These results may be taken as evidence for the existence of a delocalized proximity electrical effect which is a function of the side chain Z. The exact nature of this delocalized proximity electrical effect remains to be established.

Deviation of the Unsubstituted Compound.—We have excluded the value for X = H from the correlations as this value often deviates from the correlation line obtained for ortho-substituted compounds. It was shown, however, that, in the case of polarographic half-wave potentials of ortho-substituted compounds, h_{calcd} was not significantly different from h_{obsd} (the value for the unsubstituted compound). In the case of nmr data of ortho-substituted compounds, 16 of 18 sets studied showed no significant difference between h_{calcd} and h_{obsd}.[7] It seemed of interest to determine whether h_{calcd} and h_{obsd} are significantly different in the case of the proton transfer equilibria studied here. A Student's t test was carried out for the significance of h_{calcd} for all sets for which significant correlation with eq 4 was obtained and h_{obsd} values were available. The results are given in Table VI. Of the 23 sets studied, 17 did not give significant differences between h_{obsd} and h_{calcd}. It would seem that the unsubstituted compound more often than not does lie on the correlation line for ortho-substituted compounds. It seems to deviate in some examples, however.

TABLE VI

SIGNIFICANCE OF h_{calcd}

Set	h_{obsd}	h_{calcd}	$\|\Delta\|h^a$	$s_h{}^b$	t^c	n^d	CL^e
1	5.17	5.28	0.11	0.244	0.451	13	20.0
2	5.28	5.25	0.03	0.342	0.088	10	<20.0
3	4.959	5.30	0.34	0.849	0.400	6	20.0
4	6.95	7.05	0.10	0.0831	1.203	5	50.0
5	5.58	5.27	0.31	0.202	1.535	6	50.0
6	8.6	8.68	0.08	0.145	0.552	9	20.0
7	5.98	5.99	0.01	0.283	0.035	5	<20.0
8	10.00	9.83	0.17	0.0562	3.024	6	90.0
9	9.89	9.99	0.10	0.119	0.840	8	50.0
10	4.60	3.82	0.78	0.0729	10.70	6	99.0
11	0.79	0.923	0.13	0.533	0.244	10	<20.0
12	4.203	3.47	0.73	0.0284	25.70	8	99.9
13	8.73	8.78	0.05	0.185	0.280	7	20.0
14	9.02	8.76	0.26	0.129	2.016	7	80.0
15	7.18	7.59	0.41	0.176	2.330	9	90.0
16	1.83	2.02	0.19	0.0914	2.079	6	80.0
17	7.07	7.59	0.52	0.191	2.723	6	90.0
18	0.340	0.767	0.43	0.0158	27.22	4	95.0
20	4.66	4.64	0.02	0.0607	0.329	6	20.0
21	4.44	4.46	0.02	0.0472	0.424	6	20.0
22	0.829	0.786	0.04	0.0472	0.847	8	50.0
27	3.75	3.68	0.07	0.0575	1.217	7	50.0

^{a} Absolute value of the difference between h_{obsd} and h_{calcd}. ^{b} Standard error of h_{calcd}. ^{c} Student's t test for the significance of h_{calcd}. ^{d} Number of points in the set. ^{e} Confidence levels for the significance of h_{calcd}.

Specific Salt Effects upon the Rates of SN1 Solvolyses[1]

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Specific kinetic salt effects upon the solvolyses of *tert*-butyl bromide, 1- and 2-methyl-*exo*-2-chloronorbornane, isobornyl chloride, and camphene hydrochloride have been examined in methanol, aqueous methanol, acetone, 1,2-dimethoxyethane, and methanol-1,2-dimethoxyethane. Anion effects are important but cation effects are small (for Li^+, Na^+, and Et_4N^+). The anion order is $ClO_4^- > OTos^- \approx NO_3^- \approx Br^- > Cl^- \approx$ no salt $> F^- > OH^-$. Isotopic and azide trapping experiments show that carbonium ions or ion pairs can return in solvolyses of camphene hydrochloride and *tert*-butyl chloride, but return is not large enough to explain the salt effects. This conclusion is supported by the observation of specific salt effects upon solvolyses of isobornyl chloride and 1-methyl-*exo*-2-chloronorbornane. Retention of configuration in the methanolysis of isobornyl chloride and camphene hydrochloride shows that methyl or hydride shifts do not occur during the lifetime of the carbonium ions. Experiments on isobornyl chloride in aqueous methanol and acetone show that chloride and perchlorate ions have little effect upon the activity coefficient of the substrate. The transition state effects appear to be related, at least in part, to solvent structure induced interactions between the carbonium-like transition state, especially with a large anion such as perchlorate.

Salt effects upon the SN1 solvolyses of alkyl halides and sulfonic esters in polar hydroxylic solvents have been widely studied. It was postulated that increase of ionic strength should assist any reaction in which a neutral molecule dissociates into ions,[3,4] and Ingold and his coworkers observed such an effect in SN1 solvolyses of secondary and tertiary alkyl halides in aqueous organic solvents. They used a simple electrostatic model to explain stabilization of the dipolar transition state, and for a limited number of salts

obtained a reasonable fit between experiment and theory by assuming that the transition state could be represented as a dipole in which the carbon–halogen bond was stretched by *ca.* 0.4 Å.[4]

They also observed a rate retardation for some SN1 solvolyses when the common halide ion competed with the solvent for the carbonium ion.[3-5] This common ion retardation becomes very important with relatively stable carbonium ions and in solvents of low nucleophilicity.[4,6]

The simple electrostatic theory of the ionic strength effect assumed that ions acted nonspecifically, as point

(1) Support of this work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) NDEA Fellow, University of California, Santa Barbara, 1965–1968.

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charges, and that the whole effect was on the dipolar transition state.[3,4] However, salts have specific effects upon the activity coefficients of nonelectrolytes in water,[7] and therefore could well have specific effects upon both the initial and transition states of an S_N1 solvolysis even in polar hydroxylic solvents. There are specific effects upon the rates of S_N1 solvolyses,[8-10] and Hammett, in particular, drew attention to the possibility that small ions of high charge density might "dry" the solvent and so reduce the reaction rate.[8] Rate retardations or unexpectedly small enhancements by lyate and other small high charge density ions have been observed for several S_N1 solvolyses in polar hydroxylic solvents.[5,8-13]

Taft and his coworkers showed that the activity coefficient of *tert*-butyl chloride in water was dependent upon the nature and concentration of electrolytes, but that for many, but not all salts, there was an approximate cancellation between the specific effects on the initial and transition states, and that the net effect fitted the simple electrostatic theory reasonably well.[14] Nonetheless, difficulties remained because there are specific salt effects upon the activity coefficients of the transition state for the solvolysis of *exo*-norbornyl bromide in aqueous dioxane.[15] Another example of specific kinetic salt effects which cannot be explained wholly in terms of initial state effects is the S_N1 solvolysis of 4-nitro-4'-phenyl diphenyl methyl chloride.[16] Also the electrostatic theory predicts a logarithmic relationship between rate and ionic strength whereas for many reactions the relationship is linear,[10] even in solvents of low dielectric constant.[17]

Perrin and Pressing have recently put forward a theoretical treatment of kinetic salt effects, based on dipole–dipole interactions between the transition state and the ion-paired electrolytes, which explains the specificity of these salt effects.[18] A special salt effect has been observed in some acetolyses, where a salt, e.g., lithium perchlorate, may assist dissociation of an ion pair,[17,19] and ion pair return in, for example, the hydrolysis of *exo*-norbornyl bromide[15] or a diarylmethyl chloride[5,16] could be affected specifically by added electrolytes.

Electrolyte effects are used extensively as mechanistic tests, and it is therefore important to find whether the specific salt effects which are observed in S_N1 solvolyses in polar hydroxylic solvents depend upon mechanistic complexity of the reaction or upon the

limitations of the simple ionic atmosphere treatment of kinetic salt effects.

Bunnett and his coworkers have observed reactions in which simultaneous substitution and elimination occur, but in which the ratio of elimination to substitution cannot be explained simply in terms of simultaneous first- and second-order reactions, suggesting the importance of specific electrolyte effects.[20,21]

Because of our earlier interest in reactions of norbornyl derivatives,[11b,22] we did much of our work with camphene hydrochloride (CmHCl, I), isobornyl chloride (iBCl, II), and 1- and 2-methyl-*exo*-chloronorbornane (III and IV).

