Table IV. Experimental Range of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for I-H/I-D

$-\rho$	k_H/k_D	$VP \times EXC \times ZPE$	$(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})_{exptl}$
0.095	1.037	0.998	1.039
	1.030	0.998	1.032
	1.023	0.998	1.025
0.275	1.037	0.994	1.043
	1.030	0.994	1.036
	1.023	0.994	1.029

range in $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$, 1.024–1.044. Table IV lists experimental values of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for I-H/I-D obtained by combining values of $VP \times EXC \times ZPE$ from Table III with the value of $k_H/k_D \pm \sigma_{k_H/k_D}$. The theoretically calculated and experimentally determined ranges of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ are in good agreement, *i.e.*, 1.024–1.044 and 1.025–1.043, respectively.[12] The observed isotope effect is thus principally if not completely determined by $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$.

The importance of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ results from its being a function of the nature of the transition state.[7,13] Consequently, calculations of "exact"[7] values of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for various transition states for I-H (I-D) are in progress, with the view of unambiguously defining the nature of the pyrolytic transition state for I-H.

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[12] Use of the $VP \times EXC \times ZPE$ values calculated at 25° yields a range in $(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})_{exptl}$, 1.026–1.047, which, within the limits of experimental precision, is equivalent to the ranges in Table IV.

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The Magnitude of Secondary α-Deuterium Isotope Effects for Limiting Solvolyses[1]

Sir:

The tendency of the solvolytic secondary α-deuterium isotope effect[2,3] to increase with decreasing disposition of the substrate toward rearside nucleophilic attack or with decreasing nucleophilicity of the solvent (or attacking group) has been used as a means of assessing the limiting nature of solvolysis.[2–8] While the lower limit of the α-deuterium isotope effect is unity or slightly less for S_N2 reactions,[3,4a,j,5] determination of the maximum value for limiting solvolyses has posed difficulties. Not only does the magnitude of α-D isotope effects depend on the degree of nucleophilic involvement, but also on the leaving group[4k] and on ion-pair partitioning effects.[7b] The highest recorded values of the α-deuterium isotope effect for secondary arenesulfonates (k_H/k_D = 1.16–1.23) in saturated systems were determined with substrates sterically susceptible to backside nucleophilic attack (Table I). α-Deuterium isotope effects in this range have often been interpreted as indicating limiting behavior.[9] These conclusions are at variance with other criteria[10] which indicate that the behavior of the substrates listed in Table I is *not* limiting. For example, their *m* values and apparent *m* values are all significantly less than the experimental maximum for a secondary substrate (Table I).[11]

We have recently presented extensive evidence indicating that 2-adamantyl derivatives, unlike simple secondary alkyl derivatives such as 2-propyl or cyclohexyl, solvolyze with little or no nucleophilic solvent participation.[10,12] For this reason we have determined the rates of solvolysis of 2-adamantyl tosylate and 2-adamantyl-*2-d* tosylate in four solvents ranging from trifluoroacetic acid (low nucleophilicity)[8d,13] to 80% ethanol (high nucleophilicity)[14] in the hope of establishing maximum experimental values of the α-deuterium isotope effect for arenesulfonate leaving groups. During the course of reporting this work, two closely related studies from Shiner's laboratory[4k,l] were brought to our attention. Shiner and Dowd showed that the 3-pentyn-2-yl system apparently was limiting and gave as high

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[1] Presented at the 13th Reaction Mechanisms Conference, Santa Cruz, Calif., July 1970.

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[9] For example, Lee and Wong:[8c] "Solvolysis of I (*endo*-norbornyl tosylate) gave an isotope effect of about 1.20 which may be regarded as normal for an S_N1 or limiting solvolysis," and Stoffer and Christen:[8e] "The solvolysis of the cyclopentyl brosylates in aqueous ethanol is thought to proceed through a limiting, S_N1, carbonium ion mechanism since the k_H/k_D for the *1-d*$_1$ compound is 1.18."

