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(10) Even AH^{-} must yield some heat upon reaction with water. Thus, the error caused by any protonation of A^{2-} with THF must be much smaller than 3%.

Carbonium Ions in Solution. 9. The Relationship between Carbocations in Superacid and Solvolysis Transition States

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Abstract: The heats of ionization, ΔH_i, of various alkyl chlorides to stable carbocations in SbF_5–solvent mixtures correlate remarkably well with the free energies of activation of limiting solvolysis of the same chlorides in ethanol. The slope of the correlation line, 0.89, suggests that "carbocation character" is very largely developed in solvolysis transition states. Simple secondary chlorides, i.e., 2-propyl, cyclopentyl, and 2-butyl, subject to nucleophilic solvent assistance, do not exhibit limiting ("pure" S_N1) behavior on ethanolysis. Uncorrected solvolysis data for these substrates do not correlate with ΔH_i (SbF_5–SO_2ClF), but the same data, corrected for the amount of nucleophilic solvent assistance, correlate well. In contrast, ΔH_i values for these same substrates in the SbF_5–CH_2Cl_2 mixture correlate better with uncorrected, rather than with corrected, solvolysis free energies, indicating that the less stable carbocations are subject to specific solvation effects. All these results confirm the long-held presumption that limiting solvolysis rates are reliable measures of carbocation stabilities. Exceptions are noted. For example, stereoisomeric 2-*exo*- and 2-*endo*-norbornyl substrates (secondary as well as tertiary) both give the same carbocation on ionization but their solvolysis rates differ by 10^2–10^3. Only the exo solvolytic data correlate with ΔH_i, showing that the exo but not the endo transition states are related closely to the resulting carbocations. ΔH_i for 2-*exo*-norbornyl chloride among all the compounds reported here displays a unique sensitivity to solvent variation relative to the other cations. Although this differential solvation effect may doubtless be interpreted in various ways, we note that it conforms with theoretical prediction that σ bridged ions should show different responses to solvation than their classical counterparts. By means of our correlations of ΔH_i vs. limiting solvolysis rates and a previous correlation with gas-phase heats of ionization estimates are made of the contribution of covalent bonding from more nucleophilic solvents (ethanol, acetic acid, and even trifluoroacetic acid) in the solvolysis transition states of methyl and ethyl tosylates. In methyl tosylate ethanolysis nucleophilic assistance by solvent reduces the free energy of activation from an estimated 58 kcal/mol for the hypothetical limiting process to the observed value of 24.5 kcal/mol.

Introduction

For over half a century organic chemists have gained powerful insight into the mechanisms of polar reactions in solution through the concept of carbonium-ion-like intermediates. The daring suggestions of Meerwein and Whitmore, especially as developed by the Ingold–Hughes school, Bartlett, and Winstein, provided a rationale both for interpreting and predicting the response of an enormous range of reactions to change in structure and conditions.[2] Solvolysis reactions, in which an amphiprotic solvent serves also as the attacking nucleophile, have been the proving ground for developing the carbonium ion theory of substitution displacement reactions, primarily through structure–rate studies. A major intellectual tool for inferring the relative stabilities of unstable carbonium ions, or ion pairs, has been the postulate[3-5] that their structures and energies are well modeled by solvolysis transition states. Thus, it has often been an article of faith that S_N1 solvolysis rates for a series of similar compounds under similar conditions generally reflect directly the stabilities of their carbocationoid intermediates. However, we know now that the reactivity–selectivity principle is not universally applicable to organic reaction rates; the reasons for failure are not clearly understood.[6] Thus, it is not a foregone conclusion that there should be a close relationship between a solvolysis transition state and a carbocation intermediate. This article deals directly with this problem.

Recently one of us with his associates[7] succeeded in demonstrating that solvolysis data involving an enormous range of substrates and solvents could be correlated in terms of a single mechanistic continuum. In this view the principal difference between S_N1 and S_N2 solvolysis is the degree of nucleophilic assistance from the solvent.[8] A treatment was proposed for correcting the rates of nucleophilically assisted solvolysis to reveal the free energies of activation which would be expected for limiting S_N1 behavior.

