

**Table X.** Atomic Coordinates for  $[\text{Fe}_2\{\mu\text{-SbCH}(\text{SiMe}_3)_2\}(\text{CO})_8]$  (6)<sup>a</sup>

atom	x	y	z	B (Å <sup>2</sup> )
Sb1	0.18849 (4)	0.25626 (3)	0.23414 (1)	3.308 (5)
Fe1	0.46510 (8)	0.05588 (6)	0.15644 (3)	3.28 (1)
Fe2	0.26089 (9)	0.35915 (7)	0.11103 (3)	3.67 (1)
Si1	0.4018 (2)	0.1941 (2)	0.38367 (7)	5.07 (3)
Si2	0.1563 (2)	0.5406 (2)	0.33793 (7)	4.50 (3)
O01	0.6202 (7)	-0.2466 (4)	0.2258 (2)	8.4 (1)
O02	0.1358 (5)	-0.0503 (4)	0.1220 (2)	6.10 (9)
O03	0.7198 (6)	-0.0179 (5)	0.0286 (2)	6.3 (1)
O04	0.7580 (5)	0.1462 (5)	0.2236 (2)	6.9 (1)
O05	-0.0753 (5)	0.2711 (5)	0.0696 (2)	6.6 (1)
O06	0.4737 (7)	0.3261 (5)	-0.0247 (2)	7.4 (1)
O07	-0.0182 (7)	0.6765 (5)	0.0980 (3e)	8.9 (1)
O08	0.5556 (5)	0.4682 (4)	0.1699 (2)	6.23 (9)
C01	0.5581 (7)	-0.1264 (5)	0.2001 (3)	5.2 (1)
C02	0.2592 (7)	-0.0021 (5)	0.1336 (2)	4.3 (1)
C03	0.6170 (7)	0.0131 (5)	0.0772 (2)	4.4 (1)
C04	0.6385 (6)	0.1180 (5)	0.1973 (2)	4.3 (1)
C05	0.0589 (7)	0.2971 (6)	0.0873 (2)	4.6 (1)
C06	0.3941 (8)	0.3347 (5)	0.0279 (2)	4.9 (1)
C07	0.0910 (9)	0.5529 (6)	0.1046 (3)	5.7 (1)
C08	0.4439 (7)	0.4201 (5)	0.1488 (2)	4.4 (1)
C1	0.3289 (6)	0.3422 (5)	0.3115 (2)	3.44 (9)
C11	0.507 (2)	-0.015 (1)	0.3600 (5)	14.8 (4)
C12	0.602 (2)	0.232 (1)	0.4292 (6)	20.5 (4)
C13	0.186 (2)	0.207 (1)	0.4497 (5)	16.1 (4)
C21	0.131 (1)	0.6868 (6)	0.2685 (3)	6.7 (2)
C22	-0.1015 (9)	0.5402 (7)	0.3647 (4)	7.4 (2)
C23	0.257 (1)	0.6135 (8)	0.4073 (4)	10.0 (2)
C11A	0.684 (3)	0.055 (2)	0.360 (1)	*****
C12A	0.409 (4)	0.273 (3)	0.465 (1)	*****
C13A	0.229 (3)	0.078 (3)	0.392 (1)	*****

<sup>a</sup> Asterisked atoms were refined isotropically.

control unit), ion source acceleration, potential of 8 kV, scanning the mass range  $m/e$  1000 to  $m/e$  50. The liquid matrix employed for the FAB ionization was commercial grade *o*-nitrophenyl octyl ether (Fluka AG, Chem.). The sample was not sufficiently soluble in glycerol or thio-glycerol for FAB-MS analysis. For the mass spectral analysis, 0.1  $\mu\text{g}$

of the sample was dissolved in approximately 3  $\mu\text{L}$  of *o*-nitrophenyl octyl ether on the FAB direct insertion probe. The mass scale was calibrated with glycerol and/or CsI dissolved in glycerol.

The mass spectrum of **15** gave intense ions at  $m/e$  980, 952, 896, 738, 644, 569, and 420. The signal at  $m/e$  980 comprises a complex pattern arising from the isotopic composition  $\text{Fe}_3\text{Sb}_2\text{Si}_4\text{C}_{23}\text{H}_{38}\text{O}_9$ . A calculated isotopic pattern<sup>30</sup> for  $\text{Fe}_3\text{Sb}_2\text{Si}_4\text{C}_{23}\text{H}_{38}\text{O}_9$  gave excellent agreement (5% error) with the experimentally observed isotopic pattern. The fragment ions observed and the corresponding isotopic patterns are also consistent with the proposed structure. For example, the intense ion at  $m/e$  952 arises by loss of 28 mass units (CO) from the molecule ion. Likewise, the signals at  $m/e$  896 and  $m/e$  728 arise by loss of 3 and 9 carbonyl ligands, respectively. Expulsion of weakly bound ligands such as CO is common for such materials.<sup>31</sup> Presumably the signal at  $m/e$  644 corresponds to loss of  $\text{Fe}_2(\text{CO})_8$ , and the signal at  $m/e$  569 corresponds to loss of  $\text{Fe}_2(\text{CO})_8$  plus  $\text{Me}_3\text{Si}$ . A series of signals beginning at  $m/e$  420 and separated by 15 mass units correspond to successive loss of methyl groups from the  $\text{Fe}_2(\text{CO})_8\text{SbCH}(\text{SiMe}_3)_2$  fragment ion. This series of ions covers the mass range  $m/e$  420-330, which corresponds to successive losses of all six methyl groups.