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[11] 2-Adamantyl tosylate gives maximum values for secondary substrates: apparent $m = 0.89$, $m = 0.91$.[10a] See ref 10a for a discussion of this use of *m* values. In addition to *m* values, other criteria such as $(k_{EtOH}/k_{AcOH})_y$[10a] and per cent inversion[4b] indicate the nonlimiting behavior of the substrates listed in Table I. See also S. Winstein and D. Trifan, *ibid.*, 74, 1147 (1952).

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Table I. α-Deuterium Isotope Effects and *m* Values for Representative Cyclic and Bicyclic Arenesulfonates

Substrate	Solvent	α-k_H/k_D (T, °C)	$m^{a,b}$	Apparent $m^{a,c}$
Cyclopentyl tosylate	CH_3CO_2H	1.16 (50)[d]		0.725[e]
Cyclopentyl brosylate	C_2H_5OH	1.187 (25)[f]		
Cyclohexyl tosylate	CH_3CO_2H	1.22 (75)[g]	0.44[i]	0.79[e]
		1.19 (50)[h]		
cis-4-*tert*-Butylcyclohexyl brosylate	C_2H_5OH	1.202 (35)[j]	0.58[k]	0.75[l]
endo-Norbornyl brosylate	80% C_2H_5OH	1.19 (55)[m]	0.54[o]	
	CH_3CO_2H	1.20 (50)[n]		0.69[e]
	HCO_2H	1.23 (25)[n]		
	70% dioxane	1.20 (50)[n]		

[a] At 25°. [b] Determined in aqueous ethanols; see A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956), and ref 10a. [c] Determined from rates of solvolysis in acetic and formic acids. [d] References 2a and 2b. [e] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952). [f] Reference 8e. [g] Reference 8b. [h] Reference 2a. [i] Reference 10a. [j] Reference 4b. [k] J. M. Harris, unpublished results for the tosylate. [l] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955). [m] Reference 7a. [n] Reference 8c. [o] J. M. Harris and D. J. Raber, unpublished results for the tosylate.

Table II. Comparison of α-Deuterium Isotope Effects for 2-Adamantyl, 3-Pentyn-2-yl, and Isopropyl Sulfonate Solvolyses

	α-k_H/k_D (T, °C)		
Solvent v/v	2-Adamantyl	3-Pentyn-2-yl tosylate	Isopropyl
80% ethanol	1.149 ± 0.003 (99.8)[a]		1.076 ± 0.002 (75.3)[a] 1.098 (25)[b]
60% ethanol	1.168 ± 0.006 (75.1)[a]	1.213 (25)[c]	1.098 ± 0.002 (65.1)[a]
50% ethanol	1.225 (25)[d]		1.114 (25)[b]
70% CF_3CH_2OH	1.228 (25)[d]	1.226 (25)[c]	1.140 (25)[b]
97% CF_3CH_2OH	1.18 ± 0.01 (75.1)[a] 1.225 (25)[d]		1.16 (25)[b]
CF_3COOH	1.26 ± 0.02 (25)[e]		1.22 ± 0.02 (25)[f]

[a] Tosylates; this work. For each value, generally five concurrent conductometric protium and deuterium runs (made using a Wayne–Kerr Autobalance Universal Bridge Model B461) were made in the same bath; the error limits reported are average deviations of the measured values and do not include other possible experimental uncertainties. [b] Brosylates; ref 4g and 4i. [c] Reference 4k. [d] Trifluoroethanesulfonates ("tresylates"); ref 4l. [e] Tosylates, determined spectrophotometrically. Error limit reported for a 68% confidence interval (see R. B. Dean and W. J. Dixon, *Anal. Chem.*, **23**, 636 (1951)) from 24 individual runs for the protium and 19 runs for the deuterium compound. Five additional sets of concurrent runs gave a lower average value, 1.20 ± 0.03. [f] Tosylate; ref 6b. We regard this value as being only provisional in view of difficulties in determining trifluoroacetic acid rates reproducibly; only two simultaneous runs were reported in ref 6b.

solvolytic α-D isotope effects as any measured.[4k] Shiner and Fisher also examined the 2-adamantyl system, but they chose to use the more reactive 2,2,2-trifluoroethanesulfonate ("tresylate") leaving group permitting work at 25°.[4l] Table II summarizes the α-D isotope effects for 2-adamantyl tosylate and tresylate,[4k] and for 3-pentyn-2-yl tosylate;[4l] data for isopropyl arenesulfonates in the same solvents are also included for comparison.

