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 SN2 reactions the effect is near unity.[8] Recent work indicates that, as expected, the exact value for an SN2 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 SN1 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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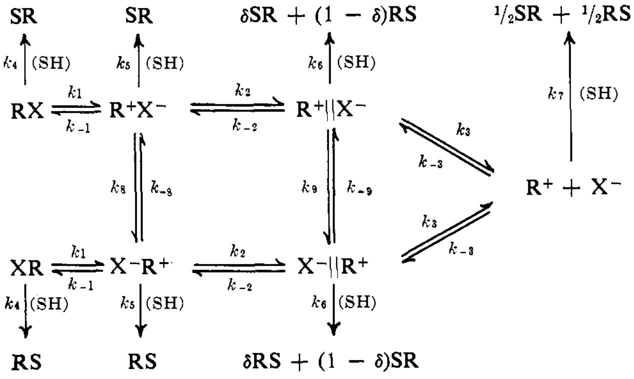
(20) Considering the widest range of solvolytic studies there is considerable evidence that at least three different carbonium ion type intermediates are important in simple solvolytic substitution, two ion pairs and the free carbonium ion.[21] Evidence also suggests that each of these, and the ground-state 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_6, 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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mediate or rate-determining nucleophilic attack on this intermediate.[10,11,22]

For rate-determining formation of the first ion pair the α-D effect should be dependent on leaving group[19] and substrate reactivity;[16,24] for rate-determining nucleophilic attack on an ion pair the isotope effect should in addition be dependent on solvent nucleophilicity.[24] Intermediate mechanisms are hard to isolate experimentally so some but not all of these expectations have been experimentally verified. The "partitioning isotope effects" observed by Murr and Donnelly[25] provide a striking independent confirmation of the difference in isotope effects between processes with k_1 rate determining and those with k_2 rate determining.

Because of the interest in the mechanism of solvolysis of adamantyl derivatives and the suggestion that 2-adamantyl toluenesulfonate solvolyzes by a nonnucleophilic mechanism,[26a–e] we thought it would be of interest to examine the α-D effects on solvolysis of a 2-adamantyl derivative. One problem which presented itself was that with the usual leaving groups the low reactivity of the compounds requires that solvolysis be done either at elevated temperatures or in strongly acidic solvents. Since we have not yet demonstrated that we can measure rates with the required accuracy, better than ±1%, under any of these conditions, we chose a more reactive sulfonate leaving group, 2,2,2-trifluoroethylsulfonate ("tresylate").[27,28]

2-Adamantyl tresylate is an easily crystallizable solid, mp 76°, which solvolyzes at a convenient rate in the usual solvents at 25°. The rate constants measured by the precise conductance method[7,9] and isotope effects are given in Table I. It is apparent that the effects (1.225–1.228) are exactly as predicted for the mechanism involving rate-determining interconversion of ion pairs.[17,19] We, therefore, agree with the classification of this reaction as not involving solvent nucleophilic participation *in the rate-determining step.* It is further seen that in accord with this mechanism the isotope effect is not dependent on solvent polarity or nucleophilicity in the range 50E–97T. Within the experimental error of the less precise measurements the effect for isopropyl brosylate in TFA does not appear significantly different.[15] Independent evidence confirms that for this solvolysis k_2 is rate determining.[10] Thus three different sulfonate esters have now been observed to give the expected maximum α-D effect of ~1.22. The fact that the α-D effect is at the maximum means that the initially formed ion pairs are undergoing internal return, *i.e.*, $k_{-1} > k_2$. Since the magnitude of this inequality is not known, care must be exercised in using the adamantyl compounds as reference substances to estimate unassisted *ionization* rates (k_1). By reference to the solvolysis rate of pinacolyl brosylate,[11] we estimate that the return to solvolysis rate ratio of the adamantyl tresylate tight ion pair (k_{-1}/k_2) is about 50. It is also apparent that α-CH_3/H ratios[26b] will depend on relative amounts of internal return.

Table I. α-D Effects on Solvolysis of 2-Adamantyl 2,2,2-Trifluoroethylsulfonate, 25°

Solvent[a]	k_H, 10^{-5} sec^{-1}	$k_H/k_{\alpha\text{-D}}$
70T	29.795	1.225 ± 0.001
97T	17.05	1.228 ± 0.001
50E	8.172	1.225 ± 0.001

[a] 97T is 97% 2,2,2-trifluoroethanol–3% water, etc. 50E is 50 vol % ethanol–50 vol % water at 25°.

We believe that carefully measured α-deuterium isotope effects provide the best probe known for determining *the degree of nucleophilic attachment to carbon in the rate-determining step* of a solvolytic substitution reaction. Isotopic substitution also has the unparalleled advantage of providing the *minimum* perturbation of the reaction under study. Thus, other criteria which have been applied such as the α-CH_3/H ratio,[26b] *m* values, $(k_{EtOH}/k_{HOAc})_Y$,[26a] and salt effects always have a much more complex relationship to mechanism and depend on the comparison of mechanisms of two or more reactions. However, since solvolysis mechanisms are reasonably complicated it is apparent that any systematic attempt to understand the details must use the entire range of techniques which has been developed. This is especially important because of the synergistic effects of information from different sources such as relative rates, isotope effects, product ratios, and stereochemical results.

Acknowledgments. We thank Professor P. v. R. Schleyer for calling the interesting 2-adamantyl system to our attention before publication of his results[26a–e] and for the exchange of manuscripts on α-D effects in the solvolysis of those compounds prior to publication.

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[22] Some confusion in the use of the term "limiting" appears inevitable. The original definition[23] was that in this class there was no covalent attachment of solvent in the transition state. By this definition rate-determining formation of the (noncovalently solvated) ion pair would be "limiting" as would rate-determining conversion of one ion pair into another or rate-determining dissociation of an ion pair. Because some reactions which had previously been classified as limiting were shown to involve rate-determining ion-pair interconversion (k_2) we have used the term in this narrower sense.[7,9] It is apparent that advancing knowledge in this field now makes a further definition of terms desirable.

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Pyrimidine Phototetramer[1]

Sir:

A photoreaction possibly involving the 1,6 head-to-head–tail-to-tail dimerization of a thymine deriva-

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