Concurrently, two of us developed rigorously authenticated methods for measuring the heats of ionization of many typical aliphatic and alicyclic halides to stable carbocations in superacidic media at low temperatures under conditions developed by Olah.[9] The method has been described[10a] as have the effects of solvent and ionic structure[10b] on thermodynamic stability. We now compare the relationship between the energies of forming carbocations as measured calorimetrically under stable ion conditions with those inferred from solvolysis

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Table I. Solvolysis Data and Derived Values Corrected for Solvent Assistance

substrate	k(R-OTs, AcOH)[a]	k(R-OTs, EtOH)[a]	k(R-Cl, EtOH)[b]	factors for nucleophilic assistance in EtOH[c]	k_{cor}[d] (R-OTs, EtOH)	k_{cor}[b,d] (R-Cl, EtOH)
2-propyl	7.7×10^{-8}	3.9×10^{-7}	3.3×10^{-11}	23 500	1.6×10^{-11}	1.4×10^{-15}
2-butyl	1.34×10^{-7}	6.0×10^{-7}	5.1×10^{-11}	3630	1.65×10^{-10}	1.40×10^{-14}
cyclopentyl	1.65×10^{-6}	2.69×10^{-6}	2.29×10^{-10}	1680	1.60×10^{-9}	1.36×10^{-13}
cyclohexyl	4.88×10^{-8}	4.6×10^{-8}	3.91×10^{-12}	256	1.80×10^{-10}	1.53×10^{-14}
2-adamantyl	5.9×10^{-9}	4.3×10^{-10}	3.6×10^{-14}	1	4.3×10^{-10} [e]	3.6×10^{-14} [e]

[a] Data from ref 7a. [b] Data calculated from the relationship $k_{RCl}/k_{ROTs} = 8.5 \times 10^{-5}$ from ref 12. [c] Factors from ref 7b. [d] Data corrected for nucleophilic solvent assistance by the method in ref 7b. [e] Corrected and uncorrected values are identical.

rates.[11a] The present results confirm and extend earlier work of Larsen[11] in "magic acid" (SbF_5–HSO_3F).

Results

Table I presents the basic data: the heats of ionization[10b] of the alkyl chlorides to the carbonium ion salts in various media and the estimated free energies of activation (uncorrected and corrected) for solvolysis of the chlorides at 25 °C in ethanol.

Heats of ionization, ΔH_i, are defined as follows:[10a,b]

$$\Delta H_i = \Delta H_s(\text{solvent}/SbF_5) - \Delta H_s(\text{solvent})$$

where $\Delta H_s(\text{solvent}/SbF_5)$ is the molar heat of solution of the chloride precursor, RCl, in a mixture of SbF_5 with a given solvent. A considerable excess, 10- to 20-fold, of SbF_5 to RCl is employed and the final concentration of R^+ "SbF_5Cl^-" (see ref 10a for references to the nature of the actual anionic species) is 10^{-4}–10^{-2} M. ΔH_s(solvent) is a corresponding molar heat of solution for RCl at high dilution in the same pure solvent (without SbF_5) under the same conditions used to measure ΔH_s (SbF_5/solvent). These measurements have been shown by a variety of methods to correspond to conversion of RCl to the carbonium ion in solution:[10b]

$$RCl + SbF_5 \rightarrow R^+ + \text{“}SbF_5Cl^-\text{”}$$

In the absence of carbocation rearrangements, ΔH_i is not affected by temperature variation within the error limits (standard deviations) shown; ΔH_i is also relatively insensitive to variations in concentration of RCl or SbF_5. Several problems, chiefly low solubility, prevented measurement of ΔH_i for the entire series of chlorides in all four solvents. However, complete ionization was shown to occur in SO_2ClF, the solvent in which we have the most ΔH_i data, and solvent effects on relative values of ΔH_i were shown to be small for all ions (except 2-norbornyl in SO_2ClF vs. CH_2Cl_2).

