obtained with *t*-butyl chloride. The choice of reference compound may be dictated by the nature of the experimental system of interest.

Experimental Section

Purification of Chemicals. 1-Adamantyl Bromide. Commercial 1-adamantyl bromide (Aldrich) was sublimed at 105 (10 mm) and 95° (0.15 mm), and was then recrystallized from pentane at −80°, mp 118.8–119.2° (lit. 119–120°).[23]

Ethanol. Ethanol was distilled from magnesium ethoxide as described by Lund and Bjerrum.[24]

Methanol. Methanol was distilled from magnesium methoxide as described by Lund and Bjerrum.[24]

Acetone. Commercial acetone was allowed to reflux with potassium permanganate, dried with Drierite, and distilled through a 24-in. Vigreux column.[25]

Dioxane. Dioxane was purified by the method of Fieser.[25] The purified solvent was stored over sodium and distilled shortly before use.

Formic Acid. The crude formic acid (Eastman, 97%) was stirred with an excess of boric anhydride for 1 week and distilled through a 24-in. Vigreux column, bp 33–34° (45 mm).[26]

Acetic Acid. Glacial acetic acid (1 l.) was refluxed with 100 ml of acetic anhydride and several milliliters of concentrated sulfuric acid. The dry acetic acid was then distilled under nitrogen through a 24-in. vacuum-jacketed column packed with glass helixes, bp 118° (1 atm).

Trifluoroethanol. Commercial 2,2,2-trifluoroethanol (Matheson Colemen and Bell) was distilled from aqueous potassium carbonate, dried with phosphorus pentoxide, and fractionally distilled through a 24-in. vacuum-jacketed column packed with glass helixes, bp 73.5–74.5°.[18]

Kinetic Methods. Rates in the aqueous solvents were determined conductometrically with a Wayne-Kerr Model B331 Impedence Bridge, capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants of 0.2–0.4, and a volume of approximately 25 ml. In a typical experiment, enough 1-adamantyl bromide to make a 10^{-3} *M* solution was placed in the conductivity cell and 20 ml of solvent was added. The cell was then sealed and equilibrated with stirring for 5 min in the constant temperature bath. The usual number of measurements taken was 12. The raw conductance data were then fitted to the first-order rate equation by means of a least-squares computer program. The solvents used for conductivity measurements give linear conductivity–concentration plots within the limits of experimental error;[27] a possible exception to this may be 80% dioxane in which the rates obtained conductometrically were faster than the titrimetric rates by almost a factor of two. The titrimetric rate constant was used for analysis of the data.

Rate constants in acetic acid and formic acid were determined by Volhard titration of hydrogen bromide, preceded by extraction of unreacted 1-adamantyl bromide as described by Winstein and Fainberg.[3c] This method was also used to check the conductometric measurements in 97% trifluoroethanol at 25°.

Acknowledgment. We thank Dr. T. W. Bentley for helpful discussions.

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The Reaction of Trityl Carbonium Ion with Water

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Abstract: The reversible reaction of trityl fluoroborate with water in acetonitrile solvent has been studied using nmr line broadening. The reaction is moderately fast on the nmr time scale ($\tau \approx 10^{-2}$ sec, 0.1 *M* cation and water) at room temperature and is approximately first order in water and zero order in cation under these conditions. The kinetic results and ^{19}F nmr studies are consistent with a model involving extensive aggregation.

The rate constants for attack of nucleophiles on carbonium ions are of considerable interest. Since in many carbonium ion reactions, relative rates such as the ratio of attack of solvent to ion-pair return or internal rotation are known,[2] the measurement of an absolute rate would generate a great deal of useful information. For the most part, owing to the high reactivity of carbonium ions, such direct measurements have been limited to relatively stable species such as highly substituted trityl ions. Early work by Grunwald[3] and Turgeon and LaMer[4] established the rates of attack of water and hydroxide ion in aqueous media on crystal violet and closely related derivatives. These reactions were slow (k_1 *ca.* 10^{-4} sec^{-1}) and could be followed by conventional spectroscopic means. More recently, the development of stopped-flow techniques has made measurement of faster reactions accessible. Taft[5] has measured the rates of reactions of a series of substituted trityl ions with water. Pseudo-first-order rate constants as rapid as 10^3 sec^{-1} were recorded for the mono-*p*-methoxytrityl cation. Ritchie[6] has studied the rates of attack on crystal violet and related ions by a large number of nucleophiles both in aqueous and nonaqueous media. Again, rapid rates were observed, especially in the nonaqueous systems. Hill[7] has recently measured the rates of reaction of water, ammonia, and hydroxide ion with tris-*p*-methoxytrityl cation by stopped flow. Nicholson and Wyatt[8] also measured

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(1) (a) Alfred P. Sloan Foundation Fellow; (b) NDEA Title IV Graduate Fellow, 1967–1969; NIH Predoctoral Fellow, 1969–1970.