When corrected for the (assumed) temperature dependence of the α-D isotope effects,[15] our results for isopropyl tosylate in 80% ethanol and for 2-adamantyl tosylate in 97% CF_3CH_2OH are seen to be in excellent agreement with the values obtained in the same solvents for isopropyl brosylate[4g] and for 2-adamantyl tresylate,[4l] respectively. According to theory, all sulfonate leaving groups should exhibit nearly the same α-D isotope effects.[4l]

The α-D isotope effect of 1.26 ± 0.02 measured for the trifluoroacetolysis of 2-adamantyl tosylate is the highest reported. However, in view of the great experimental difficulties in obtaining high precision in this solvent (see Table II, footnote *e*), we do not regard this value as being significantly different from Shiner's provisional maximum of 1.23 at 25° for sulfonate leaving groups.[4k,l] It is apparent from Table II that both 2-adamantyl and 3-pentyn-2-yl substrates give nearly identical values, at or very close to this maximum.

In contrast, with the possible exception of trifluoroacetolysis,[16] the magnitudes of the α-D isotope effects for isopropyl sulfonates are always appreciably less than this maximum value. This behavior is general, and applies to other concentrations of ethanol and trifluoroethanol–water,[4l] to water itself,[5a] and to acetic acid.[2a] These data reinforce our conclusion that the solvolyses of isopropyl derivatives generally are appreciably solvent assisted (again, with the possible exception of trifluoroacetolysis).[10,12]

However, the values of the α-D isotope effect obtained for 2-adamantyl sulfonates are not always markedly higher than other values for cyclic secondary derivatives (Table I), despite the nonlimiting behavior of these substrates revealed by other criteria (Table I and ref 11). It seems quite possible that this result is due to a nonlinear relationship between the magnitude of the α-deuterium isotope effect and the degree of backside nucleophilic involvement,[17] or to nucleophilic displacements on preformed ion pairs.[4h–l,7b] In effect, as limiting behavior[18] is approached, relatively large changes in the degree of nucleophilic solvent participation may be producing very small differences in the magnitude of the α-D isotope effects. Thus, α-D isotope effects may be less than other probes[10,12] for detecting nucleophilic solvent participation in substrates

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(15) Generally α-deuterium isotope effects around 1.15 in magnitude decrease by approximately 0.01 for each 20° rise in temperature.[4g] When corrected to the same temperature the data for the 2-adamantyl sulfonates in various solvents (Table II) give virtually the same value within reasonable experimental uncertainty. See ref 14.

(16) Compare footnotes *e* and *f* of Table II.

(17) *Cf.* H. Humski, T. Strelkov, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 693 (1969), and ref 7b.

(18) We are using the term "limiting" here and previously[10,12] to indicate the total absence of kinetically significant nucleophilic involvement of solvent (or neighboring group) in the *overall* solvolysis process as measured by k_t.

approaching limiting character. This emphasizes the need for the highest accuracy in the determination of α-D isotope effect values, an accuracy very difficult to achieve using ordinary titrimetric techniques.

Our results and those of Shiner and Fisher[41] further emphasize the unique character of the 2-adamantyl system among saturated secondary substrates. All mechanistic probes indicate the essentially limiting[18] nature of 2-adamantyl solvolyses: the large α-D effect (Table II), the high *m* values[10,11] and α-CH_3/H rate ratios,[10] per cent inversion,[19] and behavior in the presence of added strong nucleophiles, such as NaN_3.[12] In our opinion, as many experimental probes as possible should be addressed to the resolution of the mechanistic details of the solvolysis process, rather than relying on one criterion, such as secondary deuterium isotope effects alone.