Solvolysis data for the ethanolysis of secondary and tertiary alkyl chlorides were compiled by Brown and Rei[12] in 1964. Data for tertiary substrates were based on measurements made either in ethanol or 80% ethanol by a number of investigators. Values not measured in pure ethanol were calculated from 80% ethanol data. Rates of acetolysis of secondary tosylates were used to obtain estimates of the "limiting" rates of ethanolysis of the tosylates since at that time acetic acid was considered to be relatively nonnucleophilic. The rates of acetolysis were divided by an average factor of 4.4 to obtain such "limiting" ethanolysis rates of tosylates. The "limiting" rates of ethanolysis of the chlorides were then calculated by use of the factor

$$k_{RCl}/k_{ROTs} = 8.5 \times 10^{-5}$$

Since that time it has been established that acetic acid has significant nucleophilic characteristics and that secondary tosylates do not exhibit limiting behavior in that solvent.[7] A means was proposed for correcting rate constants for such solvent nucleophilicity. More recent data[7] for the solvolysis of secondary substrates (Table I) are presented in Table II after conversion to free energies of activation at 25 °C by means of the formula

$$\Delta G^{\ddagger} = 2.303RT[\log \frac{kT}{h} - \log k_{\text{solvol}}]$$
$$= 17.41 - 1.36 \log k_{\text{solvol}}$$

We have corrected the values for secondary tosylates in acetic acid by dividing the original rate constants by the established factors (Table I) for nucleophilic solvent assistance in acetic acid.[7] The corrected rate constants in Table II should represent the values that would be observed if the solvent had no nucleophilic properties. The uncorrected rates (Table I) for secondary chlorides in ethanol were obtained from data for tosylates by using Brown's factor of 8.5×10^{-5}. The net result of this treatment is to provide somewhat better estimates along the lines suggested by Brown and Rei.[12]

The free energies of activation for the ethanolysis of secondary and tertiary chlorides appear in Table I, both as uncorrected and corrected values.

Discussion

Figures 1, 2, and 3 correlate the free energies of activation for ethanolysis of the alkyl chlorides at 25 °C with the heats of ionization of the same compounds in superacid systems at low temperatures. Within this series of four solvents the *relative* heats of ionization are influenced only slightly by medium effects.[10b] Thus, SO_2F_2 and SO_2ClF are solvents of very low Lewis basicity (or nucleophilicity) in which all alkyl halides give the most exothermic heats of ionization (Table I). Within experimental error, all ΔH_i values in SO_2ClF correlate cleanly with unit slope against corresponding ΔH_i values in SO_2F_2. However, in the more nucleophilic solvents, SO_2 and CH_2Cl_2, the secondary chlorides (2-propyl, cyclopentyl, and especially 2-norbornyl) show somewhat different behavior relative to the tertiary halides than in the less nucleophilic solvents. Since differential solvent effects on the neutral halides and tertiary ions are negligible,[10b] these variations must be due to small specific solvent effects on the secondary ions in CH_2Cl_2 and SO_2. Keeping this in mind, we shall now compare the energetics of ionization with the solvolysis activation energies.

Figure 1 documents the extraordinary result that heats of ionization in SO_2ClF give an excellent correlation (with slope $= -0.89$ and $r = 0.989$) when plotted against the free energies of activation for solvolysis for all compounds provided that the secondary ions (2-propyl, 2-butyl, and cyclopentyl) are corrected for the degree of nucleophilic participation by ethanol. The corresponding line for limiting substrates (Figure 1, slope $= -0.84$, $r = 0.973$) leaves the uncorrected points for the three secondary ions several kilocalories per mole below the correlation line (black squares on Figure 1).

The overall linearity of both plots underscores dramatically

Table II. Heats of Ionization and Free Energies of Activation for Solvolysis (kcal/mol)