(2) For a general review, see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1968.

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the rate of reaction of water with this ion in aqueous dioxane. These results are consistent with the others reported.

It would be valuable to extend the rate measurements to more reactive carbonium ions in order to obtain numbers more relevant to chemical systems usually encountered in the laboratory. Noyce and Brauman[9] have estimated an upper limit on the second-order rate constant for attack of water on a monoarylmethyl cation to be *ca.* $2 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. Winstein[10] has estimated the first-order collapse of trityl cation in water to be $10^5\ \text{sec}^{-1}$ ($2 \times 10^3\ M^{-1}\ \text{sec}^{-1}$, second order). In this paper, we now report a direct measurement by nmr line-broadening techniques of the rate of reaction of D_2O with trityl cation under equilibrium conditions in acetonitrile.

Preliminary observations which led us to believe that such a measurement might be possible were the following: solutions of either 1,2,5,6-dibenzocyclohepta-1,3,5-trien-7-ol or triphenylcarbinol in acetic acid exhibited normal nmr spectra. However, when incremental amounts of strong acids such as trifluoroacetic or sulfuric acid were added, the carbinol lines broadened, collapsed, moved downfield, and finally sharpened up into the spectrum of the corresponding carbonium ion. These results are consistent with reaction 1 proceeding at

$$ROH + H^+ \rightleftarrows R^+ + H_2O \qquad (1)$$

a rate sufficient to cause averaging of the carbinol and cation spectra on the nmr timescale.

Line-broadened spectra contain information on chemical lifetimes and hence on rate constants, but analysis of the above reactions is complex because of the difficulty of determining the exact nature of the nucleophile (water, acetic acid, etc.). A system more amenable to study is trityl fluoroborate in acetonitrile (MeCN). In this case, added water caused broadening of the sharp cation lines; consequently we chose this system for quantitative work.

Experimental Section

Nmr Spectra. All nmr spectra were taken in acetonitrile and were recorded on a Varian A-60 nmr spectrometer fitted with a V-6040 variable temperature controller. Chemical shifts were measured *vs.* methylene chloride or tetramethylsilane as internal frequency standards. Care was taken at all times to adjust the rf power so that no saturation occurred during integration or line-width measurements. The temperature of the probe was measured using the observed chemical-shift difference in methanol.[11]

Solvents. Acetonitrile (Matheson Coleman and Bell, reagent grade or spectroquality) was distilled from phosphorous pentoxide and was used without further purification. Ethyl acetate (Baker and Adamson, anhydrous reagent) was used directly. Propionic anhydride (MCB, Practical) was distilled prior to use.

Aniline-2,4,6-d_3 was prepared by the method of Streitwieser and Klein;[12] deuterium incorporation was monitored by nmr. This material was converted *via* the Sandmeyer reaction[13] to **bromobenzene-2,4,6-d_3**, bp 155–157°. Bromobenzene-2,4,6-d_3 was converted through its Grignard followed by reaction with diethyl carbonate to **tri(phenyl-2,4,6-d_3)carbinol**[14] and recrystallized several times from 95% ethanol, mp 161–162° (lit.[14] mp 161–162°. The carbinol had a broad (2.8 Hz) singlet, 148 Hz downfield from CH_2Cl_2, and a sharp singlet 71 Hz upfield from CH_2Cl_2 (area 6:1). The deuterium content in the *ortho* and *para* positions was taken to be greater than 95% based on the nmr spectrum of the cation. In the hydrogen compound the peaks are clearly visible.[15]

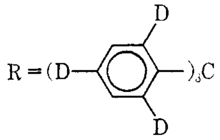
Trityl Fluoroborate. Samples of the deuterated trityl fluoroborate were prepared by the method of Dauben.[16] In a typical experiment, 500 mg of triphenylcarbinol-d_9 was dissolved in 7 ml of propionic anhydride in a Schlenk-tube apparatus where all operations could be carried out under nitrogen. This solution was cooled in a water bath, and to it was added slowly 0.5 ml of 48% HBF_4 (with stirring). The precipitated salt was filtered, washed three times with dry ethyl acetate, and the wash was removed by filtration and pumping at reduced pressure for several hours. Samples of fluoroborate prepared in this manner were yellow-orange in color; no further attempts were made to purify them. For actual kinetic runs the trityl fluoroborate was transferred to tightly capped nmr tubes either under a nitrogen atmosphere or directly in the air, with no significant difference in results. Acetonitrile solutions were stable for several days.