I   II   III   IV
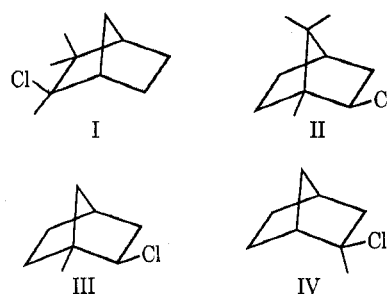
Sneen and his coworkers have studied the reaction rates and products in the presence of added nucleophiles using substrates which give "borderline" kinetic behavior[23] and explain their results in terms of simultaneous dissociation of an ion pair to give products and nucleophilic attack upon the ion pair, rather than in terms of the classical explanations based on simultaneous uni- and bimolecular mechanisms. Added salts could affect the partitioning of such an ion pair. One method of eliminating return of intermediates to reactants as a cause of specific salt effects is to use substrates, such as II and III which generate carbonium ions, which on return give the more reactive alkyl chlorides (I and IV). There are several other methods which can give information on the possible importance of return of intermediates to reactants and on the lifetime of such intermediates in reactive hydroxylic solvents: (1) examination of kinetic salt effects in solvents varying from polar hydroxylic solvents such as methanol ($Y = -1.09$) and methanol–water, 70:30 v/v ($Y = 0.96$), to relatively nonpolar solvents such as acetone–water, 90:10 v/v ($Y = -1.86$),[24] where ion pairing of electrolytes and reaction intermediates could be important; (2) rate measurements in heterogeneous systems in order to exclude effects on the activity coefficient of the substrate;[14,15] (3) solvolysis in the presence of $^{36}Cl^-$ in order to detect return of a carbonium ion or ion pair to substrate;[17b,25] (4) examination of the stereochemistry of solvolysis of the trimethylnorbornyl chlorides, to find whether the in-

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termediates last long enough for methyl or hydride shifts to occur.[26]

Examination of the kinetic salt effects showed that added chlorides did not increase reaction rate markedly, irrespective of any contribution of a common-ion effect, whereas perchlorate ions always markedly increased the rate. We therefore used 1 and 2 in the presence of chloride and perchlorate ions.

Experimental Section

Materials.—The preparation and purification of most of the alkyl chlorides has already been described. D-(+)-Camphor was converted into (+)-camphene by the method of Meerwein and Wortmann, which involves some loss of optical purity.[29] The products had values of [α]D between +58 and +64°. (The specific rotation of optically pure camphene appears to be [α]^{25}D 117.5° in toluene, and 108° in ethanol[30] showing that our material had 54–60% optical purity.) Methanol was dried by Bjerrum's method,[31] distilled, and then treated with molecular sieve. Acetone and dioxane were purified by standard methods,[31] and 1,2-dimethoxyethane (DME) was dried over sodium and then fractionally distilled.

The salts were commercial samples or were prepared by acid–base neutralization and were dried either in an oven at 150° or under vacuum in an Abderhalden drying pistol over P$_2$O$_5$.

The mixed solvents were generally made up by weight to correspond to the quoted volume:volume compositions, except for 1,2-dimethoxyethane–methanol, 80:20 v/v, which was made up by volume.

Kinetics.—Most of the reactions were followed titrimetrically by acid–base titration using lacmoid as indicator. Because of the high reactivity of camphene hydrochloride, its solvolyses in polar solvents were followed by withdrawing samples from a water-jacketed automatic pipet and quenching them in acetone at −80°.[11b] The first-order rate constants were calculated using the integrated form of the first-order rate equation and are in sec^{-1}. A few reactions in the absence of added electrolyte were followed conductrimetrically. Rate constants determined conductrimetrically agreed to within ±1% and the titrimetric rate constants within ±5%.

Isobornyl chloride was allowed to react in both homogeneous and heterogeneous conditions using methanol–water, 70:30 v/v, and acetone–water, 55:45 v/v. Aqueous dioxane could not be used as solvent under heterogeneous conditions because emulsions were formed, and the solvent compositions were chosen so that the reactions were relatively slow, but the water contents were sufficiently high that the concentration of isobornyl chloride in a saturated solution was low. For each pair of experiments, the reaction solution at 0° was divided into two equal portions, one for the homogeneous and one for the heterogeneous experiments. For the former, powdered isobornyl chloride was added, and the mixture was shaken at 0°, and then placed in a vessel, also at 0°, which contained a sintered glass filter to retain undissolved substrate, so that the filtered solution could be sucked into the reaction vessel. Atmospheric moisture was excluded by using drying tubes.

A similar type of apparatus was used for the heterogeneous experiments where solvolysis was allowed to occur at 0° in the presence of solid isobornyl chloride which was excluded from the sampling chamber by a sintered glass filter. For these experiments the reaction rate, v, was determined by plotting % reaction against time. The reaction was followed for 2–3 hr, and good

linear plots were obtained; the mean values of v, calculated between points, agreed with the graphical value within ±2%.

Isotopic Exchange.—The general procedure has already been described.[25] Radioactive inorganic chloride was used, and the unreacted alkyl chloride was extracted into petroleum ether. The alkyl chloride was solvolyzed, the chloride ion was determined by potentiometric titration, and the solution was counted using an Ekco Autoscaler N530 F. Corrections were made for background counts. Control experiments using Li^{36}Cl showed that no inorganic chloride was extracted using this procedure, and in the experiments with camphene hydrochloride the conditions for the final solvolysis were such that any isobornyl chloride would not react and could be removed by a second extraction with petroleum ether.

The relative values of the first-order rate constants of exchange, k_e, and chemical reaction, k_c, are given by

$$k_e/k_c = \log\,[100/(100 - \% \text{ exchange})]/\log\,[a/(a - x)]$$

where a and (a − x) are the substrate concentrations at the initial time and the time of sampling.

Stereochemistry.—The optical rotations were determined using either a conventional visual polarimeter or a Bendix–Ericcson electronic polarimeter. Because of a small sample size needed for the electronic polarimeter, it was used for determination of the rotations of the products, using either the Na D line or the Hg green line at 5461 Å at 20°. The rotations were all measured using ethanol solutions, excepting camphene hydrochloride whose rotation was measured in ether. For camphene they were reproducible to 3%. The starting materials and products were purified or isolated by preparative glc.

Camphene hydrochloride was prepared from camphene in the usual way, and it was converted into isobornyl chloride by dissolving it in liquid SO$_2$ and allowing the solvent to evaporate. Partial racemization occurred during this step, and when we converted camphene into isobornyl chloride by dissolving it in liquid SO$_2$ and bubbling hydrogen chloride into the solution, the isobornyl chloride was almost wholly racemized.

The details of a solvolysis are given in Table I, and Table II summarizes the results of solvolyses done under various conditions. The extent of racemization of isobornyl chloride varied from one preparation to another, and in one preparation, that used for solvolysis in the presence of Ag$_2$O, there was little racemization (Table II).

TABLE I
SOLVOLYSIS OF OPTICALLY ACTIVE CAMPHENE HYDROCHLORIDE[a]

Compd	[α]Hg, deg	[α]D, deg	[M]D, deg	% retention
Camphene hydrochloride[b]		−26.7	−46.1	
Camphene[c]	+67.5	+57.1	+77.8	99
Camphene hydrate Methyl ether[c]	−18.6	−16.8	−28.2	

[a] At 0° in MeOH with NaHCO$_3$. [b] Starting material; the camphene used in the initial preparation had [α]Hg +68.4°; [α]D +57.9°; [M]D +78.9°. [c] Products.

TABLE II
STEREOCHEMICAL COURSE OF SOLVOLYSIS OF CAMPHENE HYDROCHLORIDE AND ISOBORNYL CHLORIDE[a]

Substrate	Reagent	% optical purity of product — Cm	CmOMe
CmHCl[b]	0.2 M NaOMe	54.8 (+59.2°)	52.0 (−15.9°)
CmHCl[b]	NaHCO$_3$	52.9 (+57.1°)	55.0 (−16.8°)
CmHCl[c]	Ag$_2$O	58.7 (+63.4°)	61.0 (−18.7°)
iBCl[b]	0.2 M NaOMe[d]	25.9 (+27.9°)	24.3 (−7.44°)
iBCl[b]	0.2 M NaOMe[e]	27.6 (+29.8°)	28.4 (−8.7°)
iBCl[c]	Ag$_2$O	53.4 (+58.0°)	55.7 (−17.0°)

[a] In MeOH at 0° unless specified: Cm = camphene; CmHCl = camphene hydrochloride; CmOMe = camphene hydrate methyl ether; iBCl = isobornyl chloride. The values in parentheses are for [α]D. [b] Prepared from camphene of 53.6% optical purity, [α]D +57.9°. [c] Prepared from camphene of 59.1% optical purity, [α]D +63.8°. [d] At 59.3°. [e] At 45.1° in 1,2-dimethoxyethane–methanol, 50:50 v/v.