substrate	ΔH_i (SO_2ClF/SbF_5)[a]	ΔH_i (CH_2Cl_2/SbF_5)[a]	ΔH_i (SO_2/SbF_5)[a]	ΔH_i[c] (SO_2F_2/SbF_5)	$\Delta G^{\ddagger}$ for ethanolysis at 25 °C[e]
2-propyl chloride	−15.3 ± 0.9	−7.5 ± 1.5 (−75 °C)	−4.0 ± 0.7	−17.9 ± 0.8	31.7 (37.6)
2-butyl chloride	−15.7 ± 0.8 (−75 °C) −30.0 ± 0.8 (−25 °C)[b]			−20.4 ± 0.9	31.4 (36.3)
cyclopentyl chloride	−17.3 ± 0.9	−9.0 ± 1.0 (−75 °C)	−5.2 ± 1.0	−21.3 ± 0.7	30.5 (34.9)
1-adamantyl chloride	−21.6 ± 0.8	−11.1 ± 0.8			31.2[f]
cyclohexyl chloride	−22.5 ± 0.6[b]				32.9 (36.2)
2-*exo*-norbornyl chloride	−23.6 ± 0.8	−11.1 ± 0.4	−11.7 ± 0.8	−28.5 ± 1.0[d]	30.1
tert-butyl chloride	−25.4 ± 0.8	−15.5 ± 0.3	−12.0 ± 0.8	−29.0 ± 0.6	27.1
1-methylcyclopentyl chloride	−27.1 ± 0.6	−17.8 ± 0.5	−14.8 ± 0.8	−31.4 ± 0.8	24.6
2-phenyl-2-propyl chloride	−30.3 ± 0.3	−19.0 ± 0.6	−18.0 ± 0.4		22.1
2-methyl-2-*exo*-norbornyl chloride	−31.0 ± 1.5	−19.6 ± 0.8 (0 °C)	−18.5 ± 0.8		23.6
2-phenyl-2-*exo*-norbornyl chloride	−37.0 ± 1.2	−25.9 ± 1.2 (0 °C)	−23.8 ± 1.2		18.5

[a] Measurements at −55 °C unless shown otherwise. [b] Ion rearranges at this temperature. [c] All measurements in this column at −65 °C. [d] Chloride is not soluble in this solvent. This value estimated from *exo*-norbornyl fluoride by subtracting 1.5 kcal/mol, the average fluoride-chloride difference. [e] Data are from Brown (ref 12) as described in text. Values in parentheses are corrected for nucleophilic solvent assistance (ref 7). [f] This datum was calculated from 80% ethanol, from P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

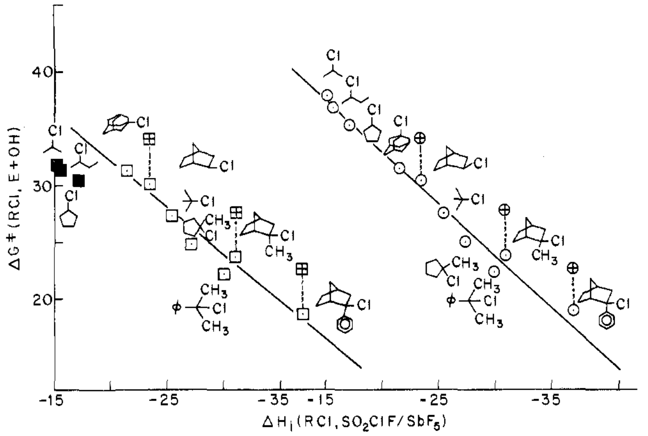

Figure 1. Correlation of free energies of activation for ethanolysis of alkyl chloride vs. heats of ionization in SO_2ClF. All points ○ on the line to the right correspond to limiting behavior, the secondary compounds being corrected according to ref 7. The left-hand line is drawn through points □ for compounds believed to give limiting ethanolysis without correction. Black squares ■ are points for uncorrected ethanolysis of secondary substrates. Crossed points ⊞ and ⊕ represent ethanolysis of 2-*endo*-norbornyl chlorides.

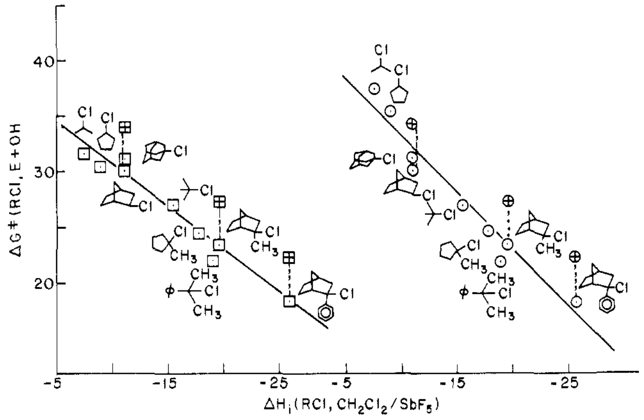

Figure 2. Correlation of free energies of activation for ethanolysis of alkyl chlorides (with and without correction of secondary compounds to limiting values) vs. heats of ionization in CH_2Cl_2/SbF_5. The points recorded with + represent the corresponding 2-*endo*-norbornyl derivatives.

the accuracy of the long-held assumption that solvolysis rates for limiting S_N1 processes are a direct reflection of carbonium ion stability. Likewise, the improved correlation for corrected secondary ions supports the Schleyer-Bentley-Schadt method[7] of estimating nucleophilic solvent participation.

