be prepared in which it is increased. Experiments directed at these goals are under way.

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Registry No. 1, 12354-84-6; **2**, 80145-87-5; **3**, 80146-08-3; **4**, 80145-86-4; **5**, 80146-01-6; **6**, 80146-02-7; **7**, 80145-83-1; **8**, 80145-84-2; **9**, 80145-85-3; **10**, 80160-32-3; cyclohexane, 110-82-7; neopentane, 463-82-1.

Deuterium Isotope Effects on the Solvolysis of 1-(1-Adamantyl)ethyl Sulfonate Esters

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In a series of papers[1-5] we have proposed that secondary alkyl sulfonates which solvolyze by a k_c limiting mechanism without internal return show α-deuterium kinetic isotope effects (α-*d* KIEs) in the range 1.15–1.16. This mechanism is exemplified by 3,3-dimethyl (pinacolyl) sulfonates which show α-d KIEs in this range in all solvents studied;[2] internal return is apparently reduced to insignificance by rapid rearrangement of the secondary to the tertiary ion in the intimate ion pair. Similar α-d KIEs are expected if the rate-determining step is attack by an oxygen nucleophile on a reversibly formed ion or ion-pair intermediate. On the other hand, if further unimolecular separation, dissociation, or β-hydrogen elimination from a reversibly formed ion pair is rate determining, the α-d KIE is expected to be in the range 1.22–1.23, values characteristic of the solvolysis of 2-adamantyl esters.[5] Of course, a mixture of these rate-determining steps would give values in between these limits. The α-d KIE may be lower than 1.15 if rate-determining loss of the leaving group is assisted by an external or internal nucleophile.

In support of an alternate mechanism of solvolysis which minimizes the importance of internal return, it has been suggested[6] that α-d KIEs lower than the limiting value of 1.22–1.23 may be due to steric effects in the initial state. In support of this contention it was reported that 1-(1-adamantyl)ethyl *p*-bromobenzenesulfonate (I-OBs) solvolyzes in 97% trifluoroethanol–3% water with an α-d KIE of only 1.11. It has been recognized for some time[7] that steric crowding tends to increase vibrational frequencies and H/D fractionation factors. However, in limiting solvolyses the transition state is expected to be less crowded than the initial state, leading to the conclusion that sterically hindered reactants should show larger not smaller α-d KIEs.

We wish to report the results of a more extensive study of the solvolysis of the title esters which shows that steric hindrance is not the cause of the reported lower isotope effect. Table I gives solvolysis rates α-d and β-d_3 rate effects and products for the title esters in nine different solvents. Two general features are of importance to the present argument.

Table I. Rates, Isotope Effects, and Product Yields for Solvolysis of 1-(1-Adamantyl)ethyl Sulfonates

solvent[a]	leaving gp[b]	k_H[c]	$k_H/k_{\alpha\text{-d}}$	$k_H/k_{\beta\text{-d}_3}$	product yields[d] sub	elimn	rearr
98H	OPms	178.5	1.116	1.120	31.5	4.4	64.1
90H	OPms	43.58	1.113	1.135	26.0	4.4	68.6
80H	OPms	39.17	1.120	1.146	26.8	7.4	65.7
97T	OBs	29.70	1.111	1.151	30.5	7.4	62.1
80T	OBs	33.49	1.119	1.153	30.6	7.5	62.0
70T	OBs	35.90	1.122	1.151	33.3	6.1	60.5
80E	OBs	0.512	1.147				
70E	OBs	1.374	1.144	1.256	66.7	13.0	20.3
60E	OBs	3.459	1.123	1.214	56.0	15.0	29.0

[a] 98H is 98% hexafluoroisopropyl alcohol–2% water; 97T is 97% trifluoroethanol–3% water; 80E is 80 vol.% ethanol–20% vol.% water, etc. [b] OPms is pentamethylbenzenesulfonate[8] and OBs is *p*-bromobenzenesulfonate. [c] *k*'s are in units of 10^{-5} s^{-1}, measured spectrophotometrically at 25 °C. Standard errors in the rate constants are generally about 0.1% and the reproducibility was about ±0.3%.[9] [d] Product yields were determined by analysis of the ^{2}H NMR spectra of reaction mixtures, initially about 0.1 M in α-d ester in the various solvents after about 10 half-lives of solvolysis. The products and the ranges, in the several solvents, of their δ values relative to external Me_4Si-d_{12} measured with a Varian HR 220 spectrometer operating at 33.8 MHz were 1-(1-adamantyl)-ethanol and ethers, 3.32–3.50; 1-(1-adamantyl)ethane, 5.80–5.91; rearranged homoadamantyl substitution products, 1.93–2.25.