The proposed fragmentation patterns for **15** have been substantiated by using FAB-TMS (tandem mass spectrometry). The specific details of these experiments on **15** and similar metal cluster ions will be presented in a separate publication.

**Acknowledgment.** The authors are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

**Supplementary Material Available:** Tables of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

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## Base-Catalyzed Reactions of Triarylmethyl Carbocations with Water

Joseph R. Gandler

Contribution from the Department of Chemistry, California State University, Fresno, California 93740. Received March 25, 1985

**Abstract:** The general base catalyzed addition of water to a series of triarylmethyl carbocations has been studied in aqueous solution with a series of substituted quinuclidines as base catalysts. Brønsted  $\beta$  values for general base catalysis range from 0.33 for trianisylmethyl carbocation, TAM ( $\text{p}K_{\text{R}^+} = 0.82$ ), to 0.52 for Malachite Green, MG ( $\text{p}K_{\text{R}^+} = 6.94$ ). There is a slight tendency for the  $\beta$  values to decrease with decreasing carbocation stability. The rate constants for the "water"-catalyzed reactions show a large positive deviation (800-fold in the case of Malachite Green) and the rate constants for the hydroxide ion catalyzed reactions a small negative deviation from Brønsted plots based on quinuclidine catalysis. These results are consistent with a concerted mechanism for the buffer-catalyzed reactions, a stepwise mechanism that proceeds through an oxonium ion intermediate for the "water"-catalyzed reactions (this mechanism corresponds to an A-1 mechanism in the microscopic reverse direction), and either a concerted or preassociation mechanism for the hydroxide ion catalyzed reactions. The positive deviation of water and the negative deviation of the hydroxide ion from the Brønsted relationship are opposite the deviations that are normally observed for these species in related reactions: compared to these related reactions, the pH range where buffer catalysis is strongest is shifted to higher pH values. These results also explain why the early attempts to find general base catalysis of the addition of water to triarylmethyl carbocations with acetate buffers proved unsuccessful.

There are two general-type mechanisms available for the reactions of alcohols to form carbocations: stepwise A-1 mechanisms

that proceed through an intermediate (an oxonium ion) either free or associated with the catalyst<sup>1</sup> and a concerted mechanism which

bypasses these intermediates. These mechanisms also apply to the reactions of related compounds, such as the hydrolyses of acetals and ortho esters which proceed via an oxocarbenium ion intermediate.<sup>4</sup>

Specific acid catalysis and large inverse solvent isotope effects support an A-1 mechanism for the reactions of alkyl alcohols and acetals,<sup>4</sup> although in the reactions of acetals, diffusion<sup>5</sup> or hemiacetal hydrolysis<sup>6</sup> can become rate-limiting in certain instances.

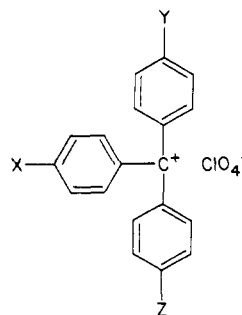
There is, however, a change from specific to general catalysis (buffer catalysis) and from large inverse solvent isotope effects to smaller solvent isotope effects in the reactions of acetals and ortho esters when bond cleavage is facilitated by increased oxocarbenium ion stability or enhanced leaving group ability.<sup>4</sup> Buffer catalysis has also been observed in the reactions of tropyl alcohol,<sup>7</sup> diferrocenylmethanol,<sup>7</sup> and triarylmethyl carbinols.<sup>8-11</sup> These results support a change to the concerted mechanism for the reactions of these substrates.<sup>4,7,11</sup>

Carboxylic acid buffers are effective catalysts for the concerted reactions of many of these substrates.<sup>4,7</sup> We were therefore surprised to learn that the early attempts to find buffer catalysis of the addition of water to triarylmethyl carbocation with acetate buffer solutions proved unsuccessful;<sup>12-14</sup> in one study, no significant catalytic effect was observed with concentrations of acetate ion up to 1.0 M.<sup>13</sup> It was later established that these reactions were instead catalyzed by more weakly acidic buffers, such as Dabco and triethylamine.<sup>8,9,11</sup> In order to better understand this result we have studied the general base catalyzed addition of water to a series of triarylmethyl carbocations, utilizing a family of substituted quinuclidines as base catalysts (pK range 7.7 to 11.5). These carbocations represent a class of carbocations that are stable in aqueous buffer solutions and provide for a wide range of carbocation stabilities (ca. 10<sup>7</sup>).<sup>15</sup> A number of groups have already shown that the addition of water to these carbocations is general base catalyzed.<sup>8-11</sup> The results of this study show that there are apparent changes in the mechanism of the solvent-catalyzed reactions compared to the solvent-catalyzed reactions of other substrates in this class. These apparent changes in mechanism are responsible for the observed catalytic effects.

## Experimental Section

**Materials.** Inorganic salts were analytical reagent grade and were used without further purification. Quinuclidine was sublimed, whereas all other materials were recrystallized prior to use. The substituted triarylmethyl carbocations were generous gifts of Professor C. D. Ritchie.

