α-, β-, and γ-Deuterium Isotope Effects in the Solvolysis of Octan-2-yl † *p*-Bromobenzenesulphonate in 88% Aqueous Trifluoroethanol and 83% Aqueous Hexafluoroisopropyl Alcohol ‡

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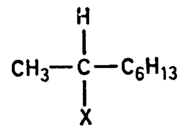
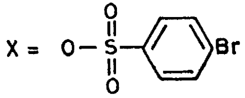
Solvolysis of octan-2-yl *p*-bromobenzenesulphonate (1) and its α-$^2H_1$, β-$^2H_3$, β-$^2H_2$ {[3,3-$^2H_2$]-(1)}, and γ-$^2H_2$ deuteriated derivatives in 88% w/w aqueous trifluoroethanol and 83% w/w aqueous hexafluoroisopropyl alcohol at 66 °C gave isotope effects k_H/k_D of 1.154, 1.250, 1.503, and 0.997 and 1.174, 1.270, 1.553, and 1.000, respectively. These results when supplemented with those earlier reported in 65% w/w aqueous ethanol represent a complete α- to γ-deuterium isotope effect spectrum in the solvolysis of a model secondary straight-chain alkyl system in aqueous hexafluoroisopropyl alcohol and a group of solvents covering a wide spectrum of nucleophilic ability and proposed as a model for the study of solvolytic reactions. The isotope effects increase in the order 65% w/w ethanol < 88% w/w trifluoroethanol < 83% w/w hexafluoroisopropyl alcohol, corresponding to the decrease in the nucleophilic properties of these media. These trends are discussed in terms of Winstein's mechanistic scheme on one hand, and some features of our unified mechanism on the other.

SECONDARY deuterium isotope effects can yield detailed information on the mechanism of solvolytic reactions.[1-4] Of particular interest is the study of such effects in media of varying nucleophilic ability reaching very low limits. In this respect, hexafluoroisopropyl alcohol, proposed by others and ourselves as a solvolytic medium of very low nucleophilicity,[5,6] should be useful. Measurements of α-, β-, and γ-effects under identical conditions for a suitably chosen substrate in a series of solvolytic media of varying nucleophilic ability including hexafluoroisopropyl alcohol should help in extending and improving knowledge in this field. These features are met in the present study which reports kinetic isotope effects, k_H/k_D, in the solvolysis of octan-2-yl *p*-bromobenzenesulphonate (1) and its α-$^2H_1$, β-$^2H_3$, β-$^2H_2$ {[3,3-$^2H_2$]-(1)}, and γ-$^2H_2$ derivatives in 87.9% aqueous trifluoroethanol (88T) and 83% aqueous hexafluoroisopropyl alcohol (83H), following the earlier reported α- and β-effects for the same compound in 65% w/w aqueous ethanol (65E).[4]



$$CH_3-\overset{H}{\underset{X}{C}}-C_6H_{13}$$

(1)



$$X = O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-C_6H_4-Br$$

Regarding earlier related studies, deuterium isotope effects have not been measured in hexafluoroisopropyl alcohol, except very recently in the solvolysis of some alicyclic systems.[7] In aqueous trifluoroethanol, isotope effect studies for secondary straight chain alkyl sulphonates are limited and do not include, to our knowledge, those for internal α-CD_2 or γ-effects.

The substrate was chosen to represent a model simple unbranched secondary system with minimum substituent effects, the study of which will also be compared eventually with simple primary and tertiary substrates, as well as with some branched systems prone to participation by neighbouring groups. It also has the advantage of both terminal and internal α-CH groups which allows for an interesting comparison. Finally, it lends itself to a convenient and reliable study of the reaction products by g.l.c., compared to short-chain systems, as previous experience in this laboratory has shown.

The solvents used belong to one of two groups of media proposed earlier for the study of solvolysis and particularly the effects of the nucleophilic (and electrophilic) properties of the medium.[6] These groups, which are aqueous mixtures of alcohols, are respectively (a) 76% w/w or 80% v/v ethanol (76E), 87.9% w/w trifluoroethanol (88T), and 83% w/w hexafluoroisopropyl alcohol (83H) and (b) 90% w/w ethanol (90E), 97% w/w trifluoroethanol (97T), and 90.5% w/w hexafluoroisopropyl alcohol (90H). The decreasing nucleophilicities within each group cover a wide spectrum and are wider for the latter group (see below and ref. 6). Compared to some other solvent systems, *e.g.* aqueous ethanol–acetic acid–formic acid–trifluoroacetic acid (TFA)[8] or aqueous aprotic solvent mixtures,§ the proposed groups have several advantages,[6] such as a common, and not low, dielectric constant within each group (31.5 and 25.8, respectively, at 40 °C) and smaller chemical differences, including acidities, between the solvents.