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α-Deuterium Effects on the Rates of Solvolysis of a 2-Adamantyl Sulfonate Ester[1]

Sir:

In earlier reported work the α-deuterium isotope effect has been developed as a criterion of solvolysis mechanism.[2–17] It has been determined that for S_N2 reactions the effect is near unity.[8] Recent work indicates that, as expected, the exact value for an S_N2 reaction varies in a systematic way with leaving group, nucleophile, and substrate reactivity;[8,12–14,18] typical observed values are in the range 0.95–1.06 per α-D (25°). For substitutions in the S_N1 category α-D effects have been shown to reach an upper limit which is characteristic of the particular leaving group and, within a narrow range, not dependent on the solvent polarity, nucleophilicity, or substrate reactivity.[7,9] This upper limit has been shown to be $\sim$1.09 for iodide, $\sim$1.125 for bromide, $\sim$1.15 for chloride, and $\sim$1.22 for sulfonate groups (at 25°).[17,19] It has been concluded that the dominant mechanism involved when these isotope effects obtain is the rate-determining conversion of one ion pair to another[19] (*e.g.*, k_2).[20] It is possible (but no evidence on the matter exists) that the effects might be slightly larger if the mechanisms were more "dissociative" and the rate-determining step involved final dissociation of an ion pair to free ions (*e.g.*, k_3).[20]

It has also been suggested that for *borderline* solvolyses the most prominent mechanisms involve either rate-determining formation of the first ion-pair inter-

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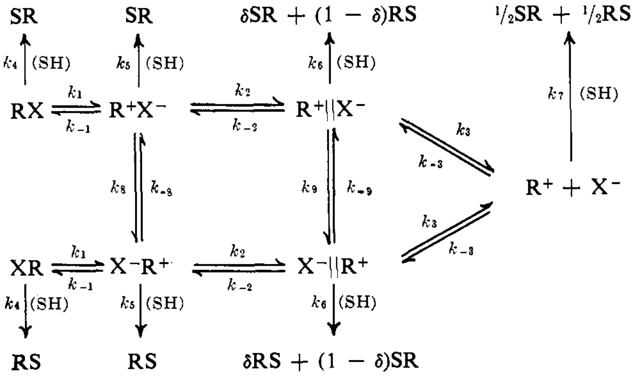
(20) Considering the widest range of solvolytic studies there is considerable evidence that at least three different carbonium ion type intermediates are important in simple solvolytic substitution, two ion pairs and the free carbonium ion.[21] Evidence also suggests that each of these, and the ground-state reactant molecule are, at least in some cases, subject to nucleophilic attack. Therefore, the following scheme represents in our view the maximally complicated scheme for a nucleophilic solvolytic substitution *supported by available evidence;* obvious additional complications are necessary to include rearrangements, elimination, and other processes. In this formulation SR represents the enantiomeric configuration to RS, etc. In the ion pairs it is assumed that a solvent molecule is present at the backside of R^+. However, with Winstein, *et al.*,[21] we do not consider the solvation to have appreciable covalent character but view it to be similar to that which obtains in the kinetically free "solvated" carbonium ion. Of the various transition states, only those for k_4, k_5, k_8, and k_7 are expected to have appreciable covalent attachment of solvent to carbon. In each case the nucleophilic attack by hydroxylic solvent is postulated to lead directly with no additional intermediates to a stable protonated substitution product which through rapid proton exchange is in equilibrium with its deprotonated form; if the products are stable under the reaction conditions the reverse of the substitution or further partitioning along its path is not considered. The evidence does not strictly rule out complications of this sort, or rule out the possibility of additional intermediates. However, in the absence of evidence that such effects are important or that the scheme is inadequate we see no reason to consider them. Thus our approach in considering the evidence on a particular solvolytic substitution is to simplify the general scheme if certain steps are not required and in particular to determine which step is the rate-determining one and which is the product-forming one.



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