M}$ ) is calculated for the equilibrium mixture obtained from  $(MeO)_3Tr^+$  and  $BzO^-$  in 90AN10W, showing that in this system the predominant species is the ester.

Complete free-energy diagrams for the hydrolyses of trityl carboxylates: The ionization rate constants of trityl carboxylates<sup>[2]</sup> and the rate constants for the consumption of tritylium ions reported in this paper shall now be combined to construct free energy diagrams for the hydrolyses of tritylium carboxylates in aqueous acetonitrile. The good correlation between  $\log k_w$  and the previously derived electrophilicity parameters E (Figure 9) shows that the E values for tritylium ions can be used to calculate rate constants for their combinations with *n*-nucleophiles by Equation (3). Therefore, all of the quantities required for the construction of free energy diagrams are now available.

In Figure 11, the covalent trityl benzoates are set on the same level. The Eyring equation was used to calculate  $\Delta G^{\dagger}$  values for the first step of the reaction cascade from directly measured ionization rate constants  $k_{\rm ion}$  (Table 8 in ref. [2]).<sup>[26]</sup>

The rate constants for the combinations of the tritylium ions with benzoate  $k_{-ion}$  in 90AN10W were calculated by Equation (3) from the E parameters given in Table 1 and the known nucleophilicity parameters of BzO<sup>-</sup> (see above). Thus, one arrives at the positions of the tritylium ions in Figure 11. As discussed above, the directly measured rate constant for the reaction of (MeO)<sub>3</sub>Tr<sup>+</sup> with BzO<sup>-</sup> is 4.4 times smaller than that calculated by Equation (3). Taking this factor into account would lower the positions of all tritylium ions in Figure 11 by 3–4 kJ mol<sup>-1</sup>, a negligible correction in view of the total spread of the reactivities. The thermodynamic stability order of the tritylium ions (affinities toward benzoate anions in 90AN10W), which has been obtained on an entirely kinetic basis ( $k_{ion}$  and  $k_{-ion}$ ), is in line with the hydroxide affinity scale  $pK_{R+}$ , which is based on equilibrium measurements in water and aqueous sulfuric acid. Figure 12 shows that the  $\Delta G^0$  values derived from kinetic ( $k_{ion}$  and  $k_{-ion}$ ) and equilibrium ( $pK_{R+}$ ) measurements

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reaction coordinate

Figure 11. Free-energy profiles for the hydrolyses of substituted trityl benzoates in 90:10 (v/v) acetonitrile/water, 25°C; constructed for  $[BzO^-]=1 \mod L^{-1}$ ; [a]  $k_w$  taken from Table 3, determined at 20°C.



Figure 12. Correlation of free energies  $\Delta G^0$  (combination of tritylium ions with BzO<sup>-</sup>, data taken from Figure 11) with  $\Delta G^0$  from pK<sub>R+</sub>; slope = 1.07,  $R^2 = 1.00$ .

correlate with a slope of 1.07 with no obvious deviations. The consistency of our kinetic data is thus confirmed.

The activation free energies for the last step in the reaction cascade of Figure 11 can again be derived from the Eyring equation. Because the relative stabilities of trityl benzoates and triarylmethanols are almost independent of the nature of the substituents on the aryl rings, all energy profiles will converge on the right of Figure 11. Readers should not be confused by the fact that  $Ar_3C$ -OH is located at approximately the same level as  $Ar_3C$ -OBz. Like in other ester hydrolyses, the equilibrium constants can be assumed to be close to one and it is the high concentration of water that is responsible for the almost quantitative hydrolyses.

Figure 11 can now be used to rationalize the kinetic phenomena reported in this and the preceding article.<sup>[2]</sup> First of all, one can recognize that the transition state of the ionization step changes significantly as one goes from trityl benzoate to the bis(dimethylamino)-substituted trityl derivative. The more electron donors that are attached, the less carbocation-like is the transition state. The origin of the observed irregularities between methyl- and methoxy-substituted tritylium systems on one side and dimethylamino-substituted ones on the other is visualized well by Figure 11. As discussed earlier, the intrinsic barriers for the reactions of the highly resonance-stabilized amino-substituted tritylium ions are particularly high. As a consequence, the transition states for the ionizations of (MeO)<sub>3</sub>Tr-OBz and (Me<sub>2</sub>N)Tr-OBz (68.9 and 69.7 kJ mol<sup>-1</sup>, respectively) as well as for the reactions of the corresponding cations with water (93.8 and 96.0 kJ mol<sup>-1</sup>, respectively) almost coincide, although (Me<sub>2</sub>N)Tr<sup>+</sup> is the much better stabilized cation. Hence, (MeO)<sub>3</sub>Tr-OBz and (Me<sub>2</sub>N)Tr-OBz ionize with similar rates, whereas (Me<sub>2</sub>N)Tr<sup>+</sup> reacts much more slowly with nucleophiles than  $(MeO)_3Tr^+$ .