**Kinetics.** Kinetics were monitored on a Gilford 240 or Cary 17D UV-vis spectrophotometer or a stopped-flow spectrophotometer interfaced with a Nicolet digital oscilloscope and a Tektronix programmable calculator. Reactions were carried out in aqueous solution at 25 °C in



MG. X=(CH<sub>3</sub>)<sub>2</sub>N; Y=(CH<sub>3</sub>)<sub>2</sub>N; Z=H  
 NO<sub>2</sub>-MG. X=(CH<sub>3</sub>)<sub>2</sub>N; Y=(CH<sub>3</sub>)<sub>2</sub>N; Z=NO<sub>2</sub>  
 MeO-DMA. X=(CH<sub>3</sub>)<sub>2</sub>N; Y=CH<sub>3</sub>O; Z=H  
 Me-DMA. X=(CH<sub>3</sub>)<sub>2</sub>N; Y=CH<sub>3</sub>; Z=H  
 TAM. X=CH<sub>3</sub>O; Y=CH<sub>3</sub>O; Z=CH<sub>3</sub>O

the presence of a large excess of buffer at ionic strength = 1.0 M, maintained with potassium chloride. Cuvettes were temperature equilibrated in the cell compartment of the spectrophotometer for a least 20 min prior to a kinetic run. All reactions followed excellent pseudo-first-order kinetics. A Beckman Model 1019 or Altrex 71 pH meter was used for pH measurements. The pK values of the substituted quinuclidine buffers were determined by potentiometric titration.

**Solvent Isotope Effects.** Solutions of KOD in deuterium oxide were prepared by dissolving KOH in deuterium oxide and then titrating these solutions against potassium hydrogen phthalate. The solvent isotope effects were determined at two base concentrations (0.020 and 0.040 M) by running concurrently, in the cell compartment of the spectrophotometer, the reactions catalyzed by both the hydroxide and deuterioxide ions.

## Results

Catalysis of the addition of water to substituted triarylmethyl carbocations follows the rate law of eq 1,<sup>8-10</sup> in which  $k_W$ ,  $k_{OH}$ , and  $k_B$  are the rate constants for the "water"-, hydroxide-, and buffer-catalyzed reactions, respectively.

$$k_{\text{obsd}} = k_B[B] + k_{OH}[\text{OH}] + k_W \quad (1)$$

The reactions were carried out so that the pH values of the buffer solutions used in the kinetic runs were always at least one unit, and generally many units, above the pK<sub>R</sub><sup>+</sup> of the carbocations. Under this condition, the reverse reactions (the reactions of the alcohols to produce the carbocations) are insignificant. Furthermore, the pH values of the buffer solutions were always high enough so that the substrate's dimethylamino groups were in their free base form. Second-order rate constants for the hydroxide ion catalyzed reactions were measured directly in dilute solutions of potassium hydroxide and were obtained from plots of  $k_{\text{obsd}}$  against hydroxide ion concentration. Second-order rate constants for the buffer-catalyzed reactions were obtained from plots of  $k_{\text{obsd}}$  against buffer base concentration at constant pH and are based on four or more buffer base concentrations. In all cases the intercepts of these plots agree well with the intercepts calculated from the known water and hydroxide ion rate constants and the measured pH. Rate constants for the water reactions were obtained from the intercepts of plots of  $k_{\text{obsd}}$  against buffer base concentration in 3-quinuclidinone or Dabco buffer solutions. In these solutions the hydroxide ion reactions do not contribute significantly to the observed rate constants.

Table I lists the second-order rate constants for the substrates studied in this work. Table I also includes a comparison of the rate constants measured in this work with rate constants that have been measured in other laboratories, generally under different conditions of ionic strength. In general, agreement is satisfactory. For example, for the buffer-catalyzed reactions we measure rate constants for the Dabco-catalyzed reaction of MG and Me-DMA with water of 0.00270 and 0.051 M<sup>-1</sup> s<sup>-1</sup>, respectively; these values compare well with values of 0.026 and 0.047 M<sup>-1</sup> s<sup>-1</sup> reported by Ritchie and co-workers.<sup>11</sup> A rate constant of 0.036 M<sup>-1</sup> s<sup>-1</sup> for the quinuclidine-catalyzed reaction of MG compares satisfactorily with Ritchie's value of 0.042 M<sup>-1</sup> s<sup>-1</sup>.<sup>11</sup> A slightly larger discrepancy is noted for the Dabco-catalyzed reaction of TAM: 80 M<sup>-1</sup> s<sup>-1</sup> (this work), and the value of 62 M<sup>-1</sup> s<sup>-1</sup> reported by Ride et al.<sup>9</sup> Table I also shows that there are, relatively, only small

(1) This mechanism involves rate-limiting formation of the oxonium ion intermediate in the presence of a base which stabilizes the transition state by hydrogen bonding. This mechanism corresponds to a preassociation mechanism<sup>2</sup> or spectator-catalyzed reaction.<sup>3</sup>

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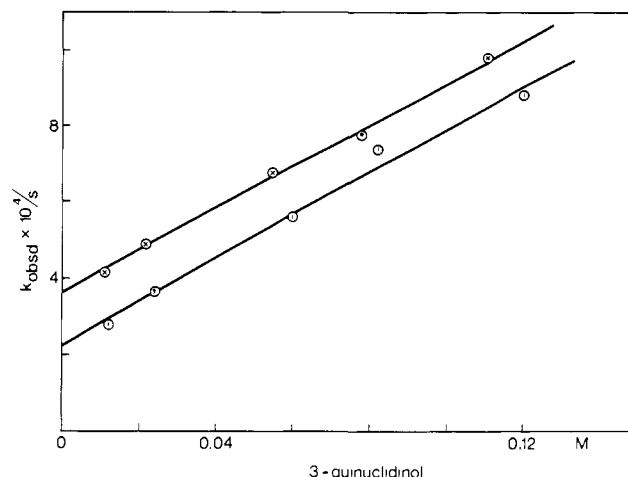
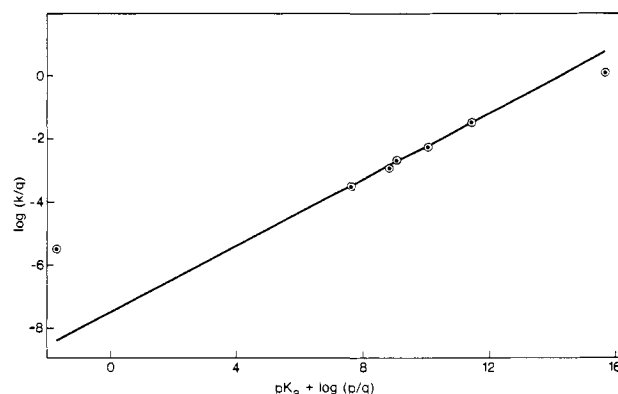
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**Table I.** Rate Constants and Reaction Conditions for the Base-Catalyzed Addition of Water to Triarylmethyl Carbocations<sup>a</sup>