(26) These shifts occur readily in aprotic solvents.[27,28]

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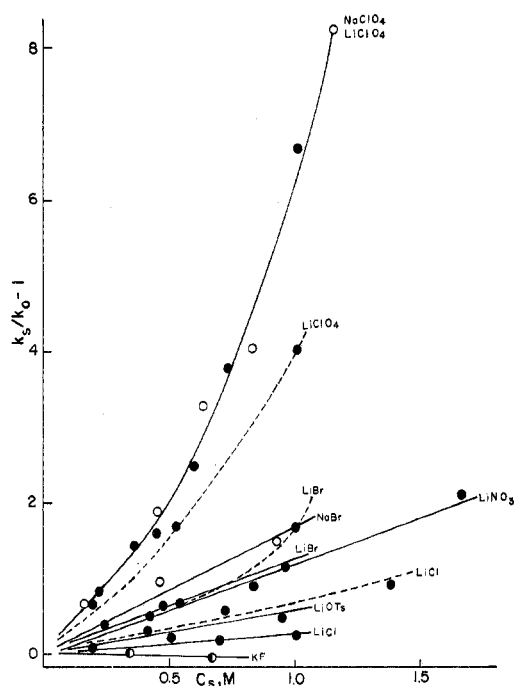
Figure 1.—Salt effects upon the methanolysis of 1-methyl-*exo*-2-chloronorbornane at 80.0° (broken line) and 2-methyl-*exo*-2-chloronorbornane at 25.0° (solid line): ●, lithium salts; O, sodium salts; ◑, potassium salts.
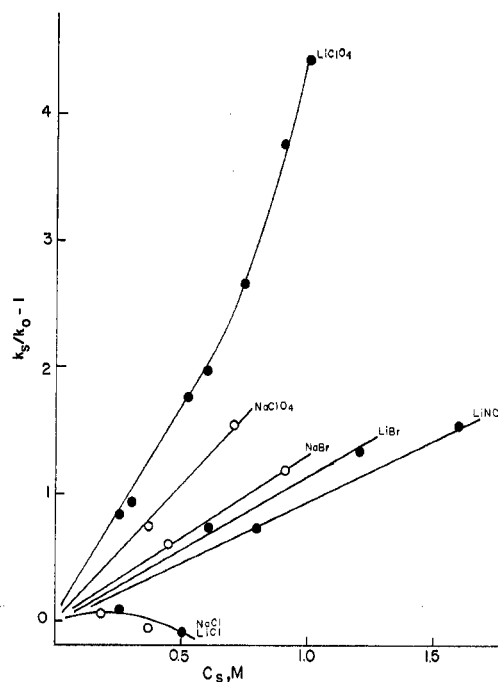
The conversion of camphene into its hydrochloride and back to camphene occurs with no loss of optical activity (Tables I and II), suggesting that both steps occur without racemization and that therefore the formation of camphene hydrate methyl ether probably also occurs without racemization. In one experiment camphene with $[\alpha]D$ +57.9° gave isobornyl chloride with $[\alpha]D$ −16.0° and $[\alpha]Hg$ −16.6°, and in another camphene with $[\alpha]D$ +63.8° gave isobornyl chloride with $[\alpha]D$ −31.5° and $[\alpha]Hg$ −32.8°. Taking $[\alpha]D$ +108° for optically pure camphene in ethanol[30] we calculate the optical purities given in Table II, $[\alpha]D$ −50° for optically pure camphene hydrochloride, and a mean value of $[\alpha]D$ −30.6° for camphene hydrate methyl ether. On the assumption that the solvolysis of isobornyl chloride proceeds without racemization, we estimate $[\alpha]D$ −59.2° and $[\alpha]Hg$ −63° for optically pure material.

Independent experiments showed that the products were optically stable in the reaction solutions, and on a Tween 60–Celite glc column at 120°.

In the course of this work, we compared the rotations of some of the materials at two wavelengths (Table III). The results for camphene confirm Hückel's earlier measurements.[32]

TABLE III
OPTICAL ACTIVITIES AT TWO WAVELENGTHS

Compd	$[\alpha]D/[\alpha]Hg$
Camphene	0.846[a]
Camphene hydrate methyl ether	0.899
Isobornyl chloride	0.979

[a] A value of 0.825 is reported by Hückel.[32]

Products.—The salt effects upon the products of methanolysis of isobornyl chloride and camphene hydrochloride were determined using glc by methods already described.[11b] Because of the insensitivity of the thermal conductivity detector used in our glc, we did not measure the amounts of the minor products such at tricyclene and isobornyl methyl ether which are formed in these solvolyses.[22,33]

Methanolysis of isobornyl chloride and camphene hydrochloride in the presence of sodium or tetraethylammonium azide

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Figure 2.—Salt effects upon the methanolysis of *tert*-butyl bromide at 25.0°: ●, lithium salts; O, sodium salts.

gave what we assume is 2,3,3-trimethylnorbornyl 2-azide, and it was extracted with the other neutral products. We were unable to separate it from camphene hydrate methyl ether by elution from an alumina column using petroleum ether, but it could be isolated by glc at 130° using a Tween–Celite column. It decomposed on heating at atmospheric pressure at *ca.* 170° but had a sharp melting point of 55° in a sealed tube. It had ir peaks at 4.8 and 8.0 μ characteristic of an azide.[34] *Anal.* Calcd for $C_{10}H_{17}N_3$: C, 63.5; H, 14.3; N, 22.2. Found: C, 63.3; H, 14.5; N, 22.0. In most experiments the amount of azide intervention was determined using glc, but with isobornyl chloride in aqueous 1,2-dimethoxyethane titration was used.

Results

Rates of Solvolysis.—Salt effects upon rate constant are illustrated for a number of reactions by plotting or tabulating $(k_s/k_0) - 1$ against C_s (Figures 1–4 and Tables IV–VIII), where k_s and k_0 are the first-order rate constants in the presence and absence of salt, and C_s is the molar concentration of salt. The values of the first-order rate constants in the absence of salt are given in Table IX.

TABLE IV
METHANOLYSIS OF ISOBORNYL CHLORIDE[a]

Salt	C_s, M	$(k_s/k_0) - 1$	b
LiCl	0.51	0.30	0.59
LiCl	1.00	0.60	0.60
LiNO₃	0.50	2.02	4.0
LiNO₃	1.19	4.11	3.5
LiNO₃	0.50	0.42[b]	0.84[b]
LiNO₃	1.19	1.15[b]	0.97[b]
LiClO₄	0.093	0.76	8.2
LiClO₄	0.52	3.09	6.0
LiClO₄	0.51	2.06[b]	4.0[b]
LiClO₄	1.03	5.20[b]	5.0[b]
NaClO₄	0.28	1.84	6.6
NaClO₄	0.56	3.60	6.4

[a] In MeOH at 0° unless specified; at 0° k_0 = 1.84 × 10⁻⁷ sec⁻¹. [b] At 45.0°, k_0 = 9.65 × 10⁻⁶ sec⁻¹.

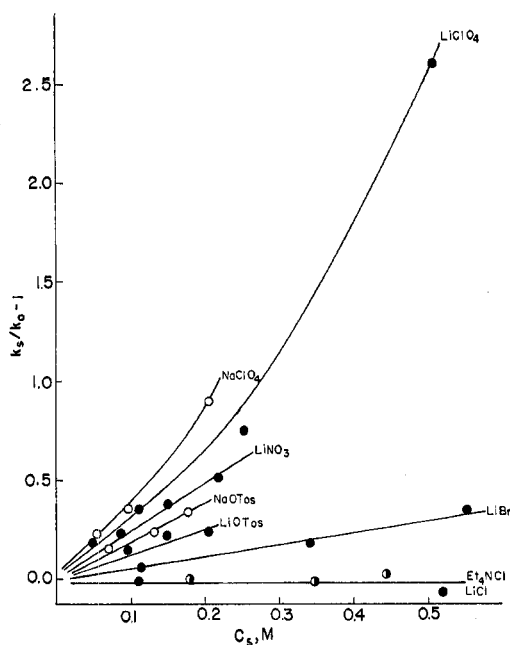(34) R. T. Cowley, "Infrared Spectroscopy," Allyn and Bacon, Boston, 1966, Chapter V.