Nmr Measurements. A freshly prepared sample of trityl fluoroborate was weighed by difference into an nmr tube, dry acetonitrile was added, and the total volume was measured. The width at half-height and the chemical shift of the cation were determined. Successive amounts of D_2O were added by microliter syringe, the exact amount determined by weighing the tube, and the spectra were recorded. Finally, sufficient D_2O was added to quench the cation completely, and the width at half-height and chemical shift of the carbinol were determined. Results were reproducible and did not change with time. Thus, during the course of the experiment, hydrolysis of acetonitrile apparently did not occur. Kolthoff and Chantooni found no evidence for hydrolysis under their rather similar conditions.[17]

Results

In order to be able to vary parameters systematically while knowing which nucleophile was present, quantitative studies were carried out on reaction 2 in MeCN. The species indicated in eq 2 are formal ones—the actual species present may be quite different (see later).

$$R^+BF_4^- + D_2O \rightleftharpoons ROD + D^+BF_4^- \qquad (2)$$



The *ortho,para*-deuterated compound was chosen in order to simplify the nmr spectra. There is reason to believe[12,18] that substitution of deuterium will have a negligible effect on rates and equilibria. D_2O was used for quantitative experiments in preference to H_2O also for simplification of the spectra. While there is, presumably, an isotope effect introduced in this way, it is likely not to be large,[7] and in any case will not affect the primary conclusions.

Some spectra of solutions of R^+ in MeCN with varying amounts of D_2O added are shown in Figure 1. Note that the initial, sharp, cation resonance broadens, shifts upfield, and ultimately sharpens into the final, carbinol resonance.

The temperature dependence of the spectra of R^+ in MeCN with added D_2O is shown in Figure 2. The

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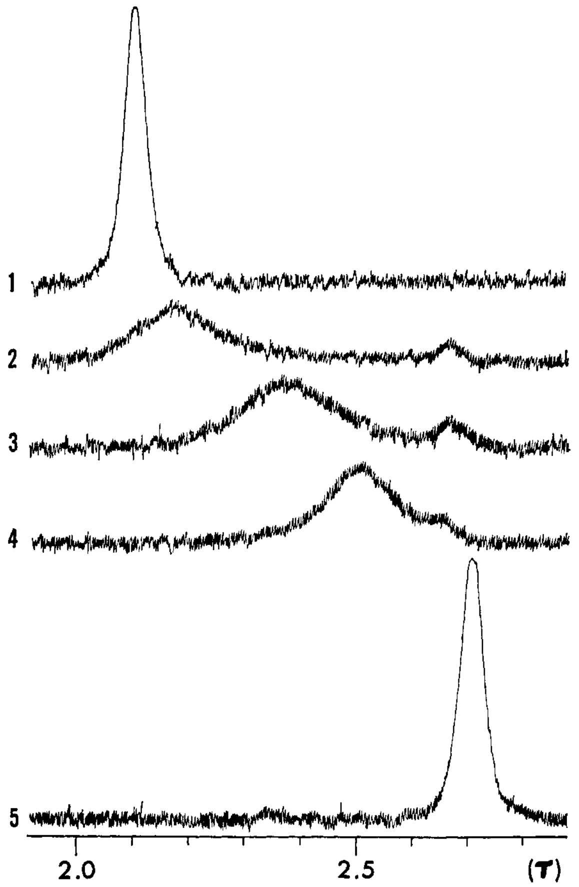

Figure 1. (1) Nmr spectrum of $R^+BF_4^-$ in MeCN. (2–4) Spectra of 1 with added increments of D_2O. (5) Spectra of 1 with excess D_2O added to quench cation; normal sharp resonance of ROD.