base catalyst (pK)	fraction of free base	10 <sup>3</sup> k, M <sup>-1</sup> s <sup>-1</sup>
<b>MG<sup>b</sup></b>		
hydroxide		760 <sup>c</sup>
deuterioxide		661
quinuclidine (11.5)	0.23	35.7 <sup>d</sup>
3-quinuclidinol (10.1)	0.33, 0.58	5.72
3-chloroquinuclidine (9.20)	0.33	1.92
Dabco (9.20)	0.64	2.66 <sup>e</sup>
2-quinuclidinone (7.53)	0.87	0.305
water <sup>f</sup> (-1.74)		0.176 <sup>g</sup>
<b>NO<sub>2</sub>-MG<sup>b</sup></b>		
hydroxide		1740 <sup>h</sup>
quinuclidine	0.20, 0.33	50.3
3-quinuclidinol	0.50	7.47
carbonate (9.64)	0.33	3.88
3-chloroquinuclidine	0.50	3.62
Dabco	0.33	2.74
3-quinuclidinone	0.75	0.320
water <sup>f</sup>		0.139 <sup>f</sup>
<b>Me-DMA<sup>b</sup></b>		
hydroxide		7600 <sup>i</sup>
quinuclidine	0.20	513
3-quinuclidinol	0.33, 0.50	93.1
Dabco	0.66	51.0 <sup>k</sup>
3-quinuclidinone	0.86	9.07
water <sup>f</sup>		5.30 <sup>f</sup>
<b>MeO-DMA<sup>b</sup></b>		
hydroxide		7200 <sup>m</sup>
quinuclidine	0.20	358
3-quinuclidinol	0.33	68.1
carbonate	0.50	27.0
Dabco	0.33	40.2
3-quinuclidinone	0.86	6.66
water <sup>f</sup>		3.05 <sup>n</sup>
<b>TAM<sup>b</sup></b>		
hydroxide		3890000 <sup>o</sup>
quinuclidine	0.25	315000
3-quinuclidinol	0.66	85100
Dabco	0.66, 0.83	80400 <sup>p</sup>
water <sup>f</sup>		9990 <sup>q</sup>

<sup>a</sup>In aqueous solution at 25 °C and *I* = 1.0 M (KCl). <sup>b</sup>MG is Malachite Green, NO<sub>2</sub>-MG is *p*-nitro-*p*'-bis(dimethylamino)triphenylmethyl cation, Me-DMA is *p*-methyl-*p*'-(dimethylamino)triphenylmethyl cation; MeO-DMA is *p*-methoxy-*p*'-(dimethylamino)triphenylmethyl cation; TAM is trianisylmethyl cation. <sup>c</sup>*k* = 2.18 M<sup>-1</sup> s<sup>-1</sup> at *I* < 0.01 M and 25 °C, ref 52; *k* = 1.60 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.003–0.10 M and 25 °C, ref 53; *k* = 1.36 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.01 M and 25 °C, ref 54; *k* = 1.59 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.01 M and 25 °C, ref 55; *k* = 1.23 M<sup>-1</sup> s<sup>-1</sup> at *I* = 1.0 M and 30 °C, ref 56; *k* = 1.65 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.01 M and 25 °C, ref 57. <sup>d</sup>*k* = 0.042 M<sup>-1</sup> s<sup>-1</sup> at 25 °C, ref 11. <sup>e</sup>*k* = 2.6 × 10<sup>-3</sup> M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.018 M and 25 °C. <sup>f</sup>Rate constant is in units of s<sup>-1</sup>. <sup>g</sup>*k* = 2.11 × 10<sup>-4</sup> s<sup>-1</sup>, ref 52; *k* = 3.8 × 10<sup>-4</sup> s<sup>-1</sup>, ref 54; *k* = 3.8 × 10<sup>-4</sup> s<sup>-1</sup>, ref 56; *k* = 4.8 × 10<sup>-4</sup> s<sup>-1</sup>, ref 57; *k* = 1.08 × 10<sup>-4</sup> s<sup>-1</sup> at *I* = 0.50 M and 20 °C, ref 58. <sup>h</sup>*k* = 5.64 M<sup>-1</sup> s<sup>-1</sup>, at *I* < 0.01 M and 25 °C, ref 11. <sup>i</sup>*k* = 1.80 × 10<sup>-4</sup> s<sup>-1</sup>, ref 11. <sup>j</sup>*k* = 17.9 M<sup>-1</sup> s<sup>-1</sup>, at *I* = 0.01 M and 25 °C, ref 11. <sup>k</sup>*k* = 47 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.04 M and 25 °C, ref 11. <sup>l</sup>*k* = 5.51 × 10<sup>-3</sup> s<sup>-1</sup>, ref 11. <sup>m</sup>*k* = 15.8 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.02 M and 25 °C, ref 11. <sup>n</sup>*k* = 4.60 × 10<sup>-3</sup> s<sup>-1</sup>, ref 11. <sup>o</sup>From ref 14, *I* = 1.0 M NaCl and 25 °C; *k* = 8615 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.013 M and 25 °C, ref 14; *k* = 4600 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.10 M and 30 °C, ref 12. <sup>p</sup>*k* = 62 M<sup>-1</sup> s<sup>-1</sup> at *I* = 0.20 M and 25 °C, ref 9. <sup>q</sup>*k* = 12.0 s<sup>-1</sup> at *I* = 0.05 M and 25 °C, ref 14; *k* = 9.2 s<sup>-1</sup> at *I* = 1.0 M (KCl), ref 14; *k* = 12.9 s<sup>-1</sup> at *I* = 0.10 M and 25 °C, ref 12; *k* = 10.2 s<sup>-1</sup> at *I* = 0.03 M and 25 °C, ref 13; *k* = 12 s<sup>-1</sup> at *I* = 0.20 M and 25 °C, ref 9.

