

REACTION OF THE TRIANISYLMETHYL CATION WITH  
WATER, HYDROXIDE AND AMMONIA

E. Alexander Hill and William J. Mueller

Departments of Chemistry, University of Minnesota, Minneapolis, Minnesota,  
and University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

(Received in USA 27 December 1967; accepted for publication 19 February 1968)

Important insight into the chemistry of carbonium ions has been gained through equilibrium studies of carbonium ion stability and kinetic studies of nucleophilic substitution reactions. However, there have been relatively few rate studies of the reactions of carbonium ions themselves, particularly the rapid reactions with water and stronger nucleophiles. The present literature in this area is largely limited to reactions of the more highly stabilized amino-substituted triarylmethane dyes<sup>1</sup>, and a recent study by Diffenbach, Sano and Taft<sup>2</sup>, which included p-methoxy-substituted triarylmethyl cations.

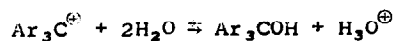
We wish to present preliminary results of our study of the reaction of the tri-p-anisylmethyl cation with water, hydroxide and ammonia using stopped flow techniques. Rate constants for the above reactions are shown in Table I. Experiments were performed by neutralizing an aqueous acid solution of the partially ionized carbinol (about 0.2M in acid and  $5 \times 10^{-6}$ M carbinol) with the appropriate base. For the reactions with water, neutralization was with acetate or formate. (Excess carboxylate or carboxylic acid was shown to have little effect on the rate.) Despite differences in the extraneous solutes present, the comparison of rates appears valid. Relative rates are not correlated by the basicity of the nucleophiles, but appear consistent with reasonable contributions from both basicity and polarizability of the nucleophile<sup>3</sup>.

**Table 1**  
**Rates of Reaction of Triarylmethyl Cation with Nucleophiles**

<u>Nucleophile</u>	<u>T<sup>o</sup></u>	<u>k<sub>1</sub> sec<sup>-1</sup></u>	<sup>a</sup> <u>k<sub>2</sub>(M<sup>-1</sup>sec<sup>-1</sup>)</u>
H <sub>2</sub> O <sup>b</sup>	25 <sup>o</sup>	12.9 <sub>+2</sub>	
	29 <sup>o</sup>	15.2 <sub>+0.3</sub>	0.28
	34 <sup>o</sup>	18.1 <sub>+0.8</sub>	
	39 <sup>o</sup>	23.1 <sub>+0.9</sub>	
OH <sup>-c</sup>	30 <sup>o</sup>		(4.6 <sub>+3</sub> )x10 <sup>3</sup>
NH <sub>3</sub> <sup>d</sup>	30 <sup>o</sup>		(2.1 <sub>+0.2</sub> )x10 <sup>3</sup>

a. Second order rate constant. Calculated for water as 55 M. b. 0.10 M HCOOH, 0.10 M NaClO<sub>4</sub>; ΔH<sup>‡</sup> = 7.1<sub>+1.0</sub> Kcal/mole, ΔS<sup>‡</sup> = 28<sub>+3</sub> e.u. c. 0.10 M NaClO<sub>4</sub>, 0.021-0.053 M NaOH. d. 0.10 M NH<sub>4</sub>ClO<sub>4</sub>, 0.081-0.176 M NH<sub>3</sub>.

In the reaction of a carbonium ion with water, it is generally implicitly assumed that the rate-determining step is coordination of the ion to water, and that proton loss is a subsequent rapid occurrence. In the current instance, we present direct evidence that such is the case. From the fractionation factor for proton and deuteron between water and hydronium ion<sup>4</sup>, the predicted isotope effect  $K_H/K_D$  for the equilibrium:



reduces approximately to:

$$\frac{K_H}{K_D} \approx \frac{[\text{>O}^{(+) - \text{H}}]^3 [\text{-OD}]^3}{[\text{>O}^{(+) - \text{D}}]^3 [\text{-OH}]^3} \approx \left(\frac{1}{1}\right)^3 \approx \left(\frac{1}{0.7}\right)^3 = 2.9$$

We observe a value of 2.7. A similar calculation for the rate, assuming that the transition state resembles protonated alcohol, leads to a solvent secondary isotope effect of 2.0, and inclusion of any primary isotope effect due to rate-determining proton transfer would increase this value. However, the observed  $K_H/K_D = 1.2$  is much smaller, leading to the conclusion that coordination with water must be rate determining. The transition state is not far displaced from the starting state along the reaction coordinate, at least in so far as bonding of the protons is concerned. (Alternatively, the protonated carbinol might be sterically prevented from hydrogen bonding, making its hydrogen frequencies atypical of an  $-O^+H_2$ .)

The effects of added salts upon the reactions with water and hydroxide were examined, and are shown in fig. 1. The lowest salt concentration is above the customary range of quantitative treatments, but the effect is in the expected direction for reaction between the oppositely charged hydroxide and carbonium ions. However, the effects of sodium perchlorate on the water and hydroxide reactions are very similar, despite the difference in charge type, and quite specific to the salt used. Qualitatively, the effect on the water reaction may be in the expected direction. If the transition state resembles an anilinium ion in its activity coefficient behavior<sup>5</sup>, increasing electrolyte concentration should destabilize it relative to the carbonium ion. The rate of reaction of the trianisylmethyl cation with water is also sensitive to solvent. In 50% acetone, the rate increases over that in water by a factor of about three ( $k_1 = 42 \pm 3 \text{ sec}^{-1}$  at  $26.5^\circ$ ). The rate increase may result specifically from a breakdown of the water structure, which increases the availability of water molecules, or more generally to the parallel between effects of increased ionic strength and solvent polarity on rates of ionic reaction.