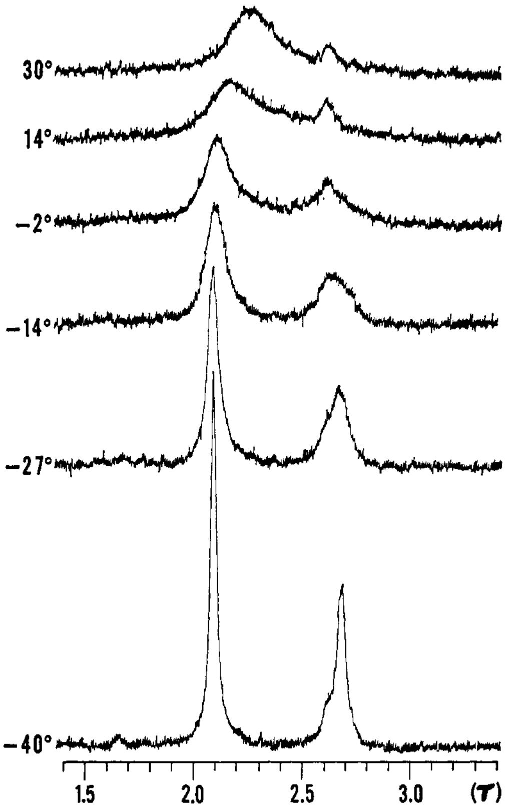

Figure 2. Temperature dependence of the nmr spectrum of $R^+BF_4^-$ in MeCN containing added D_2O.

broadened signal is observed to split (~10°), and the component signals move apart and sharpen into the cation and carbinol resonances (~−40°). The implication of these results is that reaction 2 is occurring at the probe temperature, 35°, at a rate sufficient to cause time averaging.

Inspection of the spectra always revealed the presence of an additional peak at approximately the resonance of the carbinol (see Figures 1 and 2). It is believed that this peak is due to the bistrityl ether,[19] formed in equilibrium with the cation and carbinol, eq 3. The nmr spec-

$$R^+ + \mathrm{ROD} \rightleftharpoons \mathrm{ROR} + D^+ \qquad (3)$$

trum of a solution prepared by dissolving an authentic sample[20] of the ether in acetonitrile acidified with concentrated sulfuric acid showed two peaks: one sharp unresolved multiplet appearing at approximately the chemical shift of the small peak visible in Figures 1 and 2, and a broad signal further downfield. Addition of more sulfuric acid to this solution caused a decrease in the size of the sharp multiplet and a further shift of the downfield signal accompanied by sharpening of this signal. When enough acid was added, the broad signal was seen to sharpen into the spectrum of the cation, while the upfield signal disappeared entirely. This behavior of the ether is consistent with the equilibrium shown in eq 3 and suggests very strongly that the small peak visible in aqueous solutions of trityl fluoroborate is in fact the bistrityl ether. At any rate, the small area of this peak and its small amount of broadening require that the species responsible for this resonance cannot contribute appreciably to the broadening experienced by the cation and carbinol. Conservatively, we estimate the contribution at less than 1%.

Quantitative information about rates and formal concentrations of the species present may be derived from the nmr spectra. The relative concentrations of ether and R^+ + ROD can be determined by integration of the peaks. The relative proportions of R^+ and ROD are obtained[21] from eq 4, where ω_c is the chemical shift

$$\omega_c = P_{R^+}\omega_{R^+} + P_{\mathrm{ROD}}\omega_{\mathrm{ROD}} \qquad (4)$$

of the coalesced peak and ω_{R^+}, P_{R^+}, ω_{ROD}, and P_{ROD} are the chemical shift and fraction of cation and carbinol, respectively. Given the initial concentrations, it is then possible to calculate the formal equilibrium concentrations of R^+, ROD, ROR, D_2O, and D^+ by simple material and charge balance. These concentrations for a selected series of experiments are shown in Table I.

It is possible to obtain rate information[21] in the region of rapid exchange from eq 5 and 6 where $1/T_2'$ is the

$$\frac{1}{T_2'} = \frac{P_{R^+}}{T_2^{R^+}} + \frac{P_{\mathrm{ROD}}}{T_2^{\mathrm{ROD}}} + P_{R^+}{}^2P_{\mathrm{ROD}}{}^2(\omega_{R^+} - \omega_{\mathrm{ROD}})^2(\tau_{R^+} + \tau_{\mathrm{ROH}}) \qquad (5)$$

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[19] The ether has low solubility in MeCN, although in our system the solubility is enhanced by the presence of acid. In $CDCl_3$ the ether appears as a complex multiplet centered *ca.* 0.1 ppm upfield from the carbinol which exhibits a single sharp line. A thin layer chromatogram of a solution of cation and carbinol contains the ether as shown by comparison with an authentic sample.[20]