salt effects upon the rate constants for the "water"- or quinuclidine-catalyzed reactions. These effects are in line with the small 25% decrease in the rate constant reported for the "water"-catalyzed reaction of TAM, for a change from *I* = 0.01 to 1.0 M KCl.<sup>14</sup> Our rate constants for the hydroxide ion catalyzed reactions, measured at 1.0 M KCl, are about 2–3-fold smaller than the hydroxide ion rate constants measured in other laboratories, generally at ionic strengths of less than 0.1 M. These salt effects

**Figure 1.** Dependence of  $k_{\text{obsd}}$  on quinuclidinol base concentration for the reaction of Malachite Green, MG, at 25 °C and *I* = 1.0 M (KCl); fraction of free base = 0.58 (x) and 0.33 (j).**Figure 2.** Brønsted plot for the general base catalyzed addition of water to Malachite Green, MG, at 25 °C and *I* = 1.0 M (KCl). The catalysts utilized are listed in Table I; the rate constant and pK of Dabco are statistically corrected.

are consistent with those previously reported.<sup>12,14,16</sup>

In order to avoid kinetic problems that are due to specific salt and medium effects,<sup>12,14,16,17</sup> the buffer concentrations used in the kinetic runs were generally much lower than the concentration of the potassium chloride added to maintain a constant ionic strength of 1.0 M. Plots of  $k_{\text{obsd}}$  against buffer concentration were always linear: there was no indication of curvature in these plots that is expected if specific salt or medium effects were important.

Figure 1 shows that  $k_{\text{obsd}}$  for the reaction of MG with water is directly proportional to the 3-quinuclidinol base concentration and independent of the buffer ratio. This proves that the reaction is general base catalyzed. Similar kinetic plots were obtained for the other carbocations and base catalysts (Table I, plots not shown). Buffer catalysis has been reported previously for the reactions of these substrates.<sup>8–11</sup>

Figure 2 is a Brønsted plot for the general base catalyzed reaction of MG. The rate constant and pK for Dabco are statistically corrected. Similar Brønsted plots were observed for the reactions of the other substrates (plots not shown). The Brønsted  $\beta$  values for the reactions of these carbocations are reported in Table II, along with  $pK_R$  and  $\log k_W$  values for each carbocation.

## Discussion

**General Base Catalysis.** It has been suggested that the most likely mechanism for the buffer-catalyzed reactions of triaryl-

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**Table II.** Brønsted  $\beta$  values,  $pK_{R^+}$  values, and  $\log k_w$  values for Triarylmethyl Carbocations in Water<sup>a</sup>

carbocation	$\beta^b$	$pK_{R^+}$	$\log k_w^c$
MG	0.52	6.94 <sup>d</sup>	-3.75
NO <sub>2</sub> -MG	0.55	5.24 <sup>d</sup>	-3.86
MeO-DMA	0.44	4.86 <sup>f</sup>	-2.51
Me-DMA	0.49	4.40 <sup>d</sup>	-2.27
TAM	0.33	0.82 <sup>e</sup>	1.00

<sup>a</sup> At  $I = 1.0$  M (KCl) and 25 °C. <sup>b</sup> Brønsted  $\beta$  for MG was calculated from the slope of a plot of  $\log k$  against  $pK$  of the base catalyst. The catalysts utilized are listed in Table I; Brønsted  $\beta$  values for the other carbocations were calculated relative to the value for MG by plotting  $\log k_B$  for a given carbocation against  $\log k_B$  for MG with quinuclidine, 3-quinuclidinol, Dabco, and 3-quinuclidinone, which provide a common set of base catalysts. The  $\beta$  value for TAM was calculated in the same way with quinuclidine, 3-quinuclidinol, and Dabco as base catalysts. <sup>c</sup>  $k_w$  is in units of s<sup>-1</sup>. <sup>d</sup> Reference 11. <sup>e</sup> Reference 15.

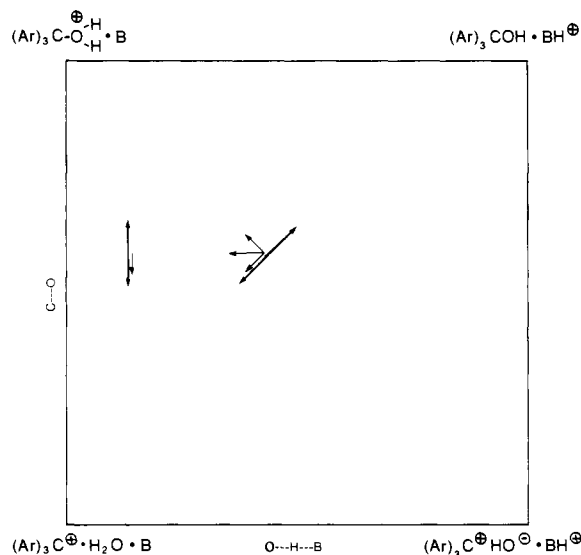
methyl carbocations with water is a concerted mechanism in which proton transfer and carbon-oxygen bond formation occur in a single step.<sup>11</sup> This is confirmed by the results reported here: general base catalysis with  $\beta$  values ranging from 0.33 to 0.57 (Table II).