Figure 3.—Salt effects upon the methanolysis of camphene hydrochloride at 0°: ●, lithium salts; O, sodium salts; ◑, tetraethylammonium salts.
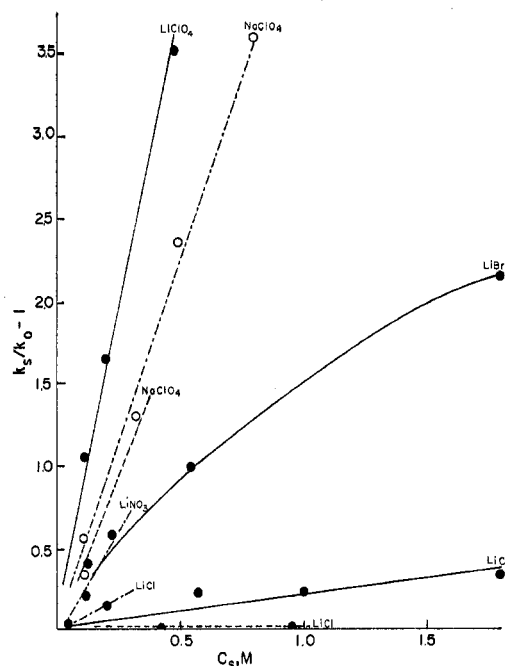

Figure 4.—Salt effects upon the methanolysis of camphene hydrochloride in 1,2-dimethoxyethane–methanol, 80:20, v/v, at 25.3° (solid line), and 0° (- - - -), and in acetone–water, 90:10 v/v, at 0° (- · -): ●, lithium salts; O, sodium salts.

TABLE V

SALT EFFECTS UPON THE METHANOLYSIS OF
2-METHYL-exo-2-NORBORNYL CHLORIDE[a]

Salt	C_s, M	$10^5 k$, sec^{-1}	b
		1.52	
		47.0[b]	
LiCl	0.69	2.14	0.59
LiCl	1.47	2.38	0.39
LiBr	0.47	2.66	1.6
LiBr	1.17	4.45	1.6
LiNO₃	0.58	2.70	1.3
LiNO₃	1.00	3.60	1.4
LiClO₄	0.53	6.55	6.3
LiClO₄	1.18	21.7	11.3
KOMe	0.05	43.4[b]	
NaOAc	0.17	50.5[b]	

[a] In MeOH at 0° unless specified.   [b] At 25.0°.

TABLE VI

SOLVOLYSIS OF ISOBORNYL CHLORIDE IN AQUEOUS METHANOL[a]

Salt	C_s	$10^5 k$, sec^{-1b}	b	$10^7 v$, mol l.$^{-1}$ sec^{-1c}	f_{RCl}	f^*
		3.52		3.00		
LiCl	0.14	3.27		3.03	0.92	0.99
LiCl	0.30	3.45		2.95	1.00	1.02
LiCl	0.38	3.70		3.09	1.02	0.97
LiCl	1.05	4.23		3.00	1.20	1.00
NaCl	0.12	3.21		3.03	0.90	0.99
NaCl	0.37	3.46		3.09	0.95	0.97
Et₄NCl	0.10	3.48		2.95	1.05	1.02
Et₄NCl	0.22	3.48		2.89	1.03	1.04
NaBr	0.10	3.44		2.84	1.04	1.06
NaBr	0.23	3.53		3.07	0.98	0.98
LiClO₄	0.44	5.73		4.64	1.06	0.65
NaClO₄	0.10	4.32	2.3	3.34	1.10	0.90
NaClO₄	0.23	5.05	1.9	3.61	1.19	0.83
NaClO₄	0.33	4.90	1.2	4.42	0.82	0.68
NaClO₄	0.45	5.44	1.5	4.61	1.00	0.65
NaClO₄	1.14	9.48	1.4	7.77	1.05	0.39

[a] In MeOH–H₂O, 70:30 v/v, at 0°.   [b] Homogeneous solution.
[c] Heterogeneous conditions.

TABLE VII

SOLVOLYSIS OF ISOBORNYL CHLORIDE IN AQUEOUS ACETONE[a]

Salt	C_s, M	$10^5 k$, sec^{-1b}	b	$10^7 v$, mol l.$^{-1}$ sec^{-1c}	f_{RCl}	f^*
		2.35		2.32		
LiCl	0.47	2.37		2.02	1.16	1.15
LiCl	1.00	2.30		1.83	1.24	1.27
LiClO₄	0.57	4.58	1.7	2.92	1.56	0.80
LiClO₄	0.74	6.08	2.1	3.38	1.78	0.69
LiClO₄	1.06	8.01	2.3	4.06	1.95	0.57

[a] In acetone–H₂O, 55:45 v/v, at 0°.   [b] Homogeneous solution.
[c] Heterogeneous conditions.

The simple electrostatic theory and the empirical extension of the Debye–Hückel treatment both predict linear relationships between log k and ionic strength.[3,4,35] Our kinetic results support Winstein's conclusion that the relationship between rate and salt concentration is linear rather than logarithmic[10,17] at least for relatively low concentrations of salt, and Tables IV–VIII and X–XIII give the initial slopes, b, of plots of (k_s/k_0) − 1 against salt concentration, C_s. There is a spread of b values, which are close to zero for chlorides, fluorides, and acetates, and which are always largest for perchlorates. However, the actual b values differ, even for substrates of similar structure, e.g., camphene hydrochloride and 2-methyl-exo-2-chloronorbornane. Although the data are not extensive, they indicate that some of the b values decrease with increasing temperature. There is no simple relation between the b values and solvent composition, except that for the solvolysis of isobornyl chloride they decrease for perchlorates in going from methanol to aqueous methanol.

(35) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Part 2.8.

TABLE VIII

SALT EFFECTS ON SOLVOLYSES OF CAMPHENE HYDROCHLORIDE[a]

		—Me$_2$CO–H$_2$O[b]—		—DMe–MeOH[c]—	
Salt	C_s, M	$(k_s/k_0) - 1$	b	$(k_s/k_0) - 1$	b
LiCl	0.028	0.03	1.0		
LiCl	0.099	0.16	1.6		
LiCl	0.410			−0.02	
LiCl	0.573			0.23[d]	0.4[d]
LiCl	0.942			−0.03	
LiCl	1.00			0.24[d]	0.2[d]
LiCl	2.36			0.43[d]	0.2[d]
Et$_4$NCl	0.075	−0.03			
Et$_4$NCl	0.13			0.22	
LiBr	0.545			0.98	1.8
LiBr	1.93			2.33	1.4
LiNO$_3$	0.104	0.20	1.9		
LiNO$_3$	0.210	0.57	2.7		
NaClO$_4$	0.108	0.55	5.1		
NaClO$_4$	0.115			0.35	3.0
NaClO$_4$	0.315			1.3	4.1
NaClO$_4$	0.491	2.33	4.7		
NaClO$_4$	0.977	4.44	4.6		
LiClO$_4$	0.103			1.06[d]	10.2[d]
LiClO$_4$	0.201			1.65[d]	8.2[d]
LiClO$_4$	0.481			3.52[d]	7.3[d]
Bu$_4$NPF$_6$	0.101			0.20[d]	2.0

[a] At 0° unless specified. [b] Me$_2$CO–H$_2$O, 90:10 v/v, at 0° $k = 6.80 \times 10^{-5}$ sec^{-1}. [c] 1,2-Dimethoxyethane–MeOH, 80:20 v/v, at 0° $k = 8.29 \times 10^{-6}$ sec^{-1}, at 25.3° $k = 1.06 \times 10^{-4}$ sec^{-1}. [d] At 25.3°.