The fact that a nearly unit slope is found implies strongly that considerable charge separation has occurred in the S_N1 transition state. It is tempting to interpret the numerical value of the slope (−0.89) in terms of the degree of charge separation in the transition state.[13-15] For the *tert*-butyl chloride solvolysis transition state, ion-pair character has been inferred with a fraction of charge separation very close to the value of this slope.[15] However, ΔH_i refers to a different thermodynamic property, for a different process, in a different solvent and at a different temperature. Such good agreement in estimates of the exact degree of charge development is noteworthy but to some degree is probably fortuitous.

Figure 2 compares the same free energies of activation for ethanolysis with heats of ionization of the chlorides in CH_2Cl_2. Again, a nearly unit slope is found for the chlorides leading to the more stable ions. However, in this solvent there is no significant difference between the quality of correlation between ΔH_i and the two sets of solvolysis data (slope for uncorrected points = −0.763, $r = 0.980$; slope for corrected points = −1.02, $r = 0.976$). We take this to mean that there is some degree of "encumbrance" of the very unstable 2-propyl and cyclopentyl ions in this medium which causes them to behave more like nucleophilically solvated ions rather than like the free carbonium ions found in SO_2ClF or SO_2F_2. There is no evidence at this time as to the nature of this "encumbrance". An obvious possibility is formation of tighter ion pairs for the less stable secondary ions. Another possibility is partial coordination with the chlorine atoms of the solvent, i.e., in the extreme $ClCH_2\text{-}Cl^+\text{-}R$.[10]

It is unlikely that this effect is due to chloronium ion formation ($R\text{-}Cl^+\text{—}R$).[10] This would lead to ΔH_i values which would be too low because of incomplete conversion of RCl to R^+, whereas the observed ΔH_i values for 2-propyl chloride and cyclopentyl chloride are "too high" in CH_2Cl_2 compared to the fully ionized stable ions if SO_2ClF is used as the standard of comparison (see ref 10b, Figure 5).

Turning to Figure 3, we find the behavior in SO_2 more like

Table III. Estimated Free Energy Contributions ($\Delta G_{N.A.}^{\ddagger}$)^a to the Observed Nucleophilically Assisted Transition State ($\Delta G_{obsd}^{\ddagger}$) from the Predicted Limiting S_N1 Solvolysis Rate Constants of Tosylates at 25 °C (kcal mol^{-1})^a

tosylate	ethanol		CH_3CO_2H		CF_3CO_2H	
	$\Delta G_{obsd}^{\ddagger}$	$\Delta G_{N.A.}^{\ddagger}$	$\Delta G_{obsd}^{\ddagger}$	$\Delta G_{N.A.}^{\ddagger}$	$\Delta G_{obsd}^{\ddagger}$	$\Delta G_{N.A.}^{\ddagger}$
methyl	24.5	33	27.2	31	29.4	27
ethyl	25.1	16	27.5	14	27.9	9
2-propyl	26.1	6	27.1	3	23.7	0

^{a} $\Delta G_{est}^{\ddagger} - \Delta G_{obsd}^{\ddagger} = \Delta G_{N.A.}^{\ddagger}$. See text for explanation.

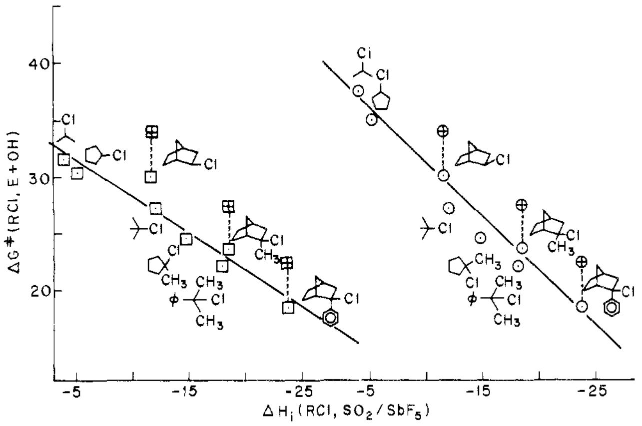

Figure 3. Correlation of free energies of activation for ethanolysis of alkyl chlorides (with and without correction of secondary compounds to limiting values) vs. heats of ionization in SO_2/SbF_5. The points recorded with + represent the corresponding 2-*endo*-norbornyl derivatives.