A concerted mechanism for the reactions of triarylmethyl carbocations may be conveniently described on a More O'Ferrall-Jencks energy diagram (Figure 3).<sup>18,19</sup> In Figure 3 the carbocation and base are located in the lower left-hand corner; proton transfer occurs along the x axis and bond cleavage along the y axis; Brønsted's  $\beta$  value serves as the measure of proton transfer.

Illustrated in the diagram of Figure 3 is a concerted mechanism with a reaction coordinate that has a significant component of both proton transfer and carbon-oxygen bond formation that is consistent with the experimental results. For example, a decrease in the stability of the carbocation will result in raising the energy of the bottom side relative to the top side of the diagram. The effects of this perturbation, both parallel and perpendicular to the reaction coordinate, and the resultant of these effects are shown in Figure 3 and predict the decrease in proton transfer ( $\beta$ ) that is observed (Table II).

The results reported here are also consistent with a vertical reaction coordinate in which the proton that is being transferred lies in a potential well: there is little or no contribution from proton transfer to motion along the reaction coordinate.<sup>20,21</sup> For a vertical reaction coordinate a decrease in the stability of the carbocation should shift the transition state parallel to the reaction coordinate and result in a decrease in carbon-oxygen bond formation (Figure 3). Little or no change is expected, however, in proton transfer. This is because as the substituents in the benzene rings are changed in this series of substrates little or no change is expected in the acidity of the oxonium ion in the upper left-hand corner of the diagram (the sums of the Hammett substituent constants are about the same for all the substrates). It is, nevertheless, difficult to rule out this possibility, because a decrease in carbon-oxygen bond formation should result in a decrease in the acidity of the proton in the transition state. If this decrease in acidity occurs and results in a weaker hydrogen bond to the catalyst, then Brønsted's  $\beta$  value would decrease, consistent with the experimental results.

**The Hydroxide Reactions.** The Brønsted plot of Figure 2 shows that the hydroxide ion falls near the Brønsted line for the reactions of MG—it shows a 3-fold negative deviation. Similar behavior was observed for the other substrates studied in this work. This result confirms previous conclusions that were based on a more limited series of catalysts (Dabco and triethylamine in the case of MG<sup>8</sup> and Dabco, triethylamine, and trimethylamine in the case



**Figure 3.** More O'Ferrall-Jencks energy surface for the addition of water to triarylmethyl carbocations catalyzed by base. Carbon-oxygen bond formation occurs along the y axis and proton transfer, measured by Brønsted  $\beta$  values, along the x axis. Two different reaction coordinates that are consistent with the experimental results are shown: one, near the center of the diagram, has components of both proton transfer and carbon-oxygen bond formation; the other only has a component of carbon-oxygen bond formation—the proton that is being transferred lies in a potential well.

of TAM<sup>9</sup>) that the hydroxide ion follows the Brønsted relationship for the reactions of these carbocations. This result contrasts with results in related systems—systems in which proton transfer and the making and breaking of bonds to heavy atoms occur in a single step—in which the hydroxide ion shows positive deviations of one to five orders of magnitude.<sup>22-27</sup> The positive deviations from the Brønsted relationship that have been observed for the hydroxide ion in related reactions has been interpreted in terms of a change in mechanism: from a concerted general base catalyzed mechanism for the buffer catalyzed reactions, to a specific base catalyzed mechanism for the hydroxide ion reactions in which the hydroxide ion acts as a nucleophile.<sup>3,23</sup> Additional evidence for this interpretation are the large negative values of  $\beta_{1g}$  observed in reactions of this class.<sup>23,30</sup> Furthermore, for reactions of this type which involve the addition or expulsion of a water or alcohol molecule to or from an electrophilic center, hydroxide ion is expected to react nucleophilically because there is little or no thermodynamic driving force for concerted base catalysis.<sup>31,32</sup>

The absence of a positive deviation for the hydroxide ion from the Brønsted relationship in the triarylmethyl carbocation reactions cannot be due to a differential electrostatic effect: a differential electrostatic effect would, relative to quinuclidine catalysts, increase not decrease the hydroxide ion rate constant in these reactions.<sup>33</sup>

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(27) Positive deviations of the hydroxide ion must also exist for the addition of water to the troylum ion<sup>7</sup> and of alcohols to nitro-activated benzenes<sup>28</sup> and 2-phenyl-1,3-dioxolium ion,<sup>29</sup> because positive deviations are observed for the "water"-catalyzed microscopic reverse of these reactions.

