ml) at 20° as described above. The amine hydrochloride was filtered off, and the hexane filtrate containing methyl diethylphosphinite (20) was cooled to −70° and was treated with hexafluoroacetone (68 mmol) over a 1.5-hr period. The mixture was allowed to reach 20° in 2 hr and was evaporated at 30° (20 mm). The product consisted mainly (ca. 85%) of dioxaphospholane 21 (δ^{31}P −13), with some (ca. 15%) oxaphosphetanes 22 (δ^{31}P +7, ca. 9%) and 23 (δ^{31}P +11, ca. 6%).

The mixture of dioxaphospholane 21 (85%) and oxaphosphetanes 22 and 23 (15%) was kept 4.5 hr at 100° in the absence of solvent, under N_2. The product still had some phospholane 21 (ca. 10%), but consisted mainly of oxaphosphetanes anti-22 (ca. 50%) and syn-23 (ca. 40%). The proportion of oxyphosphoranes 21, 22 and 23 was altered by fractional distillation, but no complete separation could be achieved. A sample of bp 25–26° (0.05 mm) obtained by distillation through an 8-in. spinning band column contained 28% of phospholane 21, 44% of anti-phosphetane 22, and 28% of syn-phosphetane 23; it had the following analysis.

Anal. Calcd for $C_{11}H_{13}O_3PF_{12}$: C, 29.2; H, 2.9; P, 6.8; F, 50.4. Found: C, 29.4; H, 3.0; P, 6.8; F, 50.5.

Attempts to Interconvert the anti-22 and syn-23 Oxaphosphetanes Derived from Methyl Diethylphosphinite and Hexafluoroacetone. Thermally. A mixture of anti-22 and syn-23 (2.3:1.0) was kept 12 hr at 100°, without significant change in the proportion of isomers. A new P-containing substance, probably due to the Wittig reaction, methyl hexafluoroisopropyl ethylphosphonate, $(C_2H_5)P(O)(OCH_3)[OCH(CF_3)_2]$, was observed at δ^{31}P ca. − 37 ppm, τ_{CH_3O} 6.22, J = 11 cps. After 1 hr at 150° and 1 hr at 180°

the ratio of phosphetanes to phosphonate (Wittig reaction) was 1.3:1.0, but the proportion of the remaining stereoisomers anti-22 to syn-23 had not changed significantly.

Thermally, with Added Hexafluoroisopropyl Alcohol, $(CF_3)_2CH-OH$. This acidic alcohol (10 mol %) was added to mixtures of anti-22 + syn-23, and the mixtures were kept 3 hr at 110°, with these results: initial mixture, 59% 22:41% 23 → 55% 22:45% 23; initial mixture, 32% 22:68% 23 → 32% 22:68% 23.

The acidic alcohol (50 mol %) was added to mixtures of anti-22 + syn-23 and the mixtures were kept 0.5 hr at 120° and 4.5 hr at 140°, with these results: initial mixture, 55% 22:45% 23 → 40% 22:60% 23; initial mixture, 34% 22:66% 23 → 40% 22:60% 23.

Reaction of Alcohols with 2,2,2-Trialkoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholenes. A given alcohol (3 molar equiv) was added to a 1.5 M solution of the indicated dioxaphospholene in benzene at 25°, in the absence of catalyst, and in the presence of various molar proportions of a tertiary amine (pyridine or 2,4,6-trimethylpyridine). The course of the reaction was followed by ^1H nmr spectrometry. The pure dioxaphospholenes corresponding to the formulas >P(OR)₃, >P(OR)₂(OR′), >P(OR)(OR′₂), and >P(OR′)₃ were available from previous work. The relative amounts of the four dioxaphospholenes present in a given reaction mixture were determined from the integration of the ^1H nmr signals of their RO and R′O groups and of their $CH_3C=CCH_3$ groups. The amounts of alcohol, ROH, produced were followed in the same manner. The results are given in Tables I and II. p-Toluenesulfonic acid had no noticeable effect on the substitution reaction of 31.

Reactions of the Tri-p-anisylmethyl Carbonium Ion with Nucleophiles[1]

C. A. Bunton* and S. K. Huang

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. Received July 29, 1971

Abstract: Kinetic salt effects upon the forward and back reaction of the tri-p-anisylmethyl carbonium ion with water have been measured. These salt effects and those upon the activity coefficient of the alcohol allow us to determine the relative stabilities of the hydronium and carbonium ions and the transition state, $X^{\mp}$. The salt order upon f_{H^+}/f_{R^+} is $LiClO_4 \sim NaClO_4 > NaBr > NaNO_3 > NaCl > LiCl >$ no salt $\sim CsCl > Me_4NCl \sim KCl$; upon $f_{H^+}/f_{X^{\mp}}$ it is $LiClO_4 \sim NaClO_4 > NaBr > NaNO_3 > NaCl \sim Me_4NCl \sim CsCl \sim$ no salt $> LiCl \sim KCl$; and upon $f_{R^+}/f_{X^{\mp}}$ it is $Me_4NCl >$ no salt $\sim CsCl > NaCl > KCl > NaBr \sim NaNO_3 > LiCl > NaClO_4 > LiClO_4$. These relative activity coefficients are considered in terms of direct and indirect interactions between the salts and the reacting species. The second-order rate constant for reaction of the carbonium and hydroxide ions is 8200 l. $mol^{-1} sec^{-1}$, and the kinetic salt order is no salt > $Me_4NCl > KCl \sim NaCl > NaBr > NaNO_3 > NaClO_4 > LiCl > LiClO_4$. The second-order rate constant for attack of azide ion is 5×10^6 l. $mol^{-1} sec^{-1}$, and the first-order rate constant for ionization of the alkyl azide is 75 sec^{-1} at 25.0° in water.

T he stability of carbonium ions in aqueous solution is of considerable importance. Stable triarylmethyl carbonium ions, e.g., Malachite Green and Crystal Violet, react relatively slowly with anionic and other nucleophiles,[2,3] but attack of water on the triphenylmethyl carbonium ion in acetonitrile is moderately fast on the nmr time scale[4] ($\tau \approx 10^{-2}$ sec), and allylic carbonium ions have half-lives of $<10^{-5}$ sec, in hydroxylic solvents.[5] Taft and his coworkers found that the reactivity of triarylmethyl carbonium ions

toward water is related to their stability relative to the alcohol.[6]

Relatively short-lived carbonium ions can be trapped in aqueous solution, for example, by azide ion or by the common ion, showing that nucleophilic anions can compete with hydroxylic solvents for the carbonium ions or ion pairs.[7]

The rates of SN1 solvolyses of alkyl halides and related compounds are subject to positive salt effects.[7,8] The effects are large, and highly specific not only in

(1) Support of this work by the National Science Foundation is gratefully acknowledged.

(2) (a) E. F. J. Duynstee and E. Grunwald, J. Amer. Chem. Soc., 81, 4542 (1959); (b) J. Dixon and T. C. Bruice, ibid., 93, 3248 (1971).

(3) C. D. Ritchie, G. A. Skinner, and V. G. Badding, ibid., 89, 2063 (1967).

(4) J. I. Brauman and W. C. Archie, ibid., 92, 5981 (1970).

(5) D. S. Noyce and S. K. Brauman, ibid., 90, 5218 (1968).

(6) R. A. Diffenbach, K. Sano, and R. W.Taft, ibid., 88, 4747 (1966).

(7) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter 7; (b) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, J. Amer. Chem. Soc., 92, 5729 (1970).