In figure 2, we present the results of a brief study of the rates of hydride abstraction from isopropanol by the trityl cation and its three p-methoxylated analogs (obtained in a manner similar to those of Bartlett

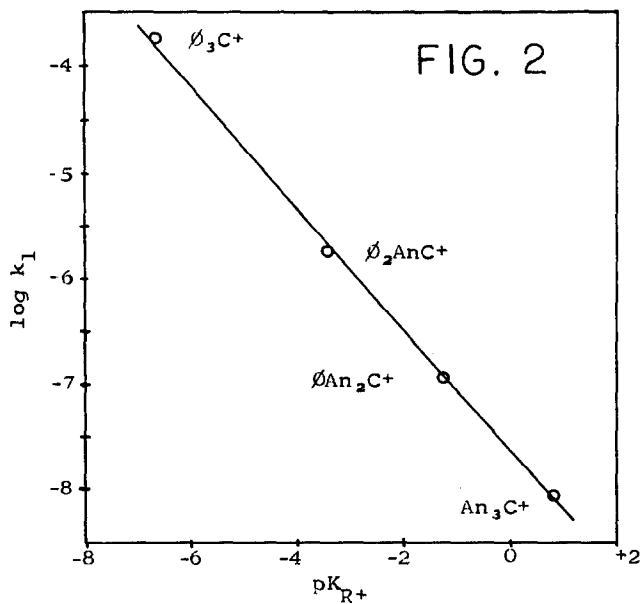
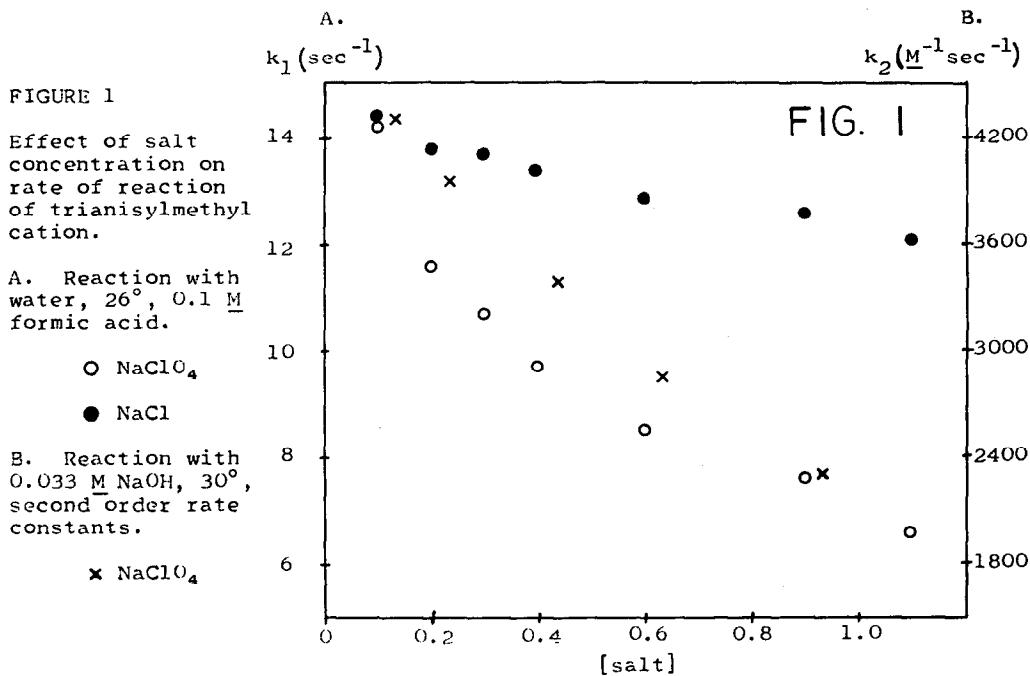


FIGURE 2

Rate vs.  $pK_{R^+}$  for reaction of para-methoxy trityl cations with 0.525 M isopropanol in 53% sulfuric acid at 25°. First order rate constants are given due to uncertainty as to degree of protonation of isopropanol.

and McCollum<sup>6</sup>). The good linear plot of slope 0.58 vs. pKa of the carbonium ion is similar to that which has been observed for phenylated trityl cations<sup>7</sup>. Taft and co-workers have found a correlation of similar slope between stability of the methoxylated trityl cations and their reaction rates with water<sup>2</sup>. Thus there appears to be a fairly precise linear correlation between rates of these two carbonium ion reactions, with quite similar dependences upon carbonium ion structure, despite the enormous difference in absolute rates of the two processes.

ACKNOWLEDGEMENT: We are indebted to the National Science Foundation for support of this research, and to Professor Rufus Lumry for use of his stopped flow apparatus.

#### REFERENCES

1. E. F. J. Duynstee and E. Grunwald, J. Am. Chem. Soc., 81, 4542(1959); C. D. Ritchie, G. A. Skinner and V. G. Badding, ibid., 89, 2063 (1967); R. Cigen, Acta Chem. Scand., 15, 1892(1961)
2. R. A. Diffenbach, K. Sano and R. W. Taft, J. Am. Chem. Soc., 88, 4747(1966)
3. J. O. Edwards, ibid., 76, 1540(1954)
4. C. G. Swain, R. F. W. Bader and E. R. Thornton, Tetrahedron, 10, 182 (1960)
5. R. H. Boyd, J. Am. Chem. Soc., 85, 1555(1963)
6. P. D. Bartlett and J. D. McCollum, ibid., 78, 1441(1956)
7. R. Grinter and S. F. Mason, Trans. Faraday Soc., 60, 497, 889(1964)