solvolyses[14]—anchimeric assistance would seem to be implicated as the accelerating factor. Similarly, α-methyl/hydrogen rate ratios in cyclopropylcarbinyl systems are found to be in the range 10^3–10^5.[3] This apparently "normal" value seemed inconsistent with the known delocalization to the cyclopropane ring.[3d] The new limiting α-CH_3/H ratio of 10^8 removes this dilemma.[15]

The following paper provides an alternative method of estimating the magnitude of solvent assistance in secondary systems.[16]

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(14) G. D. Sargent, *Quart Rev. Chem. Soc.*, 20, 301 (1966); ref 6, Vol. III, in press.

(15) *Cf.* P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, 91, 5880 (1969).

(16) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, 92, 2542 (1970).

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Solvent Assistance in the Solvolysis of Secondary Substrates. III. A Method for Estimating the Magnitude of Solvent Assistance

Sir:

The preceding papers have emphasized the marked difference in behavior between 2-adamantyl derivatives and other simple secondary substrates.[1] Such substrates, *e.g.*, isopropyl tosylate, react with considerable nucleophilic solvent participation, but this participation appears to be largely or wholly absent in the reactions of the 2-adamantyl system. In this paper, a method is suggested whereby the magnitude of solvent assistance can be put on a quantitative basis.

Definitions are in order. It is convenient to designate solvolysis processes by three rate constants, k_Δ (anchimerically assisted), k_s (nucleophilically solvent assisted), and k_c (anchimerically and nucleophilically unassisted).[2, 3] Following Winstein's usage, as the degree of assistance decreases to zero, k_Δ or k_s approaches k_c. When assistance is present, k_c is a theoretical number not directly derivable from the measured rate constant, k_t. The ratio k_s/k_c thus is a measure of the degree of nucleophilic solvent participation in the absence of anchimeric assistance; when no such participation is present $k_s/k_c = 1$.[4,5] Clearly, for bridgehead systems $k_s/k_c = 1$, because backside nucleophilic solvent participation is impossible. Other tertiary, nonbridgehead compounds behave similarly and therefore should have $k_s/k_c \cong 1$ as well.

Because of the inaccessibility of the theoretical k_c values, there has never been any way to determine k_s/k_c ratios for secondary systems. While it is clear from the literature that solvent assistance decreases along the series: alcoholic solvents > acetic acid > formic acid, the magnitude of this assistance has been a matter of uncertainty and debate.[1] The consensus has been that secondary substrates, such as isopropyl tosylate, have k_s/k_c ratios approaching 1 in formic acid,[1a] *i.e.*, nucleophilic participation by formic acid is very small.

In contrast, we have pointed out that the formolysis and acetolysis of secondary β-arylalkyl systems can be best understood in terms of two *strongly assisted* processes: k_Δ, neighboring aryl assisted, and k_s, solvent assisted.[7] Thus, according to this view, k_s/k_c for such β-arylalkyl *as well as for simple alkyl systems* should be quite large even in formic and acetic acids. A way of estimating k_s/k_c is clearly needed.

Fortunately, a model for limiting or nearly limiting behavior in secondary systems is now available.[1] The 2-adamantyl system responds to changes in solvent as do tertiary bridgehead and nonbridgehead systems[1] and should therefore also solvolyze *via* a process approaching k_c in character. In this paper, we compare the behavior of 2-adamantyl tosylate with isopropyl tosylate, a typical secondary system in which nucleophilic solvent participation is important. The requisite data are given in Table I and relative rate comparisons are presented in Table II.

The remarkable variation in relative rates—over five powers of ten—between isopropyl and 2-adamantyl tosylates in different solvents is apparent from Table II. In CF_3COOH, the least nucleophilic solvent employed,[8,9] the adamantyl compound is actually 176 times more reactive, but as the nucleophilicity of the solvent increases, so does the relative reactivity of isopropyl tosylate, which eventually becomes >1000

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(1) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, 92, 2540 (1970).