(8) S. Winstein, B. Appel, and A. Diaz, Chem. Soc., Spec. Publ., No. 19, 109 (1965).

nonpolar solvents, but even in polar hydroxylic solvents, and perchlorates are particularly effective at assisting Sn1 solvolyses.[8-12] In addition, lithium perchlorate shows a special salt effect in acetolyses where it is believed to catalyze the dissociation of a solvent separated ion pair.[8]

In all these Sn1 solvolyses it is anions of low charge density which are the most effective agents for promoting reaction. The various strong acids behave differently with respect to the H_R and H_0' acidity functions, and large low charge density anions, such as perchlorate, stabilize the trianisylmethyl carbonium ion relative to the p-nitroanilinium ion.[13,14] Perchloric acid is a better catalyst than hydrochloric acid for an A1 but not an A2 ester hydrolysis.[14] This behavior suggests that bulky anions stabilize carbonium ions, or carbonium ion-like transition states in acid reactions.

The kinetics of a number of nucleophilic substitutions involving both solvolysis and attack of an ionic nucleophile have been treated in terms of nucleophilic attack upon an ion pair, rather than the covalent substrate,[15] and there is extensive evidence for the intermediacy of ion pairs in solvolysis in relatively polar hydroxylic solvents.[16]
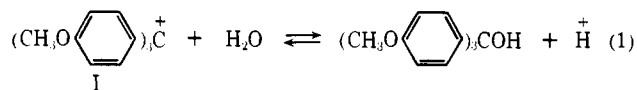
All these observations raise questions about attack upon carbonium ions by nucleophilic anions and medium effects upon these reactions.

Taft and his coworkers mention that electrolytes and nonelectrolytes retard the attack of water upon triarylmethyl carbonium ions, but give no details,[6] and there is some limited evidence on the negative salt effects of sodium chloride and perchlorate upon reactions of the tri-p-anisylmethyl carbonium ion.[17]

Dioxane, in moderate concentration, decreases the rate of formation of the tri-p-anisylmethyl carbonium ion from the alcohol in aqueous acid and speeds attack of water upon it; Nicolson and Wyatt relate these effects to changes in water activity.[18] Acetone speeds the attack of water upon the tri-p-anisylmethyl carbonium ion.[17]

Most of the systematic studies of reactions of triarylmethyl carbonium ions have been done using the stabilized dyestuff cations. In particular Ritchie and his coworkers have used several ionic nucleophiles in various solvents and conclude that reorganization of solvent structure is of key importance.[3]

The aims of the present investigation were to measure the reactivity of various nucleophiles toward the tri-p-

$$(CH_3O\langle\rangle)_3\overset{+}{C} \ + \ H_2O \ \rightleftharpoons \ (CH_3O\langle\rangle)_3COH \ + \ \overset{+}{H} \quad (1)$$

I

anisylmethyl carbonium ion (I) and the salt effects upon these reactions and upon the forward and back reactions.

Experimental Section

Materials. Tri-p-anisylmethanol was prepared by the method of Baeyer and Villiger[19] and converted into its sparingly soluble red perchlorate. Tri-p-anisylmethyl chloride (Aldrich) was used in some experiments. The aqueous solutions of electrolytes were made up using deionized water and were degassed before use.

The inorganic salts were commercial samples and were dried before use, or were prepared in solution by the neutralization of the acid with lithium or sodium hydroxide, using a pH meter. Tetramethylammonium chloride (Eastman) was dried before use. All the commercial samples of salts were neutral.

Kinetics. The reactions were followed in a Durrum–Gibson stopped-flow spectrophotometer, with the temperature maintained by recirculating water. The carbonium ion, as a solution in dilute hydrochloric acid, typically 0.05–0.1 M, was in one syringe and the nucleophile or base was in the other. In a few experiments the second syringe contained only water. (Initially we used perchloric acid but found some irreproducibility, possibly because of the low solubility of the perchlorate.) For most of the experiments in the absence of added nucleophile we used sodium acetate to neutralize the acid. In agreement with earlier work,[17] we found that small amounts of sodium acetate did not affect the reaction rate. For experiments with nonnucleophilic salts, equimolar amounts were added to the solutions in each syringe to avoid mixing problems. When azide ion was the nucleophile, a mixture of sodium azide and hydroxide was used in one syringe and hydroxide was in slight excess over the acid.

The reactions with azide and hydroxide ions were so fast that mixing was a serious problem. We therefore used a simple, readily adjustable stop on the trigger switch of the stopped-flow apparatus which allowed us to start the observation immediately after mixing was complete. We were able to follow only the final part of each reaction and had to use an expanded transmittance scale. However, the reproducibility of the results for these fast reactions is satisfactory, as is shown by the variation of k_ψ with concentration of hydroxide and azide ion. The transmission was followed on a cathode ray oscilloscope and recorded photographically. Transmissions were converted into absorbances using a Hewlett-Packard desk computer, which was also used to calculate the first-order rate constants, k_ψ (sec^{-1}). The reproducibility of the values of k_ψ is illustrated by results for duplicate experiments. Good first-order plots were obtained for up to three half-lives with correlation coefficients for a least-squares plot of at least 0.999 for reactions in which water was the nucleophile.

Most of the salt effects upon H_R and the activity coefficient of tri-p-anisylmethylcarbinol had already been measured. The measurements using KCl, CsCl, and Me$_4$NCl followed methods already described.[14] The concentration of some of the salts was restricted by solubility. Some measurements were made on the salt effects upon protonation of p-nitroaniline and diphenylamine and their activity coefficients following the methods used by Paul.[20]

Results

The observed first-order rate constants for the disappearance of the carbonium ion, R$^+$, are independent of the concentration of acetate ion ($cf.$ ref 17) and of the nature of the (dilute) acid (Table I), and directly give values of k_1^f.

Table I. Reaction of the Carbonium Ion with Water[a]

C_{H^+}, M	Medium	k_ψ, sec^{-1}
0.05	Water	15.2
0.05[b]	Water	15.0
0.05	0.1 M NaOAc	11.8
0.025	0.05 M NaOAc	12.0
0.05[b]	0.1 M NaOAc	11.5
0.05[b]	0.2 M NaOAc	11.5

[a] In aqueous solution at 25.0° with HCl unless specified. [b] HClO$_4$.

(9) G. A. Clarke, T. R. Williams, and R. W. Taft, *J. Amer. Chem. Soc.*, **84**, 2292 (1962); G. A. Clarke and R. W. Taft, *ibid.*, **84**, 2295 (1962).

(10) K. D. Michael and R. A. Clement, *Can. J. Chem.*, **39**, 957 (1961).

(11) S. Winstein, M. Hojo, and S. G. Smith, *Tetrahedron Lett.*, 12 (1960).

(12) C. A. Bunton, T. W. Del Pesco, A.M. Dunlop, and K.-U. Yang, *J. Org. Chem.*, **36**, 887 (1961).

(13) For a general review of acidity functions, see R. H. Boyd in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3.

(14) C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 1258 (1968).

(15) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 6031 (1969); R. A. Sneen and H. M. Robbins, *ibid.*, **91**, 3100 (1969).

(16) V. J. Shiner and W. Dowd, *ibid.*, **93**, 1029 (1971).

(17) E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 2565 (1968).

(18) H. Nicholson and P. A. H. Wyatt, *J. Chem. Soc. B*, 198 (1968).

(19) A. Baeyer and V. Villiger, *Ber.*, **35**, 1198 (1902).