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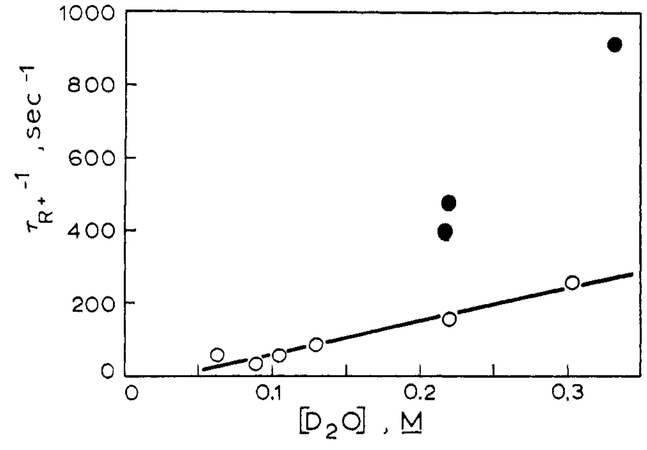

Figure 3. "First-order" plot for the reaction of $R^+BF_4^-$ with D_2O. Least-squares line does not include points for runs 5, 8, and 9 (solid circles).

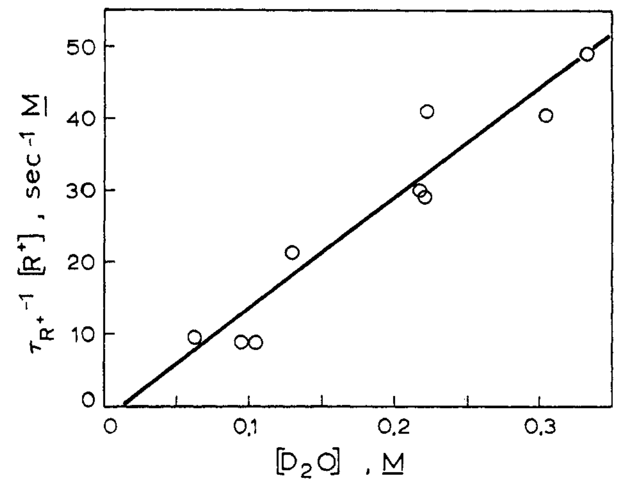

Figure 4. "Zero-order" plot for the reaction of $R^+BF_4^-$ with D_2O.

$$\frac{\tau_{R^+}}{\tau_{ROD}} = \frac{P_{R^+}}{P_{ROD}} \qquad (6)$$

half-width at half-height of the coalesced peak, $1/T_2$ is the half-width in the absence of exchange, and τ is the mean lifetime. The values of $\tau_{R^+}^{-1}$ are given in Table I. The complete line shape was also computed by using the full line-shape equation, and values of τ obtained in this way agreed satisfactorily.

Table I. Formal Concentrations and Lifetimes[a]

Run	[R$^+$]	[ROD]	[ROR]	[D$_2$O]	[D$^+$]	$\tau_{R^+}^{-1}$
1	0.176	0.036	0.011	0.063	0.058	55
2	0.296	0.040	0.016	0.089	0.072	31
3	0.167	0.050	0.011	0.105	0.072	55
4	0.245	0.088	0.017	0.129	0.123	87
5	0.075	0.145	0.007	0.217	0.159	400
6	0.185	0.130	0.027	0.219	0.183	156
7	0.158	0.141	0.034	0.303	0.210	256
8	0.078	0.150	0.006	0.219	0.163	526
9	0.054	0.183		0.332	0.183	910

[a] Concentrations in M, τ^{-1} in sec^{-1}.

Rate Constants. In order to derive rate constants it is necessary to know the rate law. In general, for a reaction with rate = $kA^aB^bC^c\cdots$, $\tau_A^{-1} = kA^{a-1}B^bC^c\cdots$. If we assume that the reaction of cation with water is first order each in D_2O and R^+, then a plot of $\tau_{R^+}^{-1}$ *vs.* [D_2O] should give a straight line with slope k. Such a plot is shown in Figure 3. It is clear from the plot that points at about 0.2 M R^+ lie on a line of slope k = 900 M^{-1} sec^{-1} while those between 0.05 and 0.1 M are considerably faster. This suggests that the reaction is first order in D_2O and less than first order in R^+.