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† For reasons of clarity, the IUPAC rule numbering the radical position in an alkyl radical such as (1) has not been followed. The same holds for the nomenclature of the deuterium labelled derivatives.

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§ The use of aprotic solvents and their mixtures with protic ones, like aqueous acetone and dioxan, should be discouraged as a rule in solvolytic studies, for hindering the necessary [4] detection of primary reaction products; also because the further reaction of unstable primary displacement products, *e.g.* oxonium species, may cause misleading kinetic observations. This may apply to several mechanistic arguments in the literature.

Thus, solvolytic differences to be observed between these media should be easier and more reliably associated with the factor of nucleophilicity (and electrophilicity) of the medium.[6] They also allow more reliable and convenient rate and product measurements than, *e.g.*, TFA,[6,9,10] and give stable solvolysis products which is not the case in TFA.[6,9,10] This allows the determination of *primary* reaction products, the significance of which has been emphasized.[4] Furthermore, the nucleophilicity range of these systems is not any narrower, since 90H and to a lesser extent 83H approach TFA very closely in nucleophilic properties.

RESULTS AND DISCUSSION

Kinetic study of the solvolysis of (1), $[\alpha\text{-}^{2}\mathrm{H}_{1}]$-(1), $[\beta\text{-}^{2}\mathrm{H}_{3}]$-(1), $[\beta\text{-}^{2}\mathrm{H}_{2}]$-(1), and $[\gamma\text{-}^{2}\mathrm{H}_{2}]$-(1) in 88T and 83H at 66 °C yielded the results shown in Tables 1 and 2. The corresponding isotope effects in 65E, when available, are also reported (Table 2). Although 65E is not a part of the group of solvents 76E–88T–83H, it is nevertheless very similar to one of them (76E). Each study involved several sets of experiments performed at different periods. In all cases good first-order kinetics were observed for 15—85% reaction. The near identity of the respective isotope effects between the different sets shows the reproducibility achieved and enhances the dependability of the results.

Comparison of the present isotope effects in 88T with the few available values for related solvolyses shows that the effects observed for the $\alpha\text{-}^{2}\mathrm{H}_{1}$ and $\beta\text{-}^{2}\mathrm{H}_{3}$ derivatives are within the usual ranges, especially if allowance is also made for small differences associated with the temperature dependence.[1a,4c] Thus, the β-effect of the $\alpha\text{-CD}_3$ group in 88T (1.250) is essentially the same as that reported for CD_3 for propan-2-yl *p*-bromobenzenesulphonate solvolysing in 97T at 45 °C (1.256).[1a] The α-isotope effect of 1.154 in the same solvent compares well with the known values of 1.140 [1a,11] and 1.165 [1a] for

TABLE 1

Rates and α-, β-, and γ-deuterium isotope effects in the solvolysis of octan-2-yl *p*-bromobenzenesulphonate (1) in 87.9% w/w aqueous trifluoroethanol (88T) at 66.0°

Set of experiments [a]	(1)	$[\alpha\text{-}^{2}\mathrm{H}_{1}]$-(1)	$[\beta\text{-}^{2}\mathrm{H}_{3}]$-(1)	$[\beta\text{-}^{2}\mathrm{H}_{2}]$-(1)	$[\gamma\text{-}^{2}\mathrm{H}_{2}]$-(1)
			$10^{2}\,k/\mathrm{min}^{-1}$ [b]		
1	6.277 ± 0.016 (14)	5.445 ± 0.036 (12)	5.068 ± 0.035 (14)	4.216 ± 0.030 (14)	
2	6.125 ± 0.026 (11)	5.292 ± 0.021 (6)	4.861 ± 0.037 (8)	3.995 ± 0.031 (6)	
3	6.127 ± 0.048 (11)	5.335 ± 0.024 (10)	4.874 ± 0.020 (11)	4.108 ± 0.030 (7)	
4	6.135 ± 0.026 (22)				6.155 ± 0.033 (15)
			$k_{\mathrm{H}}/k_{\mathrm{D}}$		
1		1.153 ± 0.008	1.238 ± 0.009	1.489 ± 0.011	
2		1.157 ± 0.007	1.260 ± 0.011	1.533 ± 0.014	
3		1.149 ± 0.010	1.257 ± 0.011	1.491 ± 0.016	
4					0.997 ± 0.007
Average [c]		1.154 ± 0.005	1.250 ± 0.006	1.503 ± 0.008	0.997 ± 0.007

[a] Within each set the experiments were conducted under the same conditions. For the different sets conducted at different periods, at most slight differences were involved in the experimental conditions. [b] Rate constants represent the average of those obtained for the number of experiments given in parentheses. Uncertainties are standard errors. [c] Weighted average of the respective $k_{\mathrm{H}}/k_{\mathrm{D}}$ values in sets 1—4.