that in Figure 1. Both lines are drawn to include as many points as possible—that for the uncorrected secondaries has a coefficient of correlation of $r = 0.958$ compared to $r = 0.982$ for the corrected data. The corrected line has a higher slope (−0.95 compared to −0.66) when points for 2-propyl, cyclopentyl, and norbornyl are included, but this is done at the expense of moving it away from some of the tertiary chlorides—notably *tert*-butyl.

The position of 2-norbornyl chloride varies relative to *tert*-butyl chloride and the other tertiaries—its ΔH_i is quite close to that of *tert*-butyl chloride in SO_2ClF and SO_2 but considerably closer to 2-propyl and cyclopentyl chloride in CH_2Cl_2. In contrast the adamantyl chloride ΔH_i is 4 kcal/mol less exothermic than that for *tert*-butyl chloride both in SO_2ClF and CH_2Cl_2.

Nucleophilic Contribution to Free Energy of Activation. We have shown that ΔH_i values correlate with corresponding gas-phase ionization data.[10b] The data are few and the errors are large so that the exact slope of the line is uncertain. However, it appears that differential gas-phase heats of ionization are attenuated by at least a factor of ⅔ on transfer to SO_2ClF. We have now extrapolated that correlation using the gas-phase ΔH_i values for hydride transfer from methane and ethane[16] to estimate ΔH_i values in SO_2ClF which would be expected if methyl chloride and ethyl chloride were to be converted to the corresponding free carbonium ion pairs in SO_2ClF. We find that this hypothetical ΔH_i for ionizing ethyl chloride would be ca. 24 kcal/mol more endothermic than for ionizing *tert*-butyl chloride. The corresponding difference for methyl chloride is ca. 45 kcal/mol. Furthermore, we can extrapolate the "uncorrected" solvolysis line of Figure 1 to include $\Delta G_{obsd}^{\ddagger}$ for the actual ethanolysis of methyl tosylate (24.5 kcal/mol) and ethyl tosylate (25.1 kcal/mol). Extrapolating the "corrected" line, the estimated $\Delta G_{est}^{\ddagger}$ values for the hypothetical, limiting S_N1 solvolysis of the two tosylates at 25 °C follow: MeOTs, ca. 58 kcal/mol; EtOTs, ca. 41 kcal/mol. The difference between these estimated limiting values and the solvent-assisted ones ($\Delta G_{est}^{\ddagger} - \Delta G_{obsd}^{\ddagger}$) is therefore a measure of the nucleophilic contribution from the solvent to the ethanolysis of these two substrates. For methyl tosylate this contribution ($\Delta G_{N.A.}^{\ddagger}$) is ca. 33 kcal/mol; for ethyl tosylate the value is ca. 16 kcal/mol.

Table III compares the results of such a treatment for solvolyses of methyl, ethyl, and 2-propyl tosylates in three solvolysis media. The results are the first quantitative estimates known to us which evaluate the enormous involvement of solvent with the substrate carbon in the methyl and ethyl transition states.

Solvolyses Which Do Not Correlate with Ionization. Occasionally, two isomeric chlorides with quite different solvolysis rates will ionize in superacid to form the same ion. At least one of the ionizations necessarily involves a rearrangement. In such cases, correlation can succeed for only one of the two chlorides—the one whose solvolysis transition state is modeled better by the free carbonium ion in superacid. Thus, cyclohexyl chloride and 1-methylcyclopentyl chloride both yield only the 1-methylcyclopentyl cation in superacid media.[10b] Obviously, the solvolysis transition state for the tertiary chloride will be closer to the ion since the ionization occurs without rearrangement. In contrast, solvolysis of cyclohexyl substrates yields very little 1-methylcyclopentyl product.[17]