(2) The terminology adopted here is that first proposed by Winstein.[3] One of the best summaries of Winstein's work may be found in a series of lectures presented in Milan, in Oct 1965: S. Winstein, Chimica Teorica, Conferenze, VIII Corso Estivo di Chimica, Accademia Nazionale dei Lincei, Rome, 1965, p 239 ff.

(3) (a) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958); (b) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 73, 2700 (1951); (c) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, 79, 4146 (1957); (d) S. Winstein, private communication.

(4) Similarly, k_Δ/k_c is a measure of anchimeric assistance. Such ratios appeared in the early literature[6] until it was realized that for most systems k_s might not be identical with k_c. The more commonly employed k_Δ/k_s ratios often give a distorted impression of the magnitude of anchimeric assistance, especially when $k_s \gg k_c$.[2,7]

(5) These definitions have certain important mathematical consequences. The equation, $k_t = k_s + k_\Delta$, is a proper one because k_s and k_Δ processes are regarded as being discrete. However, equations such as $k_t = k_s + k_\Delta + k_c$ are *not proper* and should not be used, since k_c is not regarded as a discrete process, but merely the limit to which k_s and k_Δ tend as assistance vanishes. If a different view of solvolysis mechanisms is taken, *e.g.*, that SN1 and SN2 processes are competitive and discrete, then Winstein's terminology should not be used.

(6) *E.g.*, S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 70, 821 (1948); S. Winstein and E. Grunwald, *ibid.*, 70, 828 (1948).

(7) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, 91, 4297, (1969); also see C. J. Lancelot and P. v. R. Schleyer, *ibid.*, 91, 4291, 4294, 4296 (1969); J. M. Harris, C. J. Lancelot, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, 91, 7508 (1969).

(8) (a) P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *ibid.*, 87, 5169 (1965); (b) A. Streitwieser, Jr., and G. A. Doffon, *Tetrahedron Lett.*, 1263 (1969).

(9) I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, 91, 5635 (1969), and references therein cited. Also see A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, 91, 5637 (1969); P. C. Myhre and K. S. Brown, *ibid.*, 91, 5639 (1969); P. C. Myhre and E. Evans, *ibid.*, 91, 5641 (1969).

Table I. Solvolysis Rates for 2-Adamantyl and Isopropyl Tosylates

Tosylate	Solvent	Temp, °C	k_1, sec^{-1}[a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
2-Adamantyl	50% EtOH	100.1	$(4.36 \pm 0.09) \times 10^{-3}$	24.8	−3.4
		76.6	$(4.34 \pm 0.02) \times 10^{-4}$		
		25.0	7.70×10^{-7}[b]		
	60% EtOH	100.1	$(1.95 \pm 0.05) \times 10^{-3}$	25.7	−2.4
		76.6	$(1.78 \pm 0.01) \times 10^{-4}$		
		25.0	2.49×10^{-7}[b]		
	80% EtOH	100.3	$(2.91 \pm 0.01) \times 10^{-4}$[a,c]	26.9	−3.0
		76.6	$(2.31 \pm 0.05) \times 10^{-5}$[c]		
		25.0	2.41×10^{-8}[b]		
	100% EtOH	25.0	3.87×10^{-10}[d]		
	CH$_3$COOH	100.25	$(1.04 \pm 0.04) \times 10^{-4}$[a,c]	28.1[e]	−2.1[e]
		76.50	$(7.46 \pm 0.19) \times 10^{-5}$[a,c]		
		25.0	5.94×10^{-9}[b,e]		
	HCOOH	76.75	$(8.68 \pm 0.33) \times 10^{-3}$	25.9	+5.6
		50.20	$(3.79 \pm 0.18) \times 10^{-4}$		
		25.0	1.16×10^{-5}[b]		
	CF$_3$COOH	25.0	$(3.67 \pm 0.01) \times 10^{-3}$	16.6	−13.9
		0.0	$(2.57 \pm 0.01) \times 10^{-4}$		
Isopropyl	50% EtOH[f]	25.0	1.47×10^{-5}		
	60% EtOH[b,f]	25.0	8.79×10^{-8}		
	80% EtOH[b,f]	25.0	2.94×10^{-5}		
	100% EtOH[b]	25.0	4.07×10^{-7}[f]		
			(7.22×10^{-7}[g])		
	CH$_3$COOH[7]	25.0	7.74×10^{-8}	24.7	−8.2
	HCOOH[7]	25.0	3.69×10^{-5}	19.5	−13.3
	CF$_3$COOH[b,h]	25.0	2.08×10^{-5}	19.9	−13.2