TABLE IX

FIRST-ORDER RATE CONSTANTS IN THE ABSENCE OF ADDED SALT[a]

				—Solvent—		
		70%	20%	55%	90%	80%
		MeOH–	MeOH–	Me$_2$CO–	Me$_2$CO–	DME–
Substrate	MeOH	H$_2$O	DME	H$_2$O	H$_2$O	H$_2$O
tert-BuBr	36.7[b]					
1-MBCl (III)	320[c]					
2-MBCl (IV)	15.2					
	470[b]					
iBCl (II)	0.18	35.2		23.5		
	96.5[d]					
CmHCl (I)	72.7		8.3		68.0	148
			104[b]			

[a] Values of $10^6 k$ sec^{-1}, at 0° unless specified; the solvent compositions are in vol %, i.e., 70% MeOH–H$_2$O is 70:30 MeOH–H$_2$O v/v. [b] At 25.0°. [c] At 80.0°. [d] At 45.0°.

TABLE X

VALUES OF b PARAMETERS FOR SOLVOLYSIS OF tert-BUTYL BROMIDE[a]

Salt	b
LiCl	∼0
NaCl	∼0
LiBr	1.2
NaBr	1.4
LiNO$_3$	0.9
LiClO$_4$	3.4
NaClO$_4$	2.2

[a] In MeOH at 25.0°.

For small rate enhancements most of the data are fitted equally well by linear or logarithmic relationships, but for the larger rate enhancements plots of log k against salt concentration curve downward.

We used few cations, but the anion order is generally ClO$_4^-$ > NO$_3^-$ ≈ Br$^-$ ≈ OTos$^-$ ≈ PF$_6^-$ > Cl$^-$ ≈ OAc$^-$ > F$^-$ > OR$^-$ with perchlorate being

TABLE XI

VALUES OF b PARAMETERS OF SOLVOLYSIS OF 1- AND 2-METHYL-exo-2-CHLORONORBORNANE[a]

	—Substrate—	
Salt	sec-RCl[b]	tert-RCl
LiCl	0.8	0.3
LiCl		0.5[c]
LiBr	1.1	1.6
LiBr		1.6[c]
NaBr		2.0
LiNO$_3$		1.2
LiNO$_3$		1.4[c]
LiOTos		0.7
LiClO$_4$	3.3	3.7
LiClO$_4$		6.3[c]
NaClO$_4$		4.3
NaOAc		0.4
KOMe		−1.6
KF		∼0

[a] In MeOH at 25.0° unless specified; sec- and tert- denote the secondary 1,2 derivative and the tertiary 2,2 derivative, respectively. [b] At 80.0°. [c] At 0°.

TABLE XII

VALUES OF b PARAMETERS FOR SOLVOLYSIS OF ISOBORNYL CHLORIDE[a]

		—Solvent—	
		70:30	55:45
Salt	MeOH	MeOH–H$_2$O	Me$_2$CO–H$_2$O
LiCl	0.6	∼0	∼0
Et$_4$NCl		∼0	
NaCl		∼0	
NaBr		∼0	
LiNO$_3$	4.0		
LiNO$_3$	0.9[b]		
LiClO$_4$	6.5		
LiClO$_4$	4.0[b]	1.5	1.7
NaClO$_4$	6.5	2.0	

[a] At 0° unless specified. [b] At 45.0°.

TABLE XIII

VALUES OF b PARAMETERS FOR SOLVOLYSIS OF CAMPHENE HYDROCHLORIDE[a]

		—Solvent—	
		90:10	80:20
Salt	MeOH	Me$_2$CO–H$_2$O	DME–MeOH
LiCl	∼0	1.0	∼0
LiCl			0.1[b]
Et$_4$NCl	∼0	∼0	
LiBr	0.6		1.3[b]
LiOTos	1.6		
NaOTos	1.8		
LiNO$_3$	2.4	3.7	
Bu$_4$NPF$_6$	1.9		
Bu$_4$NPF$_6$			
LiClO$_4$	3.0		
LiClO$_4$			
NaClO$_4$	4.1	4.5	4.2
NaClO$_4$			4.8[b]

[a] At 0° unless specified. [b] At 25.3°.

much more effective than the other anions. Chloride ion generally has little effect except for the methanolysis of 1-methyl-exo-2-chloronorbornane (III) at 80°, and it sometimes retards reaction, even when a common ion retardation is improbable. This salt order is qualitatively similar to that upon the relative stabilities of the trianisyl cation and the p-nitroanilinium ion.[36]

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

Ionic association can be very important; for example, specific salt effects upon the rates of SN2 reactions can be explained in terms of ion pairing of the nucleophilic anion with a cation to give an unreactive ion pair,[37] and an ion-paired salt might show no rate-enhancing ionic strength effect for the SN1 reactions considered in this discussion, but ion pairing appears not to be all important in our systems, because lithium and sodium perchlorate and lithium nitrate are strong electrolytes in methanol, and lithium and sodium chloride are strong in methanol–water containing 0.8 mol fraction of methanol,[38] but nonetheless exhibit very different kinetic salt effects. Conductance measurements show that tetraethylammonium chloride is a stronger electrolyte than either lithium chloride or bromide in methanol, and conductivity measurements on lithium halides in aqueous acetone suggest that lithium chloride exists as a tight ion pair whereas, with lithium bromide and especially iodide, some solvent molecules are bound in the ion pair,[39,40] but there is again no simple relation between the kinetic salt effects and ion pairing of the electrolyte.

For salts in which the cation is large, e.g., tetrabutylammonium, there can be considerable association even in water, because disruption of the water structure is minimized by ion pairing, and this association appears to be important in hydroxylic solvents but not in an aprotic solvent such as acetonitrile.[41]

Another factor which suggests that ionic association is not all important is that the salt order upon reaction rate is qualitatively similar in solvents ranging from good ionizing solvents like methanol and aqueous acetone to poor ionizing solvents such as 1,2-dimethoxyethane–methanol.

The specificity of these kinetic salt effects cannot therefore be ascribed wholly to ionic association, and its role seems to be relatively small for the better ionizing solvents.

Initial and Transition State Effects.—In methanol–water, 70:30 v/v, and acetone–water, 55:45 v/v, the solvolysis of isobornyl chloride is slow, compared with its rate of dissolution. In a saturated solution the activity of isobornyl chloride is constant and the Brønsted–Bjerrum rate equation gives[14,15]

$$v_s/v_0 = 1/f^*$$

where v_s and v_0 are the rates in the presence and absence of salt, and f^* is the activity coefficient in the presence of salt, taking the pure solvent as the standard state.

For homogeneous solutions

$$k_s/k_0 = f_{RCl}/f^*$$

where k_s and k_0 are the first-order rate constants in the presence and absence of salt, and f_{RCl} is the activity coefficient of the substrate.

From the reaction rates in the saturated heterogeneous system (Tables VI and VII), we calculate the salt effects upon the transition state, and hence can calculate the activity coefficients of the initial state. The values of f_{RCl} are much less accurate than those of f^*, because they depend upon two separate sets of experiments, but in aqueous methanol only the activity coefficient of the transition state is affected by added salts. In aqueous acetone both f_{RCl} and f^* depend on the salt, but with lithium chloride the effects on f_{RCl} and f^* cancel and with lithium perchlorate they augment each other.

In these systems, return of a carbonium ion intermediate cannot be responsible for the relatively low rate in lithium chloride solution, because return would give very reactive camphene hydrochloride.

Stereochemistry.—One of the questions which arises regarding kinetic salt effects hinges on the lifetimes of the carbonium ion intermediates in the hydroxylic solvents used in this work, and in acetic acid hydride shifts occur more rapidly than solvent attack upon a number of bicyclic alkyl cations.[42] There is qualitative evidence for retention of configuration in solvolyses of camphene hydrochloride in polar hydroxylic solvents,[43] and we used methanolysis to relate the stereochemistry of trimethylnorbornyl chlorides, and their solvolysis products.
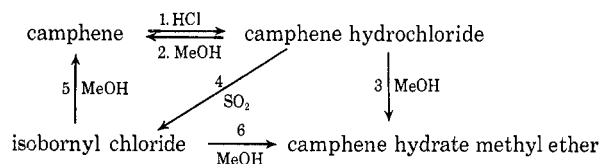
The fact that camphene can be converted into camphene hydrochloride which gives camphene with no loss of optical activity suggests that steps 1 and 2 and probably 3 occur without racemization (Tables I and II). However, the conversion of camphene hydrochloride into isobornyl chloride in liquid sulfur dioxide, step 4, causes partial racemization, but we note that the overall optical properties concerned in steps 4 and 5 and 4 and 6 are the same, suggesting that all the racemization occurs in step 4, and that the solvolyses 5 and 6 occur without racemization.