(20) M. A. Paul, *J. Amer. Chem. Soc.*, **76**, 3236 (1954).

$$R^+ + H_2O \underset{k_2{}^b}{\overset{k_1{}^f}{\rightleftarrows}} ROH + H^+$$
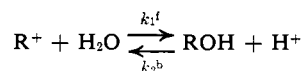
For those experiments where there was no base in the second syringe to neutralize the acid, $k_\psi = k_1{}^f + k_1{}^b$ (where $k_1{}^b$ is the first-order rate constant for the back reaction). For tri-p-anisylcarbinol pK_a = 0.82,[13] and in 0.05 M HCl k_ψ = 15.2 sec^{-1}; therefore, $k_1{}^f$ = 11.4 sec^{-1}, and $k_1{}^b$ = 3.8 sec^{-1}, and $k_2{}^b$ = 76 1. mol^{-1} sec^{-1}. This value of $k_1{}^f$ is in good agreement with the values of $k_1{}^f$ = 12.0 sec^{-1} observed when the acid was neutralized with acetate ion. Our values for $k_1{}^f$ agree reasonably well with the value of 12.9 sec^{-1} at 25.0° and with formate ion found by Hill and Mueller,[17] but are lower than the value of 27 sec^{-1} observed by Nicholson and Wyatt,[18] who did not use neutralization by a weak base but determined $k^f + k^b$.

Preliminary experiments in which R$^+$ in 0.10 M HClO$_4$ was mixed with 0.10 M NaOH gave $k_1{}^f$ = 12 sec^{-1} and an experiment with 0.05 M H$_2$SO$_4$ and 0.20 M NaOAc gave $k_1{}^f$ ~14 sec^{-1}. However, perchloric and sulfuric acid were not generally used because of the low solubility of some perchlorates and the problem of the ionization of the hydrogen sulfate ion.

Salt Effects of Salts upon the Spontaneous Reactions. Most of the salts of the strong acids decrease k^f, and increase acidity as measured by the H_R scale.[13,14]

It was necessary to have sufficient strong acid in one of the drive syringes to maintain a readily observable concentration of the carbonium ion. Generally, we used 0.1 M HCl in the syringe, so that the solution in the mixing chamber contains 0.05 M chloride ion, and the value of $k_1{}^f$ in the absence of added salt (Table II) is that for hydrolysis of R$^+$ in this solution. The

Table II. Salt Effects upon k^f and k^b

Salt	C_s, M	$k_1{}^f$, sec^{-1}	$k_1{}^f/a_{H_2O}$	$k_2{}^b$, 1. mol^{-1} sec^{-1}	$k_2{}^b/f_{ROH}$
No salt		12.0	12.0	79	79
LiCl	0.50	9.2	9.4	92	68
	1.00	6.9	7.4	101	54
	2.00	3.0	3.3	100	29
NaCl	0.50	10.8	10.9	108	85
	1.00	9.9	10.1	145	89
	2.00	8.3	8.7	276	104
KCl	0.50	10.6	10.7	100	61
	1.00	9.2	9.5	123	46
	1.50	7.6	8.0	141	33
CsCl	0.25	11.9	11.9	85	80
	0.50	11.7	11.9	90	79
	1.00	11.0	11.4	98	77
Me$_4$NCl	0.50	12.2	12.4	64	77
	1.00	13.6	14.0	54	79
	2.00	20.0	21.4	46	100
NaBr	0.25	10.1	10.2	85	86
	0.50	9.2	9.4	99	104
	0.75	8.3	8.6	126	138
	1.00	7.5	7.9	131	146
	2.00	5.2	5.7	230	289
NaNO$_3$	0.50	8.8	8.9	100	80
	1.00	7.5	7.6	145	91
	2.00	5.5	5.8	316	130
LiClO$_4$	0.50	6.9	7.1	118	142
	1.00	4.4	4.7	197	290
	2.00	2.1	2.3	610	1330
NaClO$_4$	0.50	7.4	7.5	123	135
	1.00	5.1	5.2	233	274
	2.00	2.8	3.0	970	1360

similarity of the values of $k_1{}^f$ obtained by rapidly diluting the acid, or by neutralizing it with acetate ion, shows that a change of counterion from hydronium to sodium has little effect on $k_1{}^f$, at least for low (0.05 M) electrolyte concentrations. Sodium chloride itself has small effects upon the rates of reaction, and in calculating the rate constants for the forward and back reactions of the carbonium ion, we neglect the effect of these low salt concentrations.

The salt effects upon the first-order rate constants, $k_1{}^f$, are given in Table II. Lithium and perchlorate ions are especially effective at retarding the reaction, but tetramethylammonium ion unexpectedly speeds it.

From H_R and $k_1{}^f$ in dilute NaOAc (Table III and

Table III. Salt Effects upon $H_R{}^a$

C_s, M	Salt		
	KCl	CsCl	Me$_4$NCl
0.05			−0.01[b]
0.10			−0.02[b]
0.50	0.16	0.07	−0.09[b]
0.75	0.22		
1.00	0.31	0.13	−0.21[b]
1.50	0.41		
2.00			−0.47[b]
2.00			−0.51

^{a} Values of $-\Delta H_R$, in 0.05 M HCl unless specified. ^{b} In 0.1 M HCl.

ref 14), we calculated $k_2{}^b$ = 79 1. mol^{-1} sec^{-1} (Table II), which agrees well with the value obtained by dilution. All the salts increased $k_2{}^b$ except tetramethylammonium chloride. Perchlorates markedly increase $k_2{}^b$, sodium nitrate, chloride, and bromide are less effective, and lithium, potassium, and cesium chlorides have relatively small effects.

Salt Effects upon Activity Coefficients and Acidity Functions. Most of the salt effects upon H_R and f_{ROH} (the activity coefficient of tri-p-anisylcarbinol) were available.[14] The H_R values determined in this work are shown in Table III. The activity coefficients of the alcohol follows the Setchenhow equation,[20,21] log $f_{ROH} = K_s C_s$; the values of K_s are KCl 0.42, CsCl 0.12, Me$_4$NCl −0.17. The corresponding data on p-nitroaniline and diphenylamine were taken from ref 14 and 20 or determined (Table IV). The values of $\Delta H_0'$ with added salts are from ref 14, 20, and 22.

Table IV. Salt Effects upon H_0'' and Log $f_D{}^a$

Salt	C_s, M	$-\Delta H_0''$	Log f_D
Me$_4$NCl	0.25	−0.09	−0.20
Me$_4$NCl	0.50	−0.18	−0.44
Me$_4$NCl	1.00	−0.43	−0.77
NaBr	0.50	0.15	
NaBr	1.00	0.30	0.17
NaBr	2.00	0.51	0.34
LiClO$_4$	0.50	0.13	0.02
LiClO$_4$	1.00	0.25	0.04
LiClO$_4$	2.00	0.55	0.08
NaClO$_4$	0.25	0.09	
NaClO$_4$	0.50	0.13	0.05
NaClO$_4$	1.00	0.24	0.10
NaClO$_4$	2.00	0.50	0.22

^{a} Values of $\Delta H_0''$ in 0.1 M HCl at 25.0° using diphenylamine (D); in the absence of added salt H_0'' = 1.02 (cf. ref 20).

(21) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).
(22) C. A. Bunton and J. D. Reinheimer, *J. Phys. Chem.*, **74**, 4457 (1970).

Reactions with Hydroxide Ion. The first-order rate constant for disappearance of R^+ increases approximately linearly with hydroxide ion concentration when the acid is neutralized by excess sodium hydroxide (Figure 1).