### Conclusion

Although the linear free-energy relationship  $\log k(20^{\circ}\text{C}) =$ s(N+E) cannot generally be applied to reactions involving sterically shielded systems (e.g., reactions of tritylium ions with alkenes), we have now found that it works perfectly for the decays of tritylium ions in aqueous acetonitrile. The breakdown of the inverse correlation between the electrofugalities of carbocations (rates of ionization of R-X) and their electrophilicities (rates of reactions of R<sup>+</sup> with nucleophiles) for highly stabilized carbocations appears to be a general phenomenon. As previously reported for the hydrolyses of benzhydrylium carboxylates,<sup>[25]</sup> we have now found an excellent inverse correlation between the electrophilic reactivities of methyl- and methoxy-substituted tritylium ions and the ionization rates of the corresponding trityl carboxylates. However, amino-substituted tritylium ions strongly deviate from this correlation. Because unsymmetrical aminosubstituted tritylium ions, in particular (Me<sub>2</sub>N)Tr<sup>+</sup>, are much better stabilized in solution than expected from their anion affinities in the gas phase (Figure 6), they must experience special solvation effects. Reorganization of these strongly associated solvent molecules may account for the high intrinsic barriers encountered in reactions forming  $(k_{ion})$  and quenching  $(k_w)$  these tritylium ions.

Apart from their use as protecting groups, tritylium ions also have many practical applications as hydride abstracting agents. This work has shown that there are excellent linear correlations between electrophilic reactivities ( $\log k_w, E$ ) and the  $pK_{R+}$  values as well as the calculated hydroxide affinities in the gas phase if the amino-substituted tritylium ions are excluded. Parent, methyl-, and methoxy-substituted systems can therefore be used as reference compounds for converting the manifold of published hydride abstraction rates by differently substituted tritylium ions into a common activity scale for hydride donors.<sup>[27]</sup>

#### **Experimental Section**

**Chemicals**: Acetonitrile was used as purchased (VWR, 99.9%). Water was purified by a Millipore MilliQ device (final specific resistance  $\geq 18.2 \text{ M}\Omega \text{ cm}$ ). Tetra-*n*-butylammonium acetate (Fluka,  $\geq 99\%$ ), tetra-*n*-butylammonium benzoate (Fluka,  $\geq 99\%$ ), and DABCO (Acros, 97%) were used as purchased. Tritylium tetrafluoroborates as well as trityl acetate were prepared according to synthetic procedures described previous-ly.<sup>[2]</sup>

Kinetics: In all experiments the temperature was kept constant at 20 or 25°C using a circulating water bath. Each measurement was repeated at least once, the difference in  $k_w$  not exceeding 3%. Reactions with halftimes greater than 10 s were followed by conventional UV/Vis spectrometry using a J&M TIDAS instrument equipped with an insertion quartz probe (Hellma). Faster reactions were studied with a stopped-flow UV/ Vis spectrometer (Applied Photophysics SX.18MV-R). For both techniques the tritylium tetrafluoroborates were used as substrates, their initial concentrations ranging from 10<sup>-5</sup> to 10<sup>-4</sup> mol L<sup>-1</sup>. Poorly stabilized carbocations reacting with half-lives below 10 ms were generated by laser-flash photolysis, for which the corresponding trityl acetates were used as precursors. The esters of MeTr, Me<sub>2</sub>Tr, Me<sub>3</sub>Tr, and (MeO)Tr were generated by mixing equimolar amounts of the colored tritylium tetrafluoroborates and (nBu)<sub>4</sub>N+AcO<sup>-</sup> in acetonitrile directly before the kinetic measurement, yielding colorless solutions. The laser pulse (7 ns pulse width, 266 nm, 40-60 mJ/pulse) originated from an InnoLas Spit-Light 600 Nd-YAG laser. Initial concentrations of trityl acetates ranged from  $10^{-4}$  to  $10^{-2}$  mol L<sup>-1</sup>.

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