[a] Rate constants determined conductoimetrically, unless otherwise noted. [b] Calculated from values at other temperatures. [c] Determined titrimetrically. [d] Calculated from data in other solvents using $m = 0.909$.[3,7] [e] Prior values (P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961)) are considered less accurate. [f] Calculated from the data of R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953) (m = 0.422). [g] Calculated from the data of W. Hückel and K. Tomopulos, *Justus Liebigs Ann. Chem.*, **610**, 78 (1957). [h] Calculated from the data of J. E. Nordlander and W. J. Kelly, *J. Amer. Chem. Soc.*, **91**, 996 (1969).

Table II. Isopropyl/2-Adamantyl Rate Ratios, 25°

Solvent	$\frac{k_{i\text{-PrOTs}}}{k_{2\text{-AdOTs}}}$	Minimum[a] k_s/k_c, i-PrOTs	ρ^*, alkyl Solvolysis
CF$_3$COOH	$10^{-2.25}$	10^{0}[a,b]	−7.1[8a]
HCOOH	$10^{0.5}$	$10^{2.75}$	−3.5[8a]
CH$_3$COOH	$10^{1.1}$	$10^{3.35}$	−2.6[7,8a]
50% EtOH	$10^{1.3}$	$10^{3.55}$	
60% EtOH	$10^{1.55}$	$10^{3.8}$	
80% EtOH	$10^{2.1}$	$10^{4.35}$	
100% EtOH	$10^{3.0}$	$10^{5.25}$	*Ca.* 0[c]

[a] See text.[14] [b] Assumed. [c] *Cf.* data from W. Hückel and Y. Riad, *Justus Liebigs Ann. Chem.*, **678**, 19 (1964), and A. K. Colter and R. D. Johnson, *J. Amer. Chem. Soc.*, **84**, 3289 (1962).

times *more* reactive than the 2-adamantyl tosylate. This is just what is expected from essentially k_c (anchimerically and nucleophilically unassisted) behavior of 2-adamantyl, but greater and greater solvent assistance to reaction of isopropyl tosylate.

According to theory, the relative k_c (but not k_s) rates of any two compounds should be independent of solvent.[10] We assume that there is an "inherent" k_c(isopropyl)/k_c(2-adamantyl) ratio which should be essentially independent of solvent.[13] Any deviation from this inherent ratio should then be a measure of the differing degrees to which the two compounds respond to solvent nucleophilicity.

It seems reasonable to use 2-adamantyl tosylate as a reference standard for k_c-type behavior of secondary systems. In order to estimate k_c(isopropyl), recourse is made to the results in the least nucleophilic solvent employed, CF$_3$COOH, where the isopropyl/2-adamantyl rate ratio is the smallest observed. This ratio ($10^{-2.25}$) is then taken as a provisional[14] estimate of the maximum k_c(isopropyl)/k_c(2-adamantyl),[15] a standard of reference to which the behavior in other solvents can now be compared. Column 3 of Table II provides a minimum estimate of k_s/k_c for isopropyl tosylate in each solvent.