Less trivial examples are found in the 2-norbornyl series, where both the exo and endo chlorides solvolyze at quite different rates, but presumably give common carbonium ion intermediates. Brown, Ravindranathan, Rao, and Rei[18] have shown that the exo/endo rate ratios for 2-norbornyl chloride, and its 2-methyl and 2-phenyl derivatives, are in the range 10^2–10^3. The free energies of activation of the endo isomers are thus ~3–4 kcal/mol larger than those for exo isomers. Accordingly, points (marked +) for each endo isomer have been placed *above* each of the points for *exo*-norbornyl chloride and for its 2-methyl and 2-phenyl derivatives on Figures 1, 2, and 3. Since all three *endo* points in each figure are well removed from the correlation lines it is clear that ethanolysis rates for the norbornyl derivatives with exo leaving groups correlate much better with heats of ionization than do those with endo groups.

Brown[18,19] has discussed extensively the effect of substitution on the exo/endo rate ratios in norbornyl systems in terms of Goering-Schewene free-energy diagrams[20] using equilibration to establish differences in initial state energies. In all cases the difference in $\Delta G°$ or $\Delta H°$ between endo and exo isomers is small, so that only modest contributions to rate differences can come from initial states. Thus, Goering-Schewene analyses imply unequivocally that exo/endo rate differences reflect primarily the relative energies of the transition states.

The notion that solvolysis of *exo*-norbornyl substrates involves σ participation from the nearby 1,6 bond, which is not available to assist solvolysis of the endo isomer, is the essence of the "nonclassical ion" theory of such reactions.[19] In the present case, the correlation of the three norbornyl substrates with exo leaving groups is far superior to those with endo leaving groups and implies a greater degree of product ion character for the solvolysis transition states of the exo compounds in conformity with the nonclassical ion theory. However, the fact that rather similar departures from the correlation lines (similar exo/endo rate ratios) are found for 2-norbornyl chlorides with hydrogen, methyl, and phenyl substituents at the 2 position seems to run counter to the theory since methyl and phenyl substituents should endow both endo and exo transition states with a higher degree of classical character and thus remove some or all of the advantage which the exo chloride could get from σ bridging. However, the factors which favor the exo transition state for 2-methyl-*exo*-norbornyl chloride and for 2-phenyl-*exo*-norbornyl chloride may not be the same as those providing the extra driving force for unsubstituted 2-*exo*-norbornyl chloride. This point has been debated extensively.[19]

We have noted previously[10b] (examination of Table I also makes this apparent) that the heats of ionization of the 2-norbornyl derivatives are considerably more exothermic than are those of the analogous compounds bearing other secondary groups (e.g., 2-methyl-2-*exo*-norbornyl chloride compared to *tert*-butyl or to 1-methyl-1-cyclopentyl chloride). Furthermore, ΔH_i for the 2-norbornyl ion varies to a greater degree with changes in solvent than do the ΔH_i's of the other ions implying a somewhat different combination of factors for distributing charge internally (within the ion) and externally (to solvent).[21] Two referees with diametrically opposed viewpoints on this section have expressed disappointment that we have not reached a clean-cut conclusion regarding the contribution of nonclassical stabilization of the 2-norbornyl cation. We have chosen deliberately to be circumspect in our interpretation since we feel that *by themselves* the data in this paper do not lead to a definite conclusion on this matter. We will discuss the "norbornyl problem" subsequently.

Solvolysis and the Carbocation Theory of Organic Chemistry. The correlations presented here provide extraordinary corroboration of the fundamental soundness of the "carbocation theory of organic chemistry". By this we mean the interpretation of polar reactions in terms of pathways leading through (or to) the most stable carbocation accessible to the system. One might imagine ionization to be a very complicated reaction in solvolysis solvents, yet we have found a remarkably close parallel between the energy of ion formation both in superacid (or even in the gas phase)[10b] and the energy involved in the creation of solvolysis transition states. Stabilities of a large number of carbocations (as isolated species) have already been calculated by ab initio methods and the list is growing rapidly.[22] The effects of solvation are beginning to be treated explicitly.[21] We have nearly reached the point, at last, where the details of some important prototype reactions of organic molecules in complex solvents may be understood rigorously in terms of quantum theory.

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