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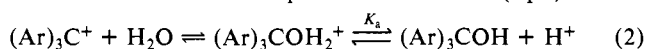
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Furthermore, rate constants for catalysis by the carbonate ion also fall on the Brønsted lines for the reactions of NO<sub>2</sub>-MG and MeO-MG (Table I, plots not shown). This result shows that electrostatic effects are not significant in these reactions and that the Brønsted behavior of the hydroxide ion is not a result of inherently different catalytic powers of nitrogen and oxygen bases. A concerted mechanism for both the hydroxide ion and quinuclidine catalyzed reactions is suggested by the common Brønsted plot in Figure 2. However, a mechanism in which the hydroxide ion stabilizes the transition state by hydrogen bonding via a preassociation mechanism<sup>2</sup> or spectator catalyzed reaction<sup>3</sup> must also be considered because these mechanisms have the advantage of proceeding via an intermediate (the oxonium ion), and thereby avoid the unfavorable transition state of a concerted mechanism in which the hydroxide ion assists nucleophilic attack by water—the rate constant for concerted catalysis by the hydroxide ion could show a negative deviation from the Brønsted relationship. In either case, the behavior of the hydroxide ion in these reactions may be a result of unfavorable solvation of the transition state for the mechanism involving direct nucleophilic attack.<sup>34</sup>

Table I shows that the hydroxide ion reacts 15% faster than deuterioxide ion in the reaction of MG: the solvent isotope effect is  $k(\text{OH}^-)/k(\text{OD}^-) = 1.15$ . This is a surprising result because deuterioxide ion is a stronger base and is generally more reactive than the hydroxide ion.<sup>35,36</sup> This result is consistent with a contribution to the observed isotope effect from a primary isotope effect that is associated with proton transfer in the transition state of a concerted mechanism. It is also, however, consistent with a mechanism involving direct nucleophilic attack, a preassociation mechanism, or spectator catalyzed reaction, since the observed isotope effect of 1.15 may be a composite of a small inverse secondary isotope effect and a normal solvent isotope effect that is due to the failure of transfer isotope effects for the substrate and transition state to cancel.<sup>37</sup>

**The Water Reactions.** Figure 2 shows that the rate constant for the "water"-catalyzed reaction of MG does not obey the Brønsted relationship but instead shows a 800-fold positive deviation. Large positive deviations of the rate constants for the "water"-catalyzed reactions of the other substrates are also observed. This result contrasts with results in related systems in which water either obeys or shows small negative deviations from the Brønsted relationship<sup>5a,25,26,28,38</sup>—these negative deviations are normally due to electrostatic effects.<sup>33,39</sup> A concerted mechanism for the "water"-catalyzed reactions has been previously suggested because rate constants for these reactions do not generally conform to the N<sup>+</sup> equation.<sup>11,41,42</sup> However, the large positive deviations of water from the Brønsted relationship that are observed here are not expected for the concerted mechanism; these deviations may instead reflect a change in mechanism: from a concerted mechanism for the buffer-catalyzed reactions to a stepwise A-1 mechanism for the "water"-catalyzed reactions—rate-limiting formation of an oxonium ion intermediate corresponds to an A-1 mechanism in the microscopic reverse direction (eq 2).



A p*K* value of -4.3 can be estimated for protonated triphenylmethyl carbinol based on a  $\rho^*$  value of -1.3, a  $\sigma^*$  value of 0.60 for the phenyl group,<sup>43</sup> and a p*K* of -1.94 for protonated

ethanol.<sup>44</sup> The  $\rho^*$  value of -1.3<sup>45</sup> is based on a value of -3.2 for the ionization of ammonium ions (XNHRR'),<sup>47</sup> assuming that  $\rho^*$  is the same for oxonium and ammonium ions,<sup>48</sup> and corrected by a factor of 2.5 for transmission of the substituent effect through an additional carbon atom.<sup>49</sup> A p*K* of -3.8 can be calculated for MG based on the value of -4.3 for triphenylmethyl carbinol, a  $\sigma^*$  value of -0.22 for the dimethylamino group,<sup>43</sup> and a Hammett  $\rho$  value of 1. On the basis of this p*K* value, a p*K*<sub>R<sup>+</sup></sub> of 7.0 for MG,<sup>11</sup> and a rate constant for attack of water on the carbocation of  $1.39 \times 10^{-4} \text{ s}^{-1}$  (Table I) a value of  $8.8 \times 10^6 \text{ s}^{-1}$  is calculated for the breakdown of the oxonium ion to give the carbocation. Similarly, a rate constant of  $1.4 \times 10^4 \text{ s}^{-1}$  is calculated for the breakdown of the oxonium ion derived from TAM (p*K*<sub>R<sup>+</sup></sub> = 0.82<sup>15</sup>). Rate constants intermediate between those for MG and TAM are calculated for carbocations of intermediate stabilities.

**The Range of Buffer Catalysis.** The small negative deviation for the hydroxide ion and the positive deviation for the water reaction from the Brønsted relationship are opposite what is normally observed in concerted reactions of this type (vide supra). These deviations mean that catalysis of these reactions will be easier to detect the stronger the base catalyst; in the microscopic reverse direction they mean that acid catalysis of the decomposition reactions will be easier to detect the weaker the acid catalyst.