Our evidence is consistent with existing evidence that the camphene hydro cation racemizes by hydride and methyl shifts when it is generated in aprotic solvents[27] (but not in the reaction of camphene with hydrogen chloride), and that it retains its optical purity in a reactive solvent such as methanol, where the lifetime of the carbonium ion is shorter than the time required for methyl or hydride shifts. In the norbornyl system, these shifts are fast on the nmr time scale except at low temperatures.[28] In various solvolyses in reactive solvents, the lifetimes of the carbonium ion like species have been estimated to be $<10^{-5}$ sec,[44] and therefore the absence of racemization in our systems is consistent with these estimates.

(37) S. Winstein, L. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, 24 (1960); N. N. Lichtin and K. N. Rao, *J. Amer. Chem. Soc.*, **83**, 2417 (1961), and references cited.

(38) C. W. Davies, "Ionic Association," Butterworths, London, 1962, Chapter 1; H. S. Harned and B. O. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold, New York, N. Y., 1957, Chapter 6; L. G. Longsworth and D. A. MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).

(39) R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *J. Amer. Chem. Soc.*, **75**, 2855 (1953); P. G. Sears, R. L. McNeer, and L. R. Dawson, *J. Electrochem. Soc.*, **102**, 269 (1955).

(40) L. G. Savedoff, *J. Amer. Chem. Soc.*, **88**, 654 (1966).

(41) (a) R. M. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963). (b) R. L. Kay and D. F. Evans, *J. Amer. Chem. Soc.*, **86**, 2748 (1964); J. L. Hawes and R. L. Kay, *J. Phys. Chem.*, **69**, 2420 (1965).

(42) J. D. Roberts and C. C. Lee, *J. Amer. Chem. Soc.*, **73**, 5009 (1951); J. D. Roberts, C. C. Lee, and W. H. Sanders, *ibid.*, **76**, 4501 (1954); P. D. Bartlett, "Non-Classical Ions," W. A. Benjamin, New York, N. Y., 1965.

(43) J. L. Simonsen, "The Terpenes," Vol. II, Cambridge University Press, Cambridge, England, 1957, p 317.

(44) S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965); D. S. Noyce and S. K. Brauman, *ibid.*, **90**, 5218 (1968).

Products. —Added lyate ion increases the amount of elimination in E1-SN1 solvolyses of isobornyl chloride and camphene hydrochloride without increasing the overall rate of solvolysis, suggesting either that the lyate ion removes the proton from the carbonium ion, whereas the solvent attacks the cationic center, or that the lyate ion changes the properties of the solvent so as to favor loss of the proton. Moreover, the loss of the proton from relatively stable carbonium ions has an enthalpy of activation of 4 kcal mol^{-1} greater than that for addition of solvent,[45] and these results suggest that a strongly basic lyate ion may be more effective than a solvent molecule in removing the proton.[11b]

The salt effects upon amount of elimination in methanolyses of isobornyl chloride and camphene hydrochloride are simple: bromide has no effect; chloride, nitrite, and acetate increase elimination; perchlorate reduces it (Table XIV and XV), and elimination in-

<div align="center">

TABLE XIV

ELECTROLYTE EFFECTS ON THE FORMATION OF
CAMPHENE FROM ISOBORNYL CHLORIDE[a]

</div>

C_{OMe^-}	Salt	C_s, M	[Camphene], mol %
0.05			30[b]
0.05	NaNO$_2$	0.30	41[b]
0.05	LiOAc	0.84	48[b]
0.20			35
0.20	NaClO$_4$	1.50	29
0.50			46
0.50	NaClO$_4$	1.50	36
1.50			70
1.50	NaClO$_4$	1.50	66
0.20			42[b]
0.20	NaClO$_4$	1.50	33[b]
0.20	LiClO$_4$	1.50	36[b,c]
0.20	LiNO$_3$	1.50	43[b,c]
0.20	LiBr	1.50	41[b,c]
0.20	LiCl	1.00	46[b,c]
0.20	Et$_4$NCl	1.50	58[b,c]

[a] At 45.1° in MeOH with NaOMe unless specified. [b] At 59.8°. [c] LiOMe.

<div align="center">

TABLE XV

ELECTROLYTE EFFECTS ON THE FORMATION OF
CAMPHENE FROM CAMPHENE HYDROCHLORIDE[a]

</div>

C_{OMe^-}	Salt	C_s, M	[Camphene], mol %
0.20			20
0.20	NaClO$_4$	1.50	15
0.50			31
0.50	NaClO$_4$	1.50	22
1.50			50
1.50	NaClO$_4$	1.50	31
0.20			22[b]
0.20	NaClO$_4$	1.50	16[b]
0.20[c]	LiCl	1.00	35[b,c]
0.50			35[b]
0.50	NaClO$_4$	1.50	25[b]

[a] At 0° in MeOH with NaOMe unless specified. [b] At 25.3°. [c] LiOMe.

creases with increasing temperature. Salt effects upon the amount of elimination have also been observed by Lucas and Hammett for the SN1-E1 solvolysis of *tert*-butyl nitrate in aqueous dioxane.[8] For sol-

volysis of α,α'-dimethyl benzyl chloride in the presence of methoxide and perchlorate ions, the amount of elimination is greater than that expected in terms of the net rates of elimination and substitution, but in this reaction salt effects upon the bimolecular component of reaction also have to be considered.[20]

The ability of the salt to increase elimination decreases with increasing acidity of the conjugate acid of the anion (Tables XIV and XV). Nitrite or acetate could act as bases toward a carbonium ion, but chloride ion would not be expected to extract a proton from a carbonium ion in a polar hydroxylic solvent.[46] It is also possible that the salt is modifying the properties of the solvent so that it attacked the carbonium ion as a base rather than a nucleophile. The salt order on the amount of elimination, Cl$^-$ > NO$_3^-$ > Br$^-$ > ClO$_4^-$, follows the ability of the anion to orient water molecules about itself, and disruption of the water structure decreases in the sequence from ClO$_4^-$ to Cl$^-$.[48] These anions could have a similar effect on the structure of methanol.

If the O–H dipoles of the hydroxylic solvent molecules are oriented toward the anion, the lone pair electrons will be more effective at removing a proton from the carbonium ion; alternatively we could suppose that solvation of the chloride ion (or other small anion) reduces the ability of the solvent to solvate the lyate ion and thereby increases its ability to extract a proton from the carbonium ion.

Anion Intervention in Solvolyses of Trimethylnorbornyl Chlorides. —One of the problems in considering the effect of electrolytes upon the fate of the carbonium ion or ion pair hinges upon the question of their lifetimes in a polar solvent. We had earlier found that addition of 1,2-dimethoxyethane increased the amount of camphene formed in the methanolysis of isobornyl chloride and camphene hydrochloride[11b] and suggested that (1) the aprotic ether could increase the basicity of the methoxide ion, by reducing hydrogen bonding between it and methanol,[49] or (2) it could solvate the carbonium ion[50] which would therefore be less susceptible to nucleophilic attack by a hydroxylic solvent but not to loss of a proton. Our observations on azide intervention support the second of these explanations, because, although 2,2,3-trimethylnorbornyl-2-azide is not formed from camphene hydrochloride and azide ion in methanol–1,2-dimethoxyethane, 10:90 v/v, it is formed in water–1,2-dimethoxyethane, 20:80 v/v, although the azide ion should be less nucleophilic in the more hydroxylic solvent.[49] (The reaction in methanolic 1,2-dimethoxyethane was not studied in detail, but the main products were camphene and isobornyl chloride.)

The results in Table XVI confirm earlier results in showing that elimination and azide attack upon the carbonium ion have enthalpies of activation which are 2–3 kcal mol^{-1} higher than that for nucleophilic attack by the solvent molecules.[45]

(45) Reference 4, Chapter VIII.

(46) There is, however, considerable evidence that proton transfer from a carbonium to a chloride ion can occur within an ion pair.[47]

(47) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963).

(48) H. S. Frank and H. G. Evans, *J. Chem. Phys.*, **13**, 507 (1945); G. R. Choppin and K. Buijs, *ibid.*, **39**, 2042 (1963).