On the basis of these minimum[14] k_s/k_c estimates, the degree of solvent participation in formic acid (>500-fold) and acetic acid (>2000-fold) solvolyses of isopropyl tosylate is seen to be substantial. This conclusion is in agreement with our interpretation of the behavior of β-arylalkyl systems.[7]

Finally, attention is called to the remarkable quantitative parallel between the minimum k_s/k_c ratios (column 3, Table II) and the ρ^* constants for solvolysis of simple secondary tosylates in various solvents (column 4, Table II).[3,7] This indicates that it may be

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(10) It is implicit in the Grunwald–Winstein treatment of solvent effects[3b,11] that compounds with the same m values should have relative rates independent of solvent.[12] This should be especially true for k_c-type substrates, whose m values should be near 1 and whose behavior should be independent of nucleophilicity.[3,11] This is idealized expectation. In practice, some dispersion in mY plots is observed, but this dispersion is not serious for similar substrates.[13]

(11) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 846 (1948).

(12) For one compound, $\log (k/k_0) = mY$; for the second, $\log k'/k_0' = m'Y$. Thus, $\log (k/k_0)/\log (k'/k_0') = m/m'$. If $m = m'$, then $\log (k/k_0) = \log (k'/k_0')$ or $k/k' = k_0/k_0'$; *i.e.*, the relative rates of the two compounds should be independent of solvent, provided solvent ionizing power (Y) is the chief factor governing the processes.

(13) We have tested and confirmed the validity of these assumptions in two new cases: *t*-butyl chloride *vs.* 1-adamantyl bromide and 2-adamantyl tosylate *vs.* di-*t*-butylcarbinyl tosylate (to be published).

(14) The solvolysis of isopropyl tosylate, even in the very weakly nucleophilic solvent, trifluoroacetic acid, may have $k_s/k_c > 1$.[8,9] Also, 2-adamantyl tosylate may have $k_s/k_c > 1$ in the more nucleophilic solvents.

(15) This ratio can be accounted for on the basis of inductive effects. If one approximates the degree of β branching in the 2-adamantyl system by $2\sigma^*_{i\text{-Pr}}$ in the Peterson[8a] CF$_3$COOH plot ($\rho^* = -7.1$, Table II), an isopropyl/2-adamantyl ratio of $10^{-2.7}$ is calculated. Obviously, other effects should also be operative.

possible to construct a solvent nucleophilicity scale applicable to a wide variety of molecules.

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(16) National Institutes of Health Postdoctoral Fellow, 1967–1969.

(17) American Can Company Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–1968; Ph.D. Thesis, Princeton University, 1970.

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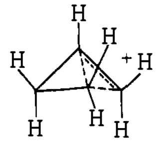
Stable Carbonium Ions. XCVIII.[1] The Nonclassical Cyclopropylcarbinyl Cation[2]

Sir:

The structure of the intermediate cation in cyclopropylcarbinyl–cyclobutyl solvolyses systems has been the subject of intensive study for many years.[3] Of the structures proposed, rapidly equilibrating unsymmetrical bicyclobutonium ions such as **1** have been most widely accepted.[3] The "bisected" structure **2** has also received support.[4] More recently a C_s symmetric ion, **5**,[5] has been suggested as the ion linking degenerate cyclopropylcarbinyl ions. The still more symmetrical (C_{3v}) tricyclobutonium ions **3** and **4** have been considered but were deemed unlikely on the basis of theoretical calculations.[5c,6]



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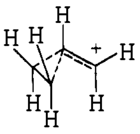

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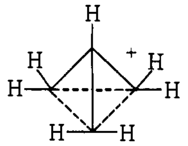

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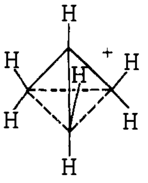

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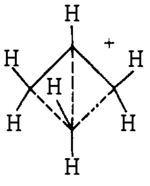

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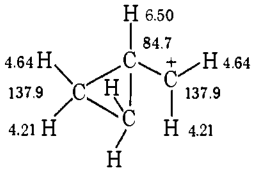
We now wish to present ^1H and ^{13}C nmr spectroscopic data on the directly observed, long-lived cyclopropylcarbinyl cation (**6**) which provide evidence for the nonclassical nature of this ion.