The second-order rate constant $k_2^f = 8200$ l. mol^{-1} sec^{-1} at 25.0°. This rate constant is subject to error, because it was necessary to use sufficient strong acid to maintain the carbonium ion concentration, and therefore the net concentration of hydroxide ion in the mixing chamber calculated allowing for twofold dilution depends upon the accuracy with which the two drive syringes introduce equal volumes into the mixing chamber. However, the points in Figure 1 fit on a reasonably good straight line even though the data were obtained at different times using three separate sets of reagent solutions. Hill and Mueller report a second-order rate constant of 4600 l. mol^{-1} sec^{-1} for this reaction at 30° and 0.1 M sodium perchlorate.[17] Allowing for temperature differences our second-order rate constant is approximately twice that reported by Hill and Mueller.[17]

Salt Effects upon Reaction with Hydroxide Ion. The simple electrostatic treatment of salt effects predicts that electrolytes will retard reactions between oppositely charged ions,[7a] as is observed for this reaction. In examining these salt effects we were faced with the problem of following a fast reaction, and we therefore chose a relatively low hydroxide ion concentration, 0.013 M, which gave a readily measurable rate constant, but the reaction with water then made an appreciable contribution to the overall reactions and the salt effects on the two reactions had to be separated. Table V

Figure 1. Reaction with hydroxide ion at 25° in the presence of 0.05 M NaCl.

Table V. Salt Effects on the Reaction with Hydroxide Ion[a]

Salt	C_s, M	k_ψ, sec^{-1}	Salt	C_s, M	k_ψ, sec^{-1}
LiCl	0.50	44.9	NaBr	0.50	51.8
LiCl	1.00	29.2	NaBr	1.00	44.9
LiCl	2.00	13.1	NaBr	2.00	31.1
NaCl	0.50	65.6	NaNO₃	0.50	52.1
NaCl	1.00	50.6	NaNO₃	1.00	39.1
NaCl	2.00	37.5	NaNO₃	2.00	30.1
KCl	0.38	69.0	LiClO₄	0.50	38.4
KCl	0.75	56.8	LiClO₄	1.00	23.5
Me₄NCl	0.25	88.3	LiClO₄	2.00	11.5
Me₄NCl	0.50	79.4	NaClO₄	0.50	43.2
Me₄NCl	1.00	88.3	NaClO₄	1.00	32.0
Me₄NCl	2.00	117	NaClO₄	2.00	18.9

[a] At 25.0° with 0.013 M NaOH and 0.025 M NaCl; in the absence of added salt $k_\psi = 112$ sec^{-1}.

gives the first-order rate constants, k_ψ, for the overall reaction, which we corrected for the reaction of water upon the carbonium ion using the values of k_1^f given in Table II. (Interpolated rate constants were used where necessary.)

The simple form of the Debye-Hückel equation predicts that for uniunivalent salts plots of log k against $C_s^{1/2}$ should be linear,[23] as has been observed for the reaction of cyanide ion with stabilized triphenylmethyl

(23) (a) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 7; (b) E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Chapter 2.9.
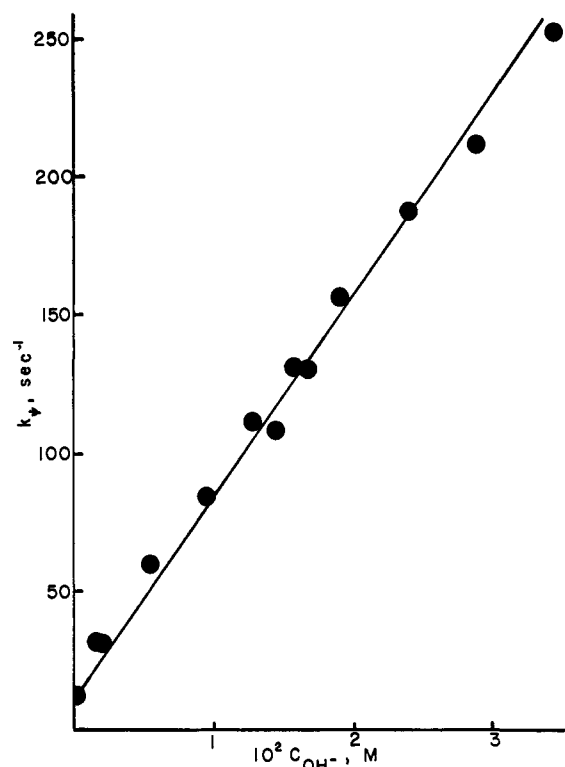
cations in low concentrations of potassium perchlorate and cyanide.[3]

Our experiments were carried out at salt concentrations much higher than those for which theoretical treatments are applicable, but plots of log k_{cor} against $C_s^{1/2}$ (where k_{cor} refers to attack of hydroxide upon the carbonium ion) were approximately linear for most salts (Figure 2). Other relations between rate constant and salt concentration, e.g., a linear dependence of log k upon $C^{1/3}$, fit the results almost as well as the square root dependence. A cube root relationship fits the activity coefficients of salts reasonably well.[23b] Dilute Me₄NCl hindered reaction as expected, with a shallow rate minimum at 0.1-0.3 M salt, and lithium salts, especially perchlorate, exhibit the largest negative salt effects.

The electrostatic treatment of kinetic salt effects predicts larger salt effects upon interionic than ion-molecule reactions. However, this is not observed in these carbonium ion reactions. The largest salt effect upon reaction of the carbonium ion with water is ca. sixfold (for 2 M NaClO₄) and slightly more than tenfold for the hydroxide ion reaction in 2 M LiClO₄, but k_2^b is increased ca. 12-fold by 2 M NaClO₄ (Tables II and V).

Reaction with Azide Ion. Reaction between azide and tri-p-anisylmethyl carbonium ion is fast so that low azide ion concentrations must be used and hydroxide ion had to be added to neutralize the strong acid.

The initial reaction with azide ion gave an "infinity" transmittance which increased over a relatively short time to a value characteristic of complete reaction, suggesting that the alkyl azide was formed reversibly, with alcohol as the thermodynamically stable product.
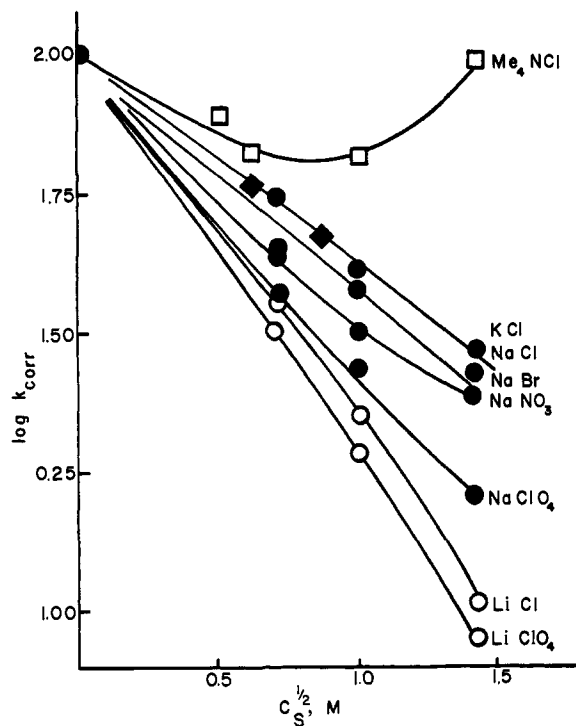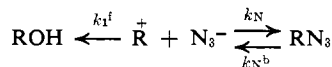
Figure 2. Salt effects upon the reaction with hydroxide ion at 25°.

$$\text{ROH} \xleftarrow{k_1^f} \overset{+}{\text{R}} + \text{N}_3^- \underset{k_N^b}{\overset{k_N}{\rightleftarrows}} \text{RN}_3$$

Provided that k_1^f is small relative to the other constant, the observed first-order rate constant for attainment of the initial "equilibrium," k_ψ, is given by

$$k_\psi = k_N^f C_{N_3^-} + k_N^b$$

In order to separate k_N^f and k_N^b, we determined the equilibrium constant, K_N, for the formation of the alkyl azide using the difference between transmittances after initial attack of azide and after complete reaction to calculate the amount of carbonium ion in equilibrium with the alkyl azide.