If we assume the reaction is first order in D_2O, we can compute an apparent second-order rate constant for eq 2 as $k_2' = (\tau_{R^+}[D_2O])^{-1}$. Then, since $k_2' = k[R^+]^{a-1}$, a plot of log k_2' *vs.* log [R^+] should give a line of slope $a - 1$. Such a plot is reasonably good and has a slope approximately equal to -1. Thus, the reaction is approximately zero order in R^+ at these concentrations. A zero-order plot of the data is shown in Figure 4. This plot accommodates the data rather well, giving a rate constant of *ca.* 150 sec^{-1}. If the data are plotted in other ways, for example half-order in cation, the fits are considerably worse than that for zero order in cation. In addition, the zero-order plot extrapolates to a rate of zero at zero water concentration, whereas the other plots do not. It should be stressed that the conclusion that the reaction is less than first order in cation can be drawn directly from the data without recourse to any kinetic treatment. Thus, runs 5, 6, and 8 make it clear that, as other concentrations are held constant, the measured lifetime of R^+ (which would be independent of R^+ concentration if first order in R^+) increases as the R^+ concentration increases. That is, R^+ actually reacts more rapidly at lower concentrations.

From the temperature dependence of the spectra, an estimate of the activation energy of *ca.* 6.5 kcal/mol can be made.

Discussion

The results obtained in this work describe the behavior in MeCN solvent of trityl cation in equilibrium with triphenylcarbinol. The cation reacts with deuterium oxide in a reaction which is first order in D_2O and considerably less than first order in cation with a moderately fast rate constant. In order to understand the results it is necessary to recognize the limitations in interpretation. The concentrations of water and acid used in the rate expressions are formal concentrations, whereas in fact, the protons are solvated by water.[17] Thus, the kinetically reactive nucleophile may be present in concentrations lower than the formal ones, and the rate constants must therefore be taken as lower limits.

It is of some interest to see if the nucleophile is actually "free" water; that is, water which is not tied up in solvating protons. From the data and equilibrium constants given by Kolthoff and Chantooni,[17] the amount of free water in equilibrium with acid in MeCN can be estimated. When an attempt was made to interpret the rates in terms of the calculated free water, a rather poor correlation was found. (The free water correlated roughly with formal water, comprising *ca.* 10–20% of the total.) It is possible that only free water actually acts as the nucleophile; our analysis suggests that this will not change the results significantly.

Since the formal concentrations of all the species are available, it is in principle possible to calculate equilibrium constants corresponding to reactions 1 and 2. When this is done, the values are found to drift considerably, an effect undoubtedly due to changes in the activities of water and hydrogen ion over the region examined. There is no convenient way to correct for these changes in activity, and we therefore do not attach much significance to these constants.

The process by which cation is converted to carbinol is a multistep one, eq 7. We have assumed that the

$$R^+ + D_2O \rightleftharpoons ROD_2^+ \rightleftharpoons ROD + D^+ \qquad (7)$$

reaction with water is the slow step, since proton transfers are probably fast. In experiments in which H_2O was used, we observed only one sharp singlet for hydroxylic protons, a result which is consistent with fast proton transfer. Hill[7] has also dealt with this question and showed that the rates show only a small isotope effect in changing from H_2O to D_2O, again suggestive of the first step being slow. Since the equilibrium constant for the second step is not known, we cannot evaluate the rate constant for loss of water from protonated carbinol.

It is instructive to compare our results with other experiments and estimates. There are no direct measurements reported for unsubstituted trityl cation, and measurements[5-8] on more stabilized ions suggest that the rate constant for reaction with water should be greater than 10 M^{-1} sec^{-1} (in aqueous solution) for trityl itself. The estimate by Winstein[10] of a collapse rate constant of *ca.* 10^3 M^{-1} sec^{-1} in aqueous solution seems quite reasonable in these terms—particularly since that for a monoarylmethyl cation has been estimated[9] at $\sim 10^5$ M^{-1} sec^{-1}. Our results indicate that the reaction in MeCN must be at least as fast, and probably faster than the estimates. Assuming that the true reaction is first order in R^+, the real second-order rate constant must be greater than 10^3 M^{-1} sec^{-1} (Figure 3, Table I).