Catalysis by buffer species will be observed only if they compete effectively with the reactions catalyzed by solvent species.<sup>50</sup> For base-catalyzed reactions this depends on the value of the Brønsted coefficient, as well as the relative values of the rate constants for the hydroxide ion, "water", and buffer catalyzed reactions.<sup>50</sup> For base catalyzed reactions the contribution to  $k_{\text{obsd}}$  from a hydroxide ion catalyzed reaction is  $\log k_{\text{OH}^-} = \log k_{\text{OH}^-}(1.0) - 14 + \text{pH}$ , in which  $\log k_{\text{OH}^-}$  is the second-order rate constant for the hydroxide ion catalyzed reaction, 1.0 is the hydroxide ion concentration (mol/L) at pH 14, and  $\log k_{\text{OH}^-}$  is the contribution to the observed rate constant from the hydroxide ion catalyzed pathway. The contribution to  $k_{\text{obsd}}$  from buffer base catalyzed pathways is described, in turn, by the Brønsted relationship  $\log k_B = \beta(\text{p}K) + C$ , in which  $\log k_B$  is the second-order rate constant for the buffer-catalyzed reaction. Since  $\log(k_{\text{OH}^-})_{\text{calcd}} = \log k_{\text{OH}^-} + D = 15.7\beta + C$ , then  $\log k_B = \beta\text{p}K + \log k_{\text{OH}^-} + D - 15.7\beta$ , in which  $D$  is the deviation of the hydroxide ion rate constant from the Brønsted relationship (positive for negative deviations and negative for positive deviations),  $\log(k_{\text{OH}^-})_{\text{calcd}}$  is the hydroxide ion second-order rate constant calculated from the Brønsted relationship, and 15.7 is the p*K* of water. If we assume that a 50% increase in  $k_{\text{obsd}}$  due to buffer catalysis is detectable, and if we limit ourselves to solutions in which the fraction of the buffer in the free base form is 0.5 (1.0 M base), then the pH values at which the rate of the buffer catalyzed reactions equal the rate of the hydroxide ion and water catalyzed reactions, respectively, define and approximate p*K* range in which buffer catalysis can be observed for any given reaction (eq 3 and 4). In these equations,<sup>51</sup>

$$\text{p}K_{\text{high}} = (15.7\beta - 14 - D)/(\beta - 1) \quad (3)$$

$$\text{p}K_{\text{low}} = (\log(k_W/k_{\text{OH}^-})/\beta) - (D/\beta) + 15.7 \quad (4)$$

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$pK_{\text{high}}$  and  $pK_{\text{low}}$  are the highest and lowest  $pK$  values, in the range of  $pK$  values in which catalysis may be observed. For example, for the reaction of MG,  $D = 0.55$ ,  $\beta = 0.53$ , and  $\log(k_{\text{W}}/k_{\text{OH}}) = -3.85$ . Therefore,  $pK_{\text{high}} = 13.3$  and  $pK_{\text{low}} = 7.4$ . This  $pK$  range is consistent with the fact that buffer catalysis is only barely detectable with 3-quinuclidinone which has a  $pK$  of 7.5. Furthermore, these results also explain why the early attempts to find general acid-base catalysis in these reactions with acetate buffer solutions ( $pK = 4.75$ ) proved unsuccessful.<sup>12-14</sup>

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## On the Incidence of Internal Ion Pair Return during Solvolysis of *sec*-Alkyl Benzenesulfonates<sup>1</sup>

Cristina Paradisi<sup>2</sup> and Joseph F. Bunnett\*

Contribution from the University of California, Santa Cruz, California 95064.

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**Abstract:** For solvolyses of four *sec*-alkyl benzenesulfonates, in which the alkyl group is isopropyl (**1**), cyclopentyl (**2**), 2-adamantyl (**3**), and 3,3-dimethyl-2-butyl (**4**), in  $\text{CF}_3\text{COOH}$  and selected other solvents, overall solvolysis rates and rates of equilibration of excess oxygen-18, originally in sulfonyl sites, between alkoxy and sulfonyl sites in unsolvolyzed ester have been determined. An improved method for oxygen-18 analysis has been developed; it reports the  $^{18}\text{O}$  content in both the alkoxy and sulfonyl moieties and is much simpler to employ than methods previously used. On the assumption that oxygen equilibration occurs via internal return from intimate ion pairs, the results indicate internal return to be extensive (>53%) in the case of **3** in three solvents, significant but of lesser magnitude for **1** and **2**, and undetectable in the case of **4**. These results oblige reinterpretation of solvolysis rate correlations that have been based on the premise that 2-adamantyl *p*-toluenesulfonate solvolyzes with rate-determining ionization. Questions concerning the nature of intimate ion pair intermediates are examined.

The solvolysis of *sec*-alkyl arenesulfonates in protic solvents such as water, alcohols, or carboxylic acids is indicated by many lines of evidence to occur via ionic intermediates with the probable concurrence in some cases of direct nucleophilic participation by the solvent.<sup>3-7</sup>

Ionization of an alkyl arenesulfonate forms a carbocation and an arenesulfonate ion, initially as an intimate (or contact, or tight) ion pair. The two ions may then partially separate to form a loose or solvent-separated ion pair, and the latter may dissociate to free ions.<sup>4,7</sup>

Much attention has been given to how much "internal return", to regenerate the substrate, occurs from the intimate or tight ion

pair first formed by heterolysis. Such internal return may conceivably occur whether the carbocation is bare or "nucleophilically solvated".<sup>5</sup> Several kinds of evidence have shown that ion pair solvolysis intermediates may revert to the original substrates,<sup>4</sup> but most of the substrates involved were such as to afford carbocations, such as allylic carbenium ions, with significant stabilizing features, and much of the "return" revealed was from solvent-separated or even dissociated ion pairs.

Solvolyses of plain *sec*-alkyl halides and arenesulfonates have some characteristics suggestive of ionic intermediates, for example, strong kinetic dependence on the polarity of solvents and on polar effects of substituents. Much of what we understand of the mechanism of solvolysis of *sec*-alkyl arenesulfonates has been inferred on the basis of indirect criteria such as kinetic isotope effects<sup>10,11</sup> and reactivity correlations,<sup>5,12-14</sup> but many of the inferences made have failed to win general acceptance.

In these circumstances it is curious that sparse use has been made of what "is probably the single most powerful tool for the detection of ion pairs in solvolysis reactions", namely, oxygen isotope scrambling in the substrate during solvolysis of a sulfonate

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