(1) Although the α-deuterium effect is low in fluorinated alcohol solvents, it is solvent dependent and not nearly so low in some ethanolic solvents. Therefore, some factor other than initial state crowding must be the most important cause of the lower effects.[10]

(2) The β-d_3 effects show variations with solvent parallel to the variations in α-d effects, strongly suggesting a common origin; since there is no reason to expect a low initial state fractionation factor for the methyl group, such a cause for the low α-d effect is unlikely.

We know of no cause for such large changes in isotope effects for a given reactant, as are illustrated in Table I, other than a change in the rate-determining step.[11] The only way for the mechanism of solvolysis of these esters to change, since S_N2 attack is out of the question,[12] is for internal return to take place in at least some of the solvents or for neighboring group participation to change drastically with solvent.[14]

We note that in the 70E and 80E solvents the α-d effects are very close to the values of 1.15–1.16 characteristic of pinacolyl (3,3-dimethyl-2-butyl) esters in a variety of solvents and that the β-d_3 effects also are close to the values of 1.19–1.21 for the pinacolyl analogues.[2] If the small fraction of elimination product were formed from an ion or ion-pair intermediate, this could contribute an increase of a few percent in the β-d_3 effects but only if there is a significant proportion of internal return.

The fact that the solvents in which the isotope effects are low also give the greatest proportions of rearranged substitution suggests that the lowering of the effects is due to the rearranged or partially rearranged structure of the transition state. If the bond to the oxygen of the leaving group is replaced by a tran-

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(11) Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9002–9012.
(12) It has been suggested that pinacolyl sulfonate esters are subject to "nucleophilic solvation",[13] despite their neopentyl type structure and low S_N2 reactivity with strong nucleophiles. It is apparent that any such effect cannot be the cause of the variation in α and β isotope rate effects here reported because the larger effects, which would correspond to lesser nucleophilic involvement, are in the more nucleophilic solvents.
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sition-state bond to carbon, the α-d effect would be expected to be reduced to about 1.07 and the β-d_3 effect to about 1.00.[15]

In our view the mechanism involves first the formation of the unrearranged tight ion pair which can undergo substitution, elimination, rearrangement, or return. Since the rearrangement rate is retarded, in comparison with the pinacolyl analogue, relatively larger yields of unrearranged products are found, and internal return becomes more competitive. Furthermore, in the less nucleophilic fluorinated alcohol solvents, attack on the unrearranged ion is slower than in the ethanol solvents, leading to relatively more internal return and larger proportions of rearrangement.

What cannot be sorted out definitively from the isotope effects are the following: (a) The extent of internal return in the ethanolic solvents, because the majority of the product is unrearranged substitution and the isotope effects are not strongly influenced by internal return under these circumstances; (b) whether reverse rearrangement of the tertiary ion is faster than its reaction with solvent to form the rearranged substitution product. A steady-state treatment of this mechanism using expected values for the single-step isotope effects[16] gives a satisfactory fit to the data and suggests that in the fluorinated alcohol solvents the reverse rearrangement is competitive and that internal return dominates further reaction by factors between 1 and 3. The details of this analysis will be published along with additional results on other secondary adamantyl carbinyl esters.

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Registry No. 1-(1-Adamantyl)ethanol *p*-bromobenzenesulfonate, 80206-36-6; 1-(1-adamantyl)ethanol pentamethylbenzenesulfonate, 80206-37-7.

(15) Calculations in ref 11 show that replacing an α chlorine by carbon has very little effect on a CH/CD fractionation factor. As shown in ref 1, the maximum isotope effect for a chlorine leaving group is about 1.15 while the maximum for a sulfonate leaving group is about 1.23. It follows that the effect on an initial state fractionation factor caused by replacing α oxygen by α carbon is about 1.23/1.15 or 1.07. β substituents have little effect on α CH/CD fractionation factors as long as the β carbon does not have a vacant orbital.