The azide ion reaction was examined at two concentrations of hydroxide ion, 0.002 and 0.016 M, and 0.05 M NaCl (Figure 3). Plots of k_ψ vs. azide concentration are reasonably linear, considering that these fast reactions are only just within the range of the instrument and the problem of neutralizing the strong acid, and give a second-order rate constant $k_N^f \approx$ 5 × 10⁶ l. mol⁻¹ sec⁻¹ (k_N^b is much smaller than $k_N^f \cdot$ $C_{N_3^-}$). The error bars in Figure 3 represent ±10%.

The association equilibrium constant, K_N, and k_N^b (Table VI) were calculated using the experiments with

Table VI. Equilibrium Constant for Formation of Alkyl Azide[a]

$10^5 C_{NaN_3}$, M	Absorbance[b]	C_{R^+}/C_{RN_3}	K_N, l. mol⁻¹	k_N^b, sec⁻¹
5.0	0.028	3.6	7.2 × 10⁴	70
6.25	0.025	4.3	6.9 × 10⁴	73
12.5	0.016	8.0	6.4 × 10⁴	78
25.0	0.009	16	6.3 × 10⁴	80
50.0	0.004	31	6.3 × 10⁴	80

[a] At 25.0° with 0.002 M NaOH and 0.05 M NaCl. [b] At the initial "equilibrium"; the absorbance of R⁺ before reaction is 0.142.
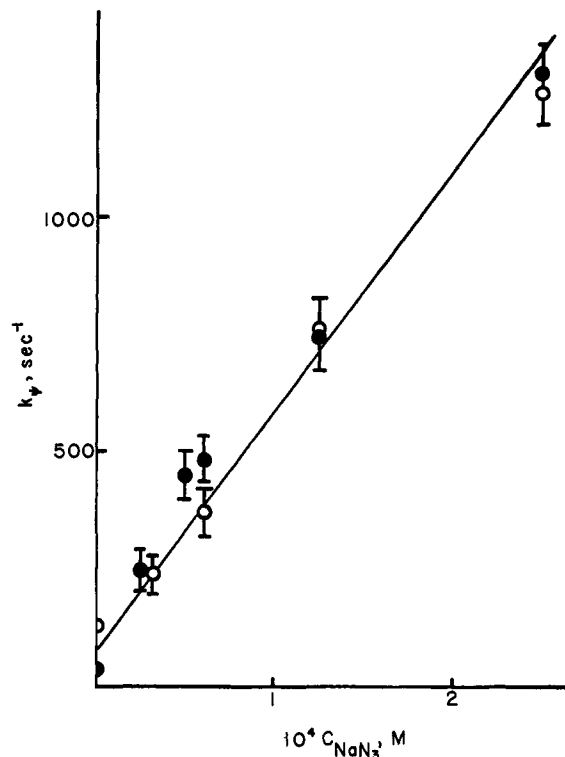

Figure 3. Reaction with azide ion at 25° in the presence of 0.05 M NaCl; ● with 0.002 M NaOH; ○ with 0.016 M NaOH.

the higher azide concentrations, because then there is least interference from the reactions with hydroxide ion and water. A problem in choosing optimum conditions is that if the azide ion concentration is too low, there is competition with hydroxide ion, and if it is too high the concentration of carbonium ion after the initial azide reaction is very small.

Despite its lower basicity and its lower nucleophilicity in S_N2 reactions, azide is much more reactive than hydroxide ion toward the tri-p-anisylmethyl carbonium ion (Figures 1 and 3).

Most alkyl azides are stable under solvolytic conditions, but Ritchie and his coworkers have determined the equilibrium constant for the dissociation of the azide of p-nitro(Malachite Green),[3] for which $K = 6.2$ × 10⁻⁴ mol l.⁻¹ in methanol at 25°. The second-order rate constant for attack of azide ion upon p-nitro-(Malachite Green) is 6.2 × 10⁴ l. mol⁻¹ sec⁻¹, so that the first-order rate constant for ionization of the azide is approximately 40 sec⁻¹. (The rate constants for attack of azide ion in methanol–methoxide ion could not be measured with the other carbonium ions studied by Ritchie and his coworkers.[3]) The equilibrium constant for dissociation of tri-p-anisylmethyl azide is 1.6 × 10⁻⁵ mol l.⁻¹ in water and is not much smaller than that found for the azide of p-nitro(Malachite Green) in methanol, suggesting that equilibrium constants are much less sensitive to structural changes than rate constant for nucleophilic attack upon the carbonium ion.[3]

For the ionization of tri-p-anisylmethyl azide in water at 25.0°, $k_N^b \approx 75$ sec⁻¹. The difference in Y values for water and methanol is 4.58,[24] and assuming that $m \sim 1$ for the ionization of the alkyl azide we

(24) Reference 23b, Chapter 2.6.

Figure 4. Salt effects upon the relative activity coefficients of the carbonium ion and the transition state.
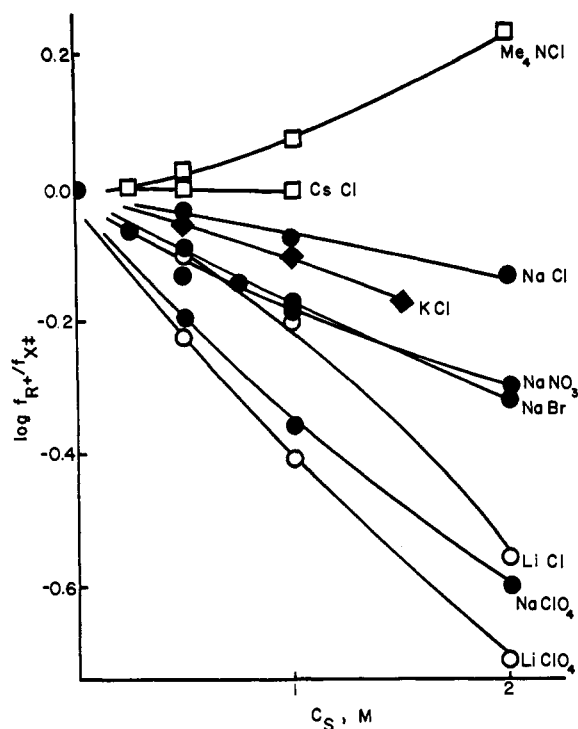

Figure 5. Salt effects upon the relative activity coefficients of the hydronium ion and the transition state.

calculate an approximate rate constant of 2×10^{-3} sec^{-1} in methanol. Tri-p-anisylmethyl azide is therefore less reactive than the azide of p-nitro(Malachite Green) by a factor of approximately 2×10^4. We can also compare azide with other leaving groups, e.g., acetate. For the methanolysis of triphenylmethyl acetate, $k_\psi = 3.2 \times 10^{-4}$ sec^{-1} interpolated at 25° in methanol,[25] and the calculated value in water, taking $m \sim 1$, is 12.3 sec^{-1}.

The three p-methoxy groups should increase the rate of an S$_N$1 solvolysis by approximately 10^9 (calculated taking $\sigma^+ = -0.78$ and $\rho = -4.0$[26]), and therefore the calculated first-order rate constant for the solvolysis of triphenylmethyl azide in water at 25° is 7.5×10^{-8} sec^{-1}. This rate comparison, based on large extrapolations of solvent and substituent effects, suggests that an alkyl azide should solvolyze by an S$_N$1 mechanism by a factor of $\sim 10^8$ more slowly than the corresponding acetate. All existing evidence shows that azide is a very poor leaving group from saturated carbon even though hydrazoic acid (pK = 4.72)[27] is not especially weak. These calculations also suggest that tri-p-anisylmethyl acetate and formate should be extremely reactive in water, as expected from the absence of any rate enhancement when the carbonium ion is trapped in the presence of acetate or formate ion (Table I and ref 17).