The less than first-order dependence on R^+ is striking. If R^+ were present primarily in the form of ion pairs and only free R^+ were kinetically reactive, then the reaction would be half-order in R^+. However, our data indicate that the reaction is fit considerably better by a rate law which is zero order in R^+. The result may be due to aggregation of ions in such a way that the concentration of the reactive species (in equilibrium with a large number of other aggregated, nonreactive ions) is essentially independent of total R^+ concentration. Results of this type have been observed in carbanion reactions,[22,23] where the dependence on base is first order at low concentrations and zero order at high concentrations. The kinetics in one case[23] have been approximated by assuming reactive monomeric ion pairs in equilibrium with dimers, trimers, etc., each with the same equilibrium constant, K_{eq}. Equilibria of this type give zero-order reaction when the product of K_{eq} and total concentration is greater than 100. If such an analysis is valid in our system, the concentration of reactive species must be less than 1% of the total R^+. Thus, we may expect that the bimolecular rate constant $k_2 \geq 10^5$ M^{-1} sec^{-1}. It should be noted, however, that there is no evidence for extensive aggregation in the case of other salts in MeCN, although evidence does exist for ion pairing.[24,25] It is possible that trityl cation may behave differently from other cations because of its extensive charge delocalization and great reactivity. Indeed, it may well be that aggregation is the rule, rather than the exception, for organic ions in aprotic solvents. There is certainly no reason to believe that such aggregation should be restricted to organic anions, and the anions do show quite predictable behavior in their tendency to aggregate.

A similar phenomenon of zero-order dependence on carbonium ion has been observed by Freedman, Young, and Sandel in the kinetics of chloride ion exchange between trityl chloride and trityl hexachloroantimonate.[26] The mechanism they proposed to explain this behavior is one involving rapid exchange between ion pairs followed by rate-limiting collapse to covalent halide. A similar mechanism (eq 8) could be constructed for the trityl cation–water system in which essentially all of the available water is involved in hydrating the ion pair (8a lies far to the right) and in which the slow step is collapse of this species to form the protonated carbinol (8b). If only free water were involved and its concen-

$$R^+BF_4^- + D_2O \rightleftharpoons R^+(D_2O)BF_4^- \qquad (8a)$$

$$R^+(D_2O)BF_4^- \rightleftharpoons ROD_2^+BF_4^- \qquad (8b)$$

tration were limiting, this mechanism would show zero-order dependence on cation and first-order dependence on free water. In view of the difficulty in accurately estimating the free water, we cannot rule out mechanisms of this type.

We have attempted to obtain additional information bearing on the question of aggregation in the trityl fluoroborate–MeCN system. Since it is well established[24] that B–F coupling in fluoroborates is exceedingly sensitive to the local environment, and there is substantial evidence for BF_4^- involvement in ion pairing in many solvents, we have examined the ^{19}F nmr spectra of BF_4^- salts in MeCN. The spectrum of 0.2 M tetra-*n*-propylammonium fluoroborate consists of two sharp (*ca.* <2 Hz width at half-height) peaks, ratio 1:4, at 6884 and 6889 Hz upfield from external trifluoroacetic acid.[27a] In contrast, the spectrum of 0.2 M trityl fluoroborate consists of one broad[27b] (*ca.* 7 Hz) peak at 6894 Hz. A 1:1 mixture of the two salts (*ca.* 0.1 M in each) shows only one broad (*ca.* 7 Hz) peak at 6890 Hz. It is clear from these results that there must be

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[22] (a) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Amer. Chem. Soc.*, **83**, 3688 (1961); (b) J. E. Hofmann, R. J. Muller, and A. Schriesheim, *ibid.*, **85**, 3000 (1963); (c) T. E. Hogen-Esch and J. Smid, *ibid.*, **89**, 2764 (1967).

[23] (a) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *ibid.*, **84**, 244 (1962); (b) A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Laughton, *J. Phys. Chem.*, **68**, 2916 (1964).

[24] (a) R. J. Gillespie, J. S. Hartman, and M. Parekh, *Can. J. Chem.*, **46**, 1601 (1968), and references therein; (b) K. Kuhlmann and D. M. Grant, *J. Phys. Chem.*, **68**, 3208 (1964). There is good evidence that BF_4^- associates with many cations in many solvents, although $AgBF_4$ in MeCN appears to exist as free ions.

[25] R. P. Taylor and I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, **91**, 4006 (1969). The extent of ion pairing observed by these authors for the methyltributylammonium tetraphenylboride system was small (*ca.* 10% at 0.1 M). However, Fuoss (R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959, Chapter 18) has predicted significant association of ions (greater than pairwise) at low concentration, and N. Lichtin (G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Wiley, New York, N. Y., 1968, p 142) discusses ion–triplet formation in SO_2 solutions of carbonium ions even at 10^{-2} M.

[26] H. H. Freedman, A. E. Young, and V. R. Sandel, *J. Amer. Chem. Soc.*, **86**, 4722 (1964).