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Wavelength-Controlled Production of Previtamin D_3[†]

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The photochemical conversion of provitamin D (7-dehydrocholesterol, 7-DHC) to previtamin D (P_3), thermally converted to vitamin D_3 at 37 °C, has been studied, in detail, because of the importance of yield maximization in the commercial production of the vitamin[1] (see Scheme I). Generally, the maximization of the yield has been achieved by control of the extent of the irradiation and the wavelength and/or the multiplicity of the excitation source. In one such study,[2] 254-nm light was used to prepare a mixture of 25% 7-DHC, 25% P_3, and 50% tachysterol$_3$ (T_3). This mixture, in turn, was irradiated at 0 °C in the presence of fluorenone (1 mol equiv) to sensitize the conversion of T_3 to P_3 and the P_3 converted to D_3 by a thermal reaction to give an overall yield of D_3 of 28-35%.[2,3]

In another study,[4-6] it has been shown that employment of light of 295-nm wavelength gives the maximum yield of P_3, i.e., 31-

Table I. Molecular Extinction Coefficients of Irradiation Products

λ, nm	ε 7-DHC	ε P_3	ε T_3	ε L_3
254	4500	7250	11450	4130
300	1250	930	11250	1320
330	25	105	2940	30
340	20	40	242	25
350	10	25	100	20

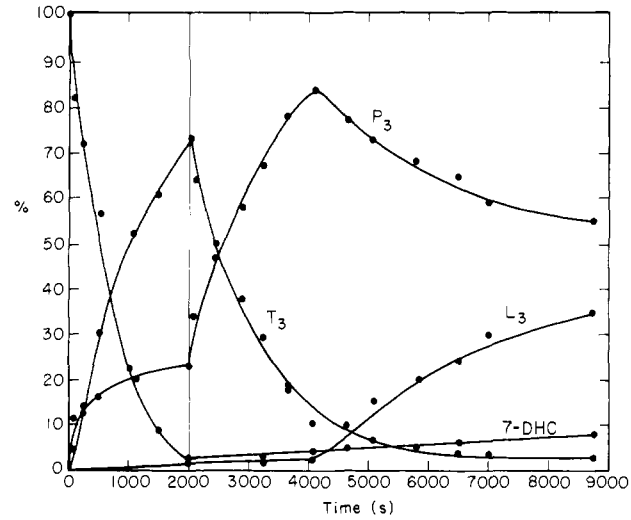

Figure 1. Reaction profile of irradiation of 7-DHC at 254 and then 350 nm.

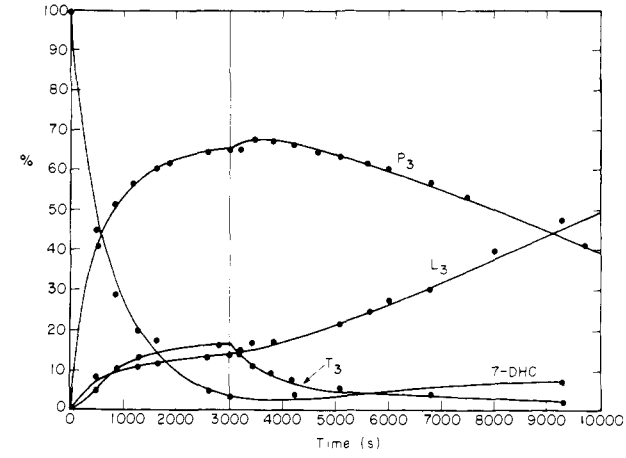

Figure 2. Reaction profile of irradiation of 7-DHC at 300 and then 350 nm.

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(7) For the irradiations at 254, 300, and 350 nm, a RPR-100 Rayonet Photochemical Reactor was used with GE-G8T5, RPR-3000A, or RPR-3500A lamps, respectively. All irradiations of 7-DHC were run in nitrogen degassed ethyl ether (sodium/benzophenone) at <5 °C (quartz Dewar, Cryocool probe). The method of analysis was the standard HPLC chromatography (see: Holic, M. F.; MacLaughlin, J. A.; Doppelt, S. H. *Science (Washington, D.C.)* **1981**, *211*, 5907).

[†]This paper is dedicated to Holger Erdmann on the occasion of his 80th birthday.

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