When cyclopropylcarbinol or cyclobutanol is dissolved in SbF_5–SO_2ClF at −80°,[7] a clear yellow-brown solution is obtained which exhibits an nmr spectrum (Figure 1) from which both ^1H and ^{13}C parameters can be obtained[8] (Table I). The one-proton methine multiplet at δ 6.50 is made up of two overlapping quartets with $J_1 = 8.0$, $J_2 = 6.5$ Hz, as shown by decoupling first the three-proton methylene doublet at δ 4.64 and subsequently the three-proton doublet at δ 4.21. When α,α-dideuteriocyclopropylcarbinol (prepared by $LiAlD_4$ reduction of cyclopropanecarboxylic acid) is ionized, the methine multiplet consists of a pair of nearly overlapping triplets, and the intensity of the methylene doublets is decreased by one-third.[9]

Using the indor technique,[10] the ^{13}C spectrum was obtained by monitoring each of the methylene doublets in turn. The spectra obtained were *identical*, giving for the methylene carbons $\delta(^{13}C)$ 137.9 ± 0.1 ppm (CS_2) and $J(^{13}CH) = 180 \pm 5$ Hz. The ^{13}C shift of the methine carbon, obtained by enhancement of the high-field proton doublet, was found to be 84.7 ppm. The conclusions drawn from the nmr spectra are that the methylene protons are nonequivalent and form two groups of equivalent protons coupled to carbons with the same chemical shift and coupling constant, *i.e.*, identical carbon atoms. The absence of geminal methylene hydrogen coupling is somewhat surprising, but it is not unreasonable since the value of J_{CH} (180 Hz) is consistent with sp^2 hybridization of the carbon atom, and J_{gem} is known to decrease to near zero in some cases.[11,12]

In order to compare the primary cyclopropylcarbinyl system (**6**) with secondary and tertiary alkylcyclo-



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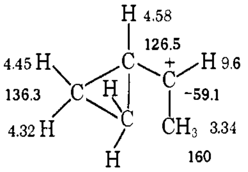

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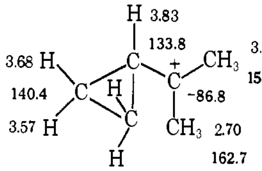

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[1] Part XCVII: G. A. Olah, D. P. Kelly, and N. Suciu, *J. Amer. Chem. Soc.*, in press.

[2] Presented in part at the 21st National Organic Chemistry Symposium, Salt Lake City, Utah, June 1969.

[3] The literature has been reviewed by K. B. Wiberg, A. H. Hess Jr., and A. J. Ashe III in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Editors, Vol. III, Wiley-Interscience, New York, N. Y., 1970, in press.

[4] P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966), and references therein.

[5] (a) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968); (b) K. B. Wiberg and G. Szeimes, *J. Amer. Chem. Soc.*, **90**, 4195 (1968); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, 90, 4303, 4311 (1968).

[6] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **No. 2**, 403 (1963).

[7] The alcohol is frozen onto the side of a test tube containing the acid solution at −78°, then gently washed into solution by a vortex mixer.

[8] A similar spectrum was obtained previously from cyclobutane, but the low-field multiplet (δ 6.5) was not well resolved: G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968). See also C. H. Lin, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1969, in which the same ion was generated from cyclopropylcarbinyl and cyclobutyl chlorides.

[9] This experiment was carried out by J. M. Bollinger.

[10] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).

[11] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, N. Y., 1969, Chapters 1–4.

[12] Ion **6** was quenched in a suspension of methanol and sodium carbonate at −78°. The presence of cyclobutyl methyl ether and cyclopropylcarbinyl methyl ether is indicated (nmr) in the products obtained. Details will be reported in a forthcoming full paper.