[27] (a) The two peaks result from fluorines bonded to ^{10}B and ^{11}B. The F–^{11}B peak is a quartet, $J \cong 0.4$ Hz. The shift and coupling are those expected.[24] (b) In the broadened peaks, the isotope shift is obscured and no coupling is apparent.

interaction between the BF_4^- and the trityl cation.[28] The broad peak for $R^+BF_4^-$ is consistent with the BF_4^- being in an asymmetric environment with broadening resulting from increased B–F coupling and quadrupole relaxation by boron.[24a] Complete line-shape analysis shows that the broadening cannot be due to exchange of fluorine between ^{11}B and ^{10}B. Ion pairing alone might be sufficient to account for the broadening; however, the single broad peak observed in the mixture of trityl and Pr_4N^+ salts suggests that more extensive aggregation may exist. Thus, the BF_4^- is in a time-averaged environment (only one peak) but is nevertheless as broad as in the absence of Pr_4N^+. In a rapid time average, the peak would be of weighted average width (4.5 Hz). The broadening is probably not due to an intermediate exchange rate, since the peak shape remained essentially unchanged when the temperature was lowered by 40°. The simplest explanation of these results is that the Pr_4N^+ salt has been incorporated into the aggregate. Thus, we believe that the ^{19}F nmr results support our hypothesis of association.

The measured "activation energy" of 6.5 kcal/mol is a composite quantity, being the sum of E_a and $\Delta H°$ for the aggregation equilibria. It is, thus, difficult to assign any simple interpretation to it, although it is rather similar to some values measured previously.[5]

The apparently faster rate of reaction 2 in MeCN compared to water may be the result of a number of factors. Ritchie[6] has stressed the importance of solvent reorganization contributions to free energies of activation. In a solvent such as MeCN which is less structured than water,[29] such reorganization effects may well be smaller. In particular, the nucleophile, water, is not the solvent in this case and reaction with it need not cause disruption of any "iceberg-like" structure. Studies by Winstein[30] suggest that nucleophilic contributions from MeCN itself are unimportant. Because the ether peak is not appreciably broadened, reversible reaction of carbonium ions with ether to produce oxonium ions cannot be an important process under our conditions. In the absence of water, any exchange between cation and carbinol is slow.

Although there are difficulties in interpreting this work, it nevertheless provides considerable insight into the behavior of carbonium ions.[31] Furthermore, the low-order dependence on cation provides evidence of aggregation for ions of this type in MeCN. Finally, the rate constant itself provides a complement to those measured for reactions in more stable systems.

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[28] In addition, Taft has observed that chemical shifts in the cationic moiety of trityl salts in MeCN are dependent upon the anion employed. R. W. Taft, personal communication.

[29] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969), and references therein.

[30] A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 5010 (1964).

[31] H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 809 (1967), measured the rate of reaction of methyl oxocarbonium ion with water, but his result is not readily compared with ours.

Gas-Phase Acidities of Alcohols

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Abstract: Relative acidities in a series of aliphatic alcohols have been determined by ion cyclotron resonance spectroscopy. The order of acidities is $(CH_3)_3CCH_2OH > (CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH > H_2O$ and $(CH_3)_3COH \approx n\text{-}C_5H_{11}OH \approx n\text{-}C_4H_9OH > n\text{-}C_3H_7OH > CH_3CH_2OH$. Phenol was found to be considerably more acidic than any of the alcohols; toluene has an acidity between that of methanol and ethanol.

Structure and reactivity relationships remain as one of the bases of physical organic chemistry. Interpretation of both rates and equilibria in terms of molecular structure permits us to explain relative reactivities as well as to predict the behavior of yet unknown compounds. Acid dissociation lies at the heart of many of these correlations for two reasons. First, acid dissociation is relatively easy to measure, and second, the proton remains a constant element in comparing a wide variety of acids. Thus, both the Hammett[2] and Branch and Calvin[3] techniques make use of acidities. It is these methods which allow us to put structure–reactivity relationships on a quantitative basis and evaluate, for example, inductive effects.

These relationships presumably deal with the intrinsic behavior of the molecules of interest. Nevertheless, it is clear that other effects may be of great importance. That this is so can be seen from examination of many phenomena in various solvents. Thus, ionization potentials, relative acidities, etc., can be changed markedly by change of solvent or removal to the gas phase.[4] The relative acidities of alcohols and hydrocarbons in various solvents serve as an example of this, although many more exist. That the solvent may play

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[1] (a) Alfred P. Sloan Foundation Fellow; (b) National Science Foundation Predoctoral Fellow, 1966–1970.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.

[3] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1941.

[4] For some interesting comments see C. D. Ritchie and R. Uschold, *J. Amer. Chem. Soc.*, **90**, 2821 (1968).