Discussion

Salt Effects upon the Water Reaction. Salts of strong acids, except tetramethylammonium chloride, increase $-H_R$, the acidity function for carbonium ion formation (Table III and ref 13, 14), retard the reaction

with water, and assist the acid-catalyzed formation of the carbonium ion (Table II). Initial state salt effects are important in many acid-catalyzed reactions[14,22,28,29] and could influence the acid heterolysis of the alcohol.

For the reaction

$$\overset{+}{R} + H_2O \rightleftarrows [X\ddagger] \rightleftarrows R\overset{+}{O}H_2 \rightleftarrows ROH + \overset{+}{H}$$
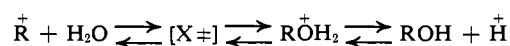
we write

$$f_{R^+}/f_{X\ddagger} = k_s^f/k^f a_{H_2O} \qquad (2)$$

$$f_{H^+}/f_{X\ddagger} = k_s^b/k^b f_{ROH} \qquad (3)$$

where the subscript s denotes reaction in the presence of added salt and the standard state is a dilute aqueous solution. For k^b and k^f we use the rate constants in 0.05 M NaCl [this low electrolyte concentration has little effect on reaction rate (Tables I and II)]. This treatment takes into account only the water molecule which is forming a new covalent bond with the carbonium ion; other interactions of water molecules are included in the activity coefficients.

These activity coefficient ratios are plotted logarithmically against salt concentration in Figures 4 and 5, and log f_{H^+}/f_{R^+} is plotted against salt concentration in Figure 6. (The value of f_{H^+}/f_{R^-} is calculated using eq 2 and 3, or directly from the salt effects upon H_R, f_{ROH},[14] and water activity.[30])

For attack of water the salt order upon $f_{R^+}/f_{X\ddagger}$ is Me$_4$NCl > no salt $\approx$ CsCl > NaCl > KCl > NaBr $\approx$ NaNO$_3$ > LiCl > NaClO$_4$ > LiClO$_4$ (Figure 4). In the transition state positive charge is developed on the incoming water molecule, and hydrogen bonding should neutralize that developing charge but not that of the carbonium ion. The electrolyte could affect the relative

(25) C. A. Bunton and A. Konasiewicz, *J. Chem. Soc.*, 1354 (1955).
(26) Reference 22, Chapter 11; H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).
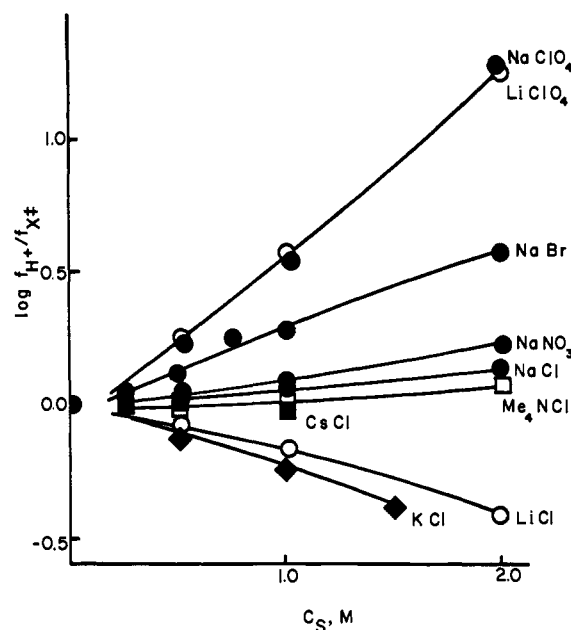(27) J. Bjerrum, *Chem. Soc., Spec. Publ.*, No. 12, 1 (1958).

(28) F. A. Long and M. A. Paul, *Chem. Rev.*, 57, 935 (1957).
(29) C. A. Bunton and J. H. Fendler, *J. Org. Chem.*, 31, 3764 (1966); C. A. Bunton, S. J. Farber, and E. J. Fendler, *ibid.*, 33, 29 (1968).
(30) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1965, Appendix 8.10; S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, 68, 911 (1964).
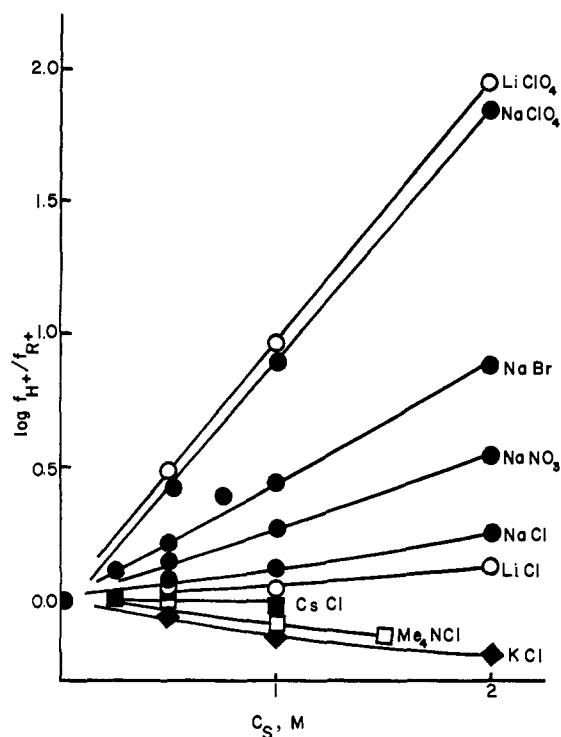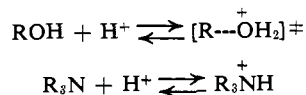
Figure 6. Salt effects upon the relative activity coefficients of the hydronium and carbonium ions.

Salt	Log $f_{H^+}/f_{X^\ddagger}$	Log f_{H^+}/f_{R^+}	Log f_{H^+}/f_{HD^+}	Log f_{H^+}/f_{HB^+}
LiCl	−0.18	0.04	0.09	0.14
NaCl	0.05	0.11	0.00	0.13
KCl	−0.24	−0.14	−0.04	0.12
CsCl	0.00	0.00		
Me₄NCl	0.00	−0.08	−0.04	0.16
NaBr	0.28	0.43	0.13	0.17
NaNO₃	0.08	0.26		0.22
LiClO₄	0.55	0.96	0.21	0.37
NaClO₄	0.55	0.89	0.15	0.33

[a] At 25.0° and 1 M salt, B = p-nitroaniline, D = diphenylamine.

stability of the carbonium ion directly by interacting with a counteranion or indirectly by changing the water structure or its hydrogen bonding ability.

Two trends appear in the salt effects: (i) anions of low charge density decrease $f_{R^+}/f_{X^\ddagger}$, i.e., stabilize the carbonium ions relative to the transition state; and (ii) lithium ions are more effective than the other larger alkali metal cations at decreasing f_{R^+}/f_X, whereas the relatively hydrophobic tetramethylammonium ion increases $f_{R^+}/f_{X^\ddagger}$. Before analyzing these trends it is useful to consider the other activity coefficient ratios.

The salt order upon $f_{H^+}/f_{X^\ddagger}$ is NaClO₄ ≈ LiClO₄ > NaBr > NaNO₃ > NaCl > Me₄NCl ≈ CsCl ≈ no salt > LiCl > KCl (Figure 5). Salt effects upon Hammett's acidity function, H_0', can be explained in terms of effects upon the Hammett base, B, and the activity of water, i.e., f_{H^+}/f_{HB^+} is governed by the activity of water, suggesting that hydrogen bonding is of key importance in determining the relative stabilities of H⁺ and HB⁺[13,31,32] but not of H⁺ and R⁺.