(49) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(50) A. Streitwieser and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888, 6233 (1957); A. Streitwieser and S. Andreades, *ibid.*, **80**, 6553 (1958).
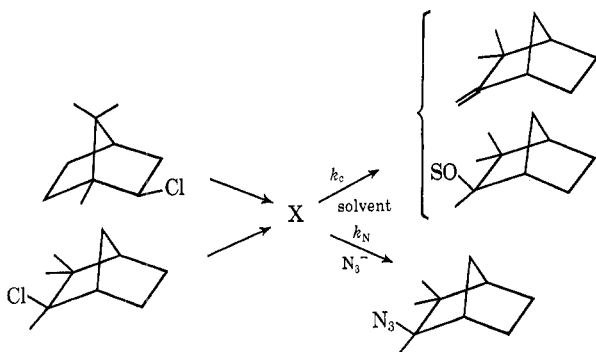
TABLE XVI

INTERVENTION BY AZIDE ION[a]

Substrate	Products, mol %		
	Cm	CmOMe	CmHN₃
CmHCl[b]	20.5	64.0	15.5
CmHCl	26.5	54.5	19.0
iBCl	25.3	54.0	20.5
iBCl[c]	36.5	40.5	23.0
iBCl[c,d]	41.0	47.0	12.0
iBCl[c,e]			16.0

[a] In methanol with 0.05 *M* NaOMe, 0.28 *M* NaN₃, and 0.04 *M* substrate, at 25.3° unless specified. [b] At 0°. [c] At 59.8°. [d] With 0.14 *M* NaN₃. [e] Water:1,2-dimethoxyethane, 20:80 v/v.

In methanolic sodium azide the products are almost the same whether the starting material is isobornyl chloride or camphene hydrochloride, showing that both substrates generate the same intermediates, either directly or by a rapid equilibration.

The simplest picture of azide intervention is shown below.

At 0° in methanol $k_N/k_c = 0.65$, whereas the experiments with ³⁶Cl give for the attack of chloride ion and methanol $k_e/k_c = 0.16$ (calculated for 1 *M* nucleophilic anions, using data in Tables XVI and XVII),

TABLE XVII

ISOTOPIC EXCHANGE BETWEEN
LITHIUM CHLORIDE AND ALKYL CHLORIDES[a]

| Substrate	Solvent[b]	C_{LiCl}, *M*	α_{ex}[c]	α_k[d]
tert-BuCl	60% aq ac	0.131	0.32	
CmHCl	MeOH	1.88	0.16[e]	0.11
CmHCl	80% aq dme	0.166	0.92 (0.60)	

[a] At 25.0° unless specified. [b] Solvents are ac = acetone, diox = dioxane, and dme = 1,2-dimethoxyethane, and the volume percentage refers to the organic component. [c] The values in parentheses are for ca. 25% reaction, the others are for 50% reaction unless specified. [d] Calculated from the rates of solvolysis using eq 2. [e] At 0°.

i.e., the chloride ion is a less effective reagent than azide ion toward the camphene hydro cation or ion pair. For solvolyses of *tert*-butyl chloride, azide and chloride have similar reactivities,[21] and, in so far as it is the less reactive carbonium ions which discriminate most between nucleophiles, these results suggest that the camphene hydro cation is less reactive than the *tert*-butyl cation toward nucleophiles. The reactivity difference could arise from both electronic and steric effects,[22b,44,51,52] and X may be a free ion or an ion

(51) N. C. Brown, *J. Chem. Soc., London, Spec. Publ.*, No. 16, 140, 175 (1962); *Chem. Brit.*, **2**, 199 (1966).
(52) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967); F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5688 (1969).

pair, or a mixture of the two, and chloride and azide ions and the solvent molecules may discriminate between the various cationic intermediates represented by X. The absence of azide attack in methanol–1,2-dimethoxyethane, 10:90 v/v, suggests that here an ion pair within a solvent cage is eliminating camphene and collapsing to isobornyl chloride, probably by the mechanism suggested by Cocivera and Winstein.[47] (We note that the situation may be different for attack upon an ion pair generated from a primary or secondary alkyl halide or tosylate in a more nucleophilic solvent.[23])

Isotopic Exchange.—The similarities of the salt effects upon the solvolyses of isobornyl chloride and 1-methyl-*exo*-chloronorbornane where return is kinetically unimportant and the other solvolyses where return is possible suggest that return is not the cause of this salt specificity, but it seemed desirable to examine the possibility of recombination of a *tert*-butyl or camphene hydro cation and a chloride ion by carrying out the solvolysis in the presence of isotopically labeled chloride ion. Only a small amount of exchange was observed (Table XVII) and the values of k_e/k_c are similar to those found earlier for solvolyses of *tert*-butyl chloride in aqueous methanol.[25]

Exchange could arise either by capture of a free carbonium ion by an external chloride ion or by iso-

$$R-Cl \rightleftharpoons \overset{+}{R} + Cl^-$$
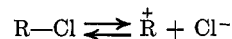
topic exchange involving an ion pair intermediate, followed by return of the ion pair to substrate.[17] Sneen

$$^{33}Cl^- + \overset{+}{R}Cl^- \rightleftharpoons {}^{36}Cl^-R^+ + Cl^-$$
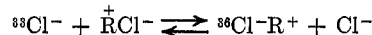
and his coworkers have considerable evidence for bimolecular reactions between nucleophiles and ion pairs generated by secondary alkyl halides,[23] and return of an ion pair generated from *p*-chlorodiphenyl methyl chloride has also been observed.[17]

On the assumption that the exchange and chemical reactions involve an intermediate I, which may be

$$R-Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \overset{k_2}{\longrightarrow} products$$
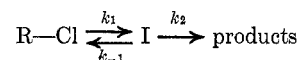
an ion pair or a carbonium ion, and assuming that *every* return of I involves isotopic exchange, the relative values of the rate constants k_e and k_c are given by

$$k_e/k_c = k_{-1} [Cl^-]/k_2, \qquad (1)$$

If I is a free carbonium ion, $k_{-1}/k_2 = \alpha$, where α is the common ion parameter.[3-5]

$$k = k_1/(1 + \alpha[Cl^-]) \qquad (2)$$

and then

$$\alpha_{ex} = k_e/k_c[Cl^-] \qquad (3)$$

Therefore, our exchange results give maximum values for capture of a free carbonium ion by chloride ion and show that return is never large enough to produce the specific salt effects which we observe with added perchlorates, *e.g.*, in the presence of 1 *M* chloride ion no more than 10% of the camphene hydro cations or ion pairs return with exchange to substrate in 1,2-dimethoxyethane–water, 80:20 v/v (Table XVII), and the rate enhancement would be small even if all this return were eliminated by an added salt. Similar con-

clusions can be drawn regarding solvolyses of *tert*-butyl chloride (Table XVII and ref 21).

Discussion

Kinetic Salt Effects.—The pattern of the overall kinetic salt effects is simple and is generally similar to those observed earlier, and, at least for the uniunivalent salts which we used, the nature of the cation is relatively unimportant. The salt order upon the rates of solvolysis of a given substrate does not depend markedly upon the temperature, the solvent, or substrate structure or upon the possibility of carbonium ion return to substrate, although these factors influence the magnitude of the kinetic salt effect.

Our experiments with isobornyl chloride under heterogeneous conditions show that initial state effects are not particularly important in mixed solvents, in agreement with experiments using *exo*-norbornyl bromide in aqueous dioxane,[15] although they are important for hydrolyses in water.[14]

Any explanation of these specific salt effects must take into account the fact that they can be observed both in systems in which there may be return of intermediates to starting material and in systems where there is no return and in which the life time of the carbonium ion is too short for methyl or hydride shifts to occur. Therefore we cannot explain all these specific salt effects in terms of a special salt effect upon the dissociation of a solvent separated ion pair, as for acetolyses,[17,19] or upon recombination of carbonium and chloride ion, or nucleophilic attack on an ion pair.[23]

The absence of a salt effect upon the activity coefficient of isobornyl chloride in aqueous methanol or acetone is understandable because the organic component of the solvent should interact most strongly with the organic substrate, whereas the salt should interact with the water. The situation in the mixed solvents is therefore completely different from that in water.[14,15]

We note also that cation effects are not large in these polar aqueous organic solvents, although in nonpolar solvents such as ether and acetic acid, a small high charge density cation such as lithium can electrophilically assist ionization.[17] Presumably small cations are so strongly solvated in polar hydroxylic solvents that they are ineffective catalysts, and the importance of such catalysis should be reduced by solvation of the departing anion. One notable exception to this generalization is the observation that the rate of hydrolysis of *p*-chlorodiphenylmethyl chloride in 80% acetone–water increases linearly with concentration of lithium perchlorate but is little affected by tetrabutyl ammonium perchlorate,[53] possibly because the latter salt is a weak electrolyte so that the perchlorate ion is less available to stabilize the carbonium ion (*cf.* ref 18).