We can draw analogies between acid-catalyzed alcohol heterolysis and amine protonation.

$$\text{ROH} + \text{H}^+ \rightleftharpoons [\text{R}\text{---}\overset{+}{\text{OH}_2}]^\ddagger$$

$$\text{R}_3\text{N} + \text{H}^+ \rightleftharpoons \text{R}_3\overset{+}{\text{N}}\text{H}$$

However, we see no close similarity between salt effects upon $f_{H^+}/f_{X^\ddagger}$ and f_{H^+}/f_{HB^+} or f_{H^+}/f_{HD^+} (Table VII). The values of f_{H^+}/f_{HB^+} were calculated using data in Tables III and IV, the Results section, and ref 14, 20, and 22. The differences between $f_{H^+}/f_{X^\ddagger}$ and f_{H^+}/f_{HB^+} are not surprising in view of the different sizes

(31) D. Rosenthal and J. S. Dwyer, J. Phys. Chem., 66, 2687 (1962); C. Perrin, J. Amer. Chem. Soc., 86, 256 (1964); M. Ojeda and P. A. H. Wyatt, J. Phys. Chem., 68, 1857 (1964).
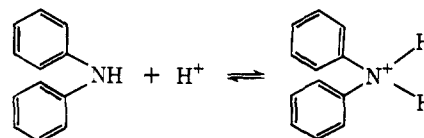(32) K. N. Bascombe and R. P. Bell, Discuss. Faraday Soc., 24, 158 (1957); P. A. H. Wyatt, ibid., 24, 162 (1957).

of the organic groups in the p-nitroanilinium ion and the transition state, and the differences between oxonium and anilinium ions. It seemed to us that the conjugate acid of diphenylamine with its bulky phenyl groups

and its two acidic protons might be a better model for the transition state than the p-nitroanilinium ion. However, there are considerable differences in the salt effects upon the activity coefficients of the transition state and this conjugate acid (Table VII) suggesting that ammonium ions are not good models for the transition state, and that hydrogen bonding is not the all important factor in the acid-catalyzed formation of the carbonium ion. (Hill and Mueller have already shown that proton loss from the conjugate acid of tri-p-anisylmethanol is not rate limiting.)[17]

Direct Interactions and the Role of Solvent Structure. Many workers have discussed environmental effects upon rates and equilibria in terms of medium effects, such as ionizing power and electrostatic ion atmosphere interactions,[7a] and specific interactions, such as hydrogen bonding[33] and special salt effects.[8] Others have considered the importance of solvent reorganization in going from initial to transition state, in particular Robertson in discussing solvolyses in water,[34] and Ritchie has applied it to reactions of stable carbonium ions with anionic nucleophiles in nonaqueous systems.[3] It appears that this concept, together with that of direct interactions, is applicable to some of our kinetic salt effects. Although the reactions of the carbonium ion with water and hydroxide ion are formally of different charge types,[7a] there are similarities in the kinetic salt effects, suggesting that changes in the stabilities of the carbonium ion are of considerable importance.

We will consider first the rate and equilibrium constant for formation of the carbonium ion, in terms of $f_{H^+}/f_{X^\ddagger}$ and f_{H^+}/f_{R^+} (Figures 5 and 6). Perchlorate ion strongly stabilizes carbonium ions relative to ions which contain acidic protons (e.g., oxonium and anilinium ions) and is particularly effective at assisting SN1 solvolyses of uncharged substrate.[8,11,12] Interionic interactions must be important, not only in low polarity solvents[8] but also in polar hydroxylic solvents, at least at high ionic strengths. The average interionic dis-

(33) A. J. Parker, Quart. Rev., Chem. Soc., 16, 163 (1962).
(34) R. E. Robertson, Progr. Phys. Org. Chem., 4, 213 (1967).

tance is 9.4 A for 1 M salt,[35] which is not large compared with the size of some of these bulky ions, and because of the lowered dielectric constant around the ions their interaction energies could be considerably larger than their translational energies. A bulky triarylmethyl carbonium ion should not be strongly hydrated and could interact with a bulky anion by virtue of electrostatic and dispersion forces and of solvent structure promoted ion pairing.[36] On this hypothesis, we assume that perchlorate ion increases $f_{H^+}/f_{X^{\pm}}$ and f_{H^+}/f_{R^+} by stabilizing the carbonium ion or the transition state. This explanation is essentially that applied earlier to anion effects upon A1 reactions and the H_R and H_0' acidity scales.[14] In postulating these interactions, we note that similar species, intimate or solvent separated ion pairs, have been postulated as reaction intermediates in solvolyses in polar hydroxylic solvents.[15,16] The salt effects upon f_{H^+}/f_{R^+} are considerably larger than those upon $f_{H^+}/f_{X^{\pm}}$, as expected in terms of a transition state intermediate in structure between a carbonium and an oxonium ion. Perchlorate ion could slow attack of water or hydroxide ion by interacting directly with the ion or transition state, in other words, stabilization by perchlorate ion should increase in the sequence $H^+ < X^{\pm} < R^+$ with decreasing charge density of the cation. (This explanation is consistent with Brønsted's original generalization that kinetic salt effects upon an ionic reaction are greatest for counterions.[37])

The kinetic effects of cations cannot be interpreted in terms of these interactions, but could result from effects upon water structure.

In considering deuterium solvent isotope effects on S_N1 solvolyses, Laughton and Robertson noted that the partial charges in the transition state will disrupt the existing water structure and set up new ion-oriented structures.[34,38] Similarly changes in water structure about the reactants should occur during formation and decomposition of a carbonium ion in water. The tri-p-anisylmethyl carbonium ion with its delocalized charge should fit into the water structure as would an uncharged solute, but formation of the transition state leads to localization of this charge. Lithium ions orient water molecules about themselves[39] and should compete with the forming oxonium ion in ordering water molecules. But the larger alkali metal cations disrupt the existing structure, whereas tetramethylammonium ions are not strongly hydrated, increase the solubility of uncharged solutes,[21] and should not hinder stabilization of the transition state by water and stabilization of the transition state relative to the carbonium ion increases in the sequence $Na^+ < K^+ < Cs^+ < Me_4N^+$ (Figure 4).

Water activity has been considered only insofar as it concerns that water molecule which forms a new covalent bond. This approach might be badly in error if there were considerable oxonium ion character in the transition state, but we see no correlation between the salt effects and water activity or the more sensitive osmotic coefficients.[30] Although the ability of anions

to increase $f_{H^+}/f_{X^{\pm}}$ and f_{H^+}/f_{R^+} increases with decreasing charge density, cation effects upon f_{H^+}/f_{R^+} are relatively small as compared with those upon $f_{R^+}/f_{X^{\pm}}$ (Figures 5 and 6). The solvated proton hydrogen bonds very strongly to water but without materially disrupting its hydrogen bonded structure[39] and, if we assume that the carbonium ion also has no marked disruptive effect on water, cations should have little effect upon f_{H^+}/f_{R^+}. Perchlorate ions have dominant effects upon $f_{H^+}/f_{X^{\pm}}$, but there is dependence on the nature of the cation for the reasons outlined earlier in our discussion of the relative stabilities of the carbonium ion and the transition state. (In these discussions separation of anionic and cationic effects can only be done qualitatively because of the strong interionic interactions at high salt concentrations.)

In considering the reaction of hydroxide with carbonium ion, we cannot separate the activity coefficients in the Brønsted rate equation, and we must consider both the ion–atmosphere salt effects, which should always inhibit reaction,[7a] and the specific salt effects. Perchlorates strongly inhibit reaction suggesting a direct interaction. Sodium chloride, bromide, and nitrate and potassium chloride have rather similar salt effects, but lithium salts inhibit strongly and tetramethylammonium chloride initially inhibits reaction as predicted by the Debye–Hückel treatment. Lithium ions could deactivate the hydroxide ion by making the coordinated water molecules more acidic, ordering the water molecules, and making solvent reorganization more difficult; cf. ref 38. The nucleophilicity and basicity of hydroxide ion are reduced both by hydrogen bonding and ion pairing. However, tetramethylammonium ion increases water–water interactions,[40] and could therefore decrease hydroxide ion hydration, and should block water molecules from hydrogen bonding to hydroxide ion without deactivating it by strong ion pairing, therefore increasing the reactivity of hydroxide ions.

Reaction with Nucleophilic Anions. The second-order rate constants at 25.0° are azide 5 × 10⁶, hydroxide 8200, and water 0.22 l. mol⁻¹ sec⁻¹. Azide ion is very reactive toward carbonium ions,[7] and the relative unreactivity of lyate ions toward some carbonium ions has been noted.[7,25,41] These differences are apparently not related to the nucleophilicities of these ions on, for example, the Swain–Scott scale.[42] Most treatments of reagent reactivity focus on the inherent reactivity of the reagent, e.g., its nucleophilicity, and on the sensitivity of the reaction to reagent reactivity, as independent parameters. On this basis it is difficult to see why hydroxide is more reactive than azide ion in S_N2 reactions, but less so for attack on a carbonium ion. However, if these parameters are not independent, one might assume that for attack on a carbonium ion, where resistance to bond making should be small, the more important factor is desolvation of the nucleophilic anion in the course of reaction.[33,34] Ignoring solvation effects, we would predict an inverse relationship between nucleophilicity and leaving ability, but azide ion is both a better nucleophile than hydroxide

(35) Reference 23b, Chapter 2.9.
(36) R. M. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963).
(37) J. N. Brønsted and A. Delbanco, *Z. Anorg. Allg. Chem.*, **144**, 248 (1925).
(38) P. M. Laughton and R. E. Robertson in ref 13, Chapter 7.
(39) Reference 23a, p 210; G. R. Choppin and K. Buijs, *J. Chem. Phys.*, **39**, 2042 (1963).

(40) H. S. Frank and M. W. Evans, *ibid.*, **13**, 507 (1945); ref 13, Chapter 36.
(41) G. R. Luces and L. P. Hammett, *J. Amer. Chem. Soc.*, **64**, 1928 (1942).
(42) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

ion, and a better leaving group, which is understandable if the solvation effects are important in controlling nucleophilicity but have less effect on leaving group ability, so that the lower Lewis basicity of the azide ion dictates leaving group ability.

Nature of the Carbonium Ions. There is extensive evidence that discrete ion pairs are intermediates in S$_N$1 solvolyses, particularly in weakly ionizing solvents, and these ion pairs either dissociate or react chemically.[8,15,16] In discussing the stabilization of tri-*p*-anisylmethyl carbonium ions or carbonium ion-like

transition states by bulky anions such as perchlorate, we suggest that interionic attractions are in part responsible, although we cannot distinguish between discrete ion pairs and very transient ionic aggregates which could be present in solutions of relatively high ionic strength. It has been noted that ion pairs formed in solvolysis may have some covalent character, and this could also be so in our systems, for example, alkyl perchlorates are generated in acidic media in which perchlorate ion acts as a nucleophile.[43]

(43) D. M. Hoffman, *J. Org. Chem.*, **36**, 1716 (1971).

Stable Carbocations. CXXVII.[1] Cyclohexenyl and Cyclopentenyl Cations and Their Methylated Derivatives

George A. Olah,* Gao Liang, and Y. K. Mo

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received July 28, 1971

Abstract: The nuclear magnetic resonance spectroscopic study of the 2-cyclohexenyl (**3a**), 1-methyl-2-cyclohexenyl (**3b**), 1,5-dimethyl-2-cyclohexenyl (**3c**), 1,3-dimethyl-2-cyclohexenyl (**3d**), 1,3,5-trimethyl-2-cyclohexenyl (**3e**), 2-cyclopentenyl (**4a**), and 1-methyl-2-cyclopentenyl (**4b**) cations is reported. Ring contraction reactions of cyclohexenyl cations to methyl-substituted cyclopentenyl cations are described. No significant 1,3-orbital interaction is observed in cyclopentenyl cations, as is revealed by carbon-13 nmr studies. Under stable ion conditions, *cis*-3-bicyclo[3.1.0]hexanol forms ion **4b** with no indication of the trishomocyclopropenyl cation.

W ith the discovery that many substituted allylic cations are stable in aqueous mineral acids,[2–6] in fluorosulfuric acid,[7–10] or in antimony pentafluoride based superacids,[11,12] the possibility was provided for the direct observation of allyl cations by spectroscopic methods (particularly by nmr) and the study of their rearrangements. In the reported stable cyclic alkenyl cations, the terminal positions of the allylic system were partially or completely alkylated (or arylated). Even though an estimate of the stability of cyclohexenyl and cyclopentenyl cations can be obtained from solvolysis studies,[13–16] there was until now no direct

observation of the unsubstituted parent cycloalkenyl cations.[7]

Bartlett and Rice[13] have found the absence of the anchimeric assistance by the double bond in the acetolysis of Δ^3-cyclopentene bromide. However, results of product studies and interpretation of rate data in some recent works[17–19] do support the presence of such an effect. In view of these data and the chemical stability of carbocations in superacid systems,[20] we have attempted to observe cycloalkenyl cations, bishomocyclopropenyl (**1**), and trishomocyclopropenyl cations, **2**.[21,22]

(1) Part CXXVI: G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972).
(2) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. T. Wisotsky, *ibid.*, **84**, 1498 (1962).
(3) N. C. Deno, H. F. Richey, N. Friedman, J. D. Hodge, J. J. House, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963).
(4) N. C. Deno and C. U. Pittman, Jr., *ibid.*, **86**, 1744, 1871 (1964).
(5) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2153 (1965).
(6) J. S. Sorensen, *ibid.*, **89**, 3782, 3794 (1967); **91**, 6397 (1969).
(7) The assumed observation of cyclohexenyl cation (G. A. Olah and W. S. Tolgyesi, *ibid.*, **83**, 5031 (1961)) must now be considered to be in error. See subsequent discussion.
(8) G. A. Olah and M. B. Comisarow, *ibid.*, **86**, 5682 (1964).
(9) N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 18.
(10) D. G. Farnum, A. Mostashari, and A. A. Hagedorn, *J. Org. Chem.*, **36**, 698 (1971).
(11) G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).
(12) G. A. Olah, *Science*, **168**, 1297 (1970).
(13) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).
(14) H. L. Goering and D. L. Towns, *J. Amer. Chem. Soc.*, **85**, 2295 (1963).
(15) M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963).
(16) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

R
1a, R = H
b, R = CH$_3$

2

In this paper we present our data on the nuclear magnetic resonance spectroscopic observation of 2-cyclohexenyl (**3a**), 1-methyl-2-cyclohexenyl (**3b**), 1,5-dimethyl-2-cyclohexenyl (**3c**), 1,3-dimethyl-2-cyclohexenyl (**3d**), 1,3,5-trimethyl-2-cyclohexenyl (**3e**), 2-cyclo-

(17) M. Hanack and K. Riedlinger, *Chem. Ber.*, **100**, 2107 (1967).
(18) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **90**, 5338 (1968).
(19) E. L. Allred and C. R. Flynn, *ibid.*, **92**, 1064 (1970).
(20) Reference 12 and references quoted therein.
(21) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3224, 3245 (1961).
(22) S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523, 6524 (1959).