Some workers have noted that these and other similar specific salt effects upon transition state stability in hydroxylic solvents appear to be caused by direct interactions between the transition state and the electrolyte.[13,36,54] Large low charge density anions and cations can bond hydrophobically in water, so as to

maximize water–water interactions, and minimize the disruption of the water structure by the large ions,[41,48,55] and such an effect could be an important factor in the specificity of kinetic salt effects. Carbonium ions are generally large and have low charge densities and are probably not strongly solvated by hydroxylic solvents, particularly if the positive charge is delocalized, and therefore they might interact with a large low charge density anion such as perchlorate, and such stabilization of the carbonium ion may be a major factor in the differential effects of salts and strong acids, upon the H_0 and H_R acidity functions and on the rates of A1 as compared with A2 solvolyses.[36] Somewhat similarly large, low charge density cations, such as tetraalkylammonium ions, stabilize the transition state of SN2 reactions relative to the nucleophilic anion.[13,54]

Effects upon the initial state have to be considered, but once this is done the salt order which we observe on these SN1 and A1 reactions is very similar to that found for anion effects upon water structure. Solvent structure dictated that ion pairing is quite different from that observed in the more usual type of Bjerrum electrostatic ion pairing which is most important in solvents of low dielectric constant and with ions of high charge density.[41]

Anion effects upon the rates of SN1 methanolysis of *tert*-butyl chloride or bromide follow the order $ClO_4^- > Br^- > NO_3^- > Cl^- \approx$ no salt $> OR^-$, and for anion effects upon water structure, measured by infrared spectral shifts, it is structure breaking anions; $ClO_4^- > Br^- > NO_3^- > Cl^-$, with OH^- and F^- being structure-making anions.[48]

Although the cation effects are generally small, several solvolyses in aqueous organic solvents are slightly faster in solutions of sodium than in lithium salts, in the opposite direction to that expected for electrophilic catalysis. Sodium disrupts the structure of water more than does lithium,[48] and to this extent the cation order is also explicable in terms of effects upon the solvent.

Much of the evidence on hydrophobic bonding relates to aqueous solutions, but protic solvents such as methanol also have considerable structure,[56] and structure could still be important in mixed aqueous organic solvents, even though the basic water structure is disrupted by addition of appreciable amounts of organic solvents (initial addition of many aprotic solvents actually enhances water–water interactions.)[57] In these organic or aqueous organic solvents it is understandable that initial state salt effects should be less important than in water, where the organic substrate must be in a cavity surrounded by water molecules instead of being solvated preferentially by the organic solvent. These solvent–structure-enforced ion pairings will depend very critically upon both the nature of the solvent and the sizes of the anion and the transition state. We should not therefore expect any simple relationship between rate and salt concentration over a wide range of solvents and substrates.

Our results also show that, as pointed out earlier,[8,9]

(53) S. Winstein, M. Hojo and S. G. Smith, *Tetrahedron Lett.*, 12 (1960).
(54) C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 5965 (1968); C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 783 (1969).

(55) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter VIII.
(56) Reference 35, Parts 2.5 and 2.6.
(57) D. N. Glew, H. D. Mark, and N. S. Rath, *Chem. Commun.*, 265 (1968).

we must be cautious in calculating the amount of common ion return kinetically, because small high charge density anions, such as hydroxide and fluoride, can retard reaction, and estimation of any rate enhancing effect of the common ion is fraught with uncertainty.[58] Use of an isotopically labeled common ion is also not the answer, because it could exchange with the leaving anion at the ion pair stage.[17]

Although we conclude that interactions between an anion and a carbonium-ion-like transition state are important factors in determining kinetic salt orders in polar hydroxylic solvents, other factors including the conventional ionic atmosphere effects and dipole-dipole effects undoubtedly contribute to the overall effect.[18] The relation between rate constant and salt concentration also suggests that more than one factor is at work.

Except for the treatment used by Perrin and Pressing,[18] most of the electrostatic treatments of kinetic salt effects predict a linear relation between log k and ionic strength (or its square root for interionic reactions).[3,35] However, Winstein and his coworkers found that kinetic salt effects in many nonpolar solvents

(58) The small rate retardations observed with fluoride or acetate ions could in principle be caused by return of a reaction intermediate to an unreactive alkyl fluoride or acetate.

were linear with ionic strength,[17a] as would be expected if there were direct 1:1 interactions between say a lithium cation and the anionic leaving group (*cf.* ref 13).

As we noted earlier our results fit neither a linear nor a logarithmic relationship between rate and ionic strength, although for many electrolytes k varies linearly with ionic strength up to moderate salt concentrations and then increases more sharply.

That part of the salt effect which involves solvent-structure-induced (hydrophobic) ion pairing could very well lead to linear relations between rate and ionic strength, whereas those caused by ionic atmosphere effects[3] and by salt effects upon the activity coefficient of the substrate[7] should follow a logarithmic relationship. Insofar as all the effects contribute to the overall effect it is not surprising that the relation between rate and ionic strength is in between linear and logarithmic.

Reactions of 2-Halo-2,3,3-trimethylbutanes in Methanol Solution. Rates and Product Ratios in Solvolysis and in Reactions with Anionic Bases[1]

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Reactions of 2-chloro-2,3,3-trimethylbutane (1a) in CH₃OH to form 2,3,3-trimethyl-1-butene (2) and 2,3,3-trimethyl-2-butyl methyl ether (3) are accelerated by added electrolytes in the order NaClO₄ > NaSC₂H₅ > NaOCH₃. The kinetic effects of NaClO₄ plus NaOCH₃ or NaSC₂H₅ are not additive. Low concentrations of NaOCH₃ cause a small rate increase but larger concentrations cause the rate to diminish. NaClO₄ does not affect the proportions of 2 and 3 formed from 1a, but NaOCH₃ and especially NaSC₂H₅ cause an increase in the fraction of olefin in the products. 1a and its bromo and iodo analogs differ, in solvolysis and in reactions with NaOCH₃ or NaSC₂H₅, in the proportions of 2 and 3 formed. The data suggest reaction in part by E1–Sn1 solvolysis and in part by the E2 mechanism, but no model to give a satisfactory quantitative account of the data has been found.

Part A

Much scientific interpretation consists of the fitting of experimental data to conceptual models, often with demonstration that certain models can and that other models cannot accommodate the data. Sometimes new models are devised *ad hoc* when none of the older ones seems adequate. However, there are occasions when experimental data outrun the supply of models; we now present data of this character.

These data concern principally rate and product studies on the solvolysis of 2-chloro-2,3,3-trimethylbutane (1a) in methanol, both in the absence and in the presence of sodium perchlorate, and on its reactions with sodium methoxide and sodium thioethoxide. For reactions of the bromo and iodo analogs of 1a, we have studied only product compositions, except for a short series of kinetic data on the iodo compound, presented in Part B. The products ob-

1a, X = Cl
b, X = Br
c, X = I

2

3
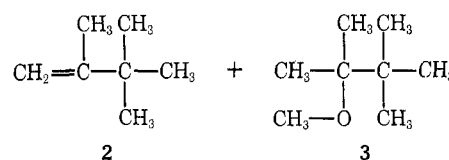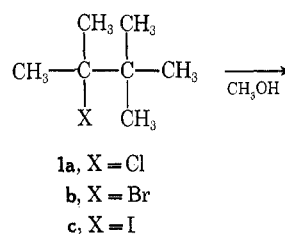
tained from all reactions are an olefin, 2,3,3-trimethyl-1-butene (2), and an ether, 2,3,3-trimethyl-2-butyl methyl ether (3). No dialkyl sulfide product was detectable in the sodium thioethoxide reactions. Our original purpose was to compare CH₃O⁻ and C₂H₅S⁻ as to their effectiveness in bringing about E2 elimination