TABLE 2

Rates and α-, β-, and γ-deuterium isotope effects in the solvolysis of octan-2-yl *p*-bromobenzenesulphonate (1) in 83% w/w aqueous hexafluoroisopropyl alcohol (83H) at 66.0°

Set of experiments [a]	(1)	$[\alpha\text{-}^{2}\mathrm{H}_{1}]$-(1)	$[\beta\text{-}^{2}\mathrm{H}_{3}]$-(1)	$[\beta\text{-}^{2}\mathrm{H}_{2}]$-(1)	$[\gamma\text{-}^{2}\mathrm{H}_{2}]$-(1)
			$10^{2}\,k/\mathrm{min}^{-1}$ [b]		
1	8.371 ± 0.017 (13)	7.131 ± 0.021 (8)	6.548 ± 0.017 (9)	5.382 ± 0.018 (7)	
2	8.165 ± 0.020 (13)	6.951 ± 0.064 (8)		5.282 ± 0.031 (8)	
3	8.285 ± 0.013 (22)				8.284 ± 0.010 (19)
4	8 529 ± 0.023 (13)		6.793 ± 0.027 (12)		
			$k_{\mathrm{H}}/k_{\mathrm{D}}$		
1		1.174 ± 0.004	1.278 ± 0.004	1.555 ± 0.006	
2		1.175 ± 0.011		1.546 ±. 0.010	
3					1.000 ± 0.002
4			1.256 ± 0.006		
Average [c]		1.174 ± 0.004	1.270 ± 0.004	1.553 ± 0.005	1.000 ± 0.002
88T [d]		1.154	1.250	1.503	0.997
65E [e]		1.118	1.167	1.333	

[a] Within each set the experiments were conducted under the same conditions. Between the different sets conducted at different periods, at most slight differences were involved in the experimental conditions. [b] Rate constants represent the average of those obtained for the number of experiments given in parentheses. Uncertainties are standard errors. [c] Weighted average of the respective $k_{\mathrm{H}}/k_{\mathrm{D}}$ values in sets 1—4. [d] $k_{\mathrm{H}}/k_{\mathrm{D}}$ values in 87.9% w/w aqueous trifluoroethanol at 66° (Table 1). [e] $k_{\mathrm{H}}/k_{\mathrm{D}}$ values in 65% w/w aqueous ethanol at 66° as obtained by interpolation of their values at 54 [4] and 73°.[4,9]

propan-2-yl and butan-2-yl *p*-bromobenzenesulphonates, respectively, in 70T at 25 °C. The corresponding α-values in 97T are 1.16 [1a,11] and 1.176.[1a] The β-isotope effect for an internal α-CD_2 group does not seem to have been measured in aqueous trifluoroethanol. The same is true for the γ-isotope effect of the β-CD_2 group which in the present case equals unity within experimental error.

No deuterium effects for straight-chain secondary alkyl groups seem to have been reported for hexafluoroisopropyl alcohol. However, a comparison with trifluoroacetic acid, in which such effects are treated as maxima for limiting solvolyses,[1a,12] is of interest. In this respect, both the $\beta\text{-}{}^{2}\mathrm{H}_{3}$ effect of 1.270 and the $\alpha\text{-}{}^{2}\mathrm{H}_{1}$ effect of 1.174, particularly the former, are considerably lower than the corresponding values of 1.46 and 1.22 in the solvolysis of propan-2-yl *p*-bromobenzenesulphonate in trifluoroacetic acid at 25 °C.[1a,12] Finally, the γ-isotope effect for $[\gamma\text{-}{}^{2}\mathrm{H}_{2}]$-(1) is equal to one. Since, to our knowledge, no other γ-deuterium isotope effects are available for the solvolysis of secondary straight-chain alkyl derivatives, no direct comparison is possible. As for such effects in other systems, which are scarce, their values are usually about unity or slightly inverse.[1a]

TABLE 3

Rates in the solvolysis of propan-2-yl (2-PrOBs) and 2-adamantyl *p*-bromobenzenesulphonate (2-AdOBs) in 65% w/w aqueous ethanol (65E), 87.9% w/w aqueous trifluoroethanol (88T), and 83 and 90.5 w/w aqueous hexafluoroisopropyl alcohols (83H and 90H)

	2-PrOBs		2-AdOBs			
Solvent	T/°C	$10^2\, k$/min^{-1} [a]	T/°C	$10^2\, k$/min^{-1} [a]	T/°C	$\frac{k_{2\text{-PrOBs}}}{k_{2\text{-AdOBs}}}$ [b]
65E	72	22.22 ± 0.15	76	2.177 ± 0.030	66	18
	52	3.40 ± 0.047	64	0.580 ± 0.032	25	48
88T	76	6.609 ± 0.012	76	11.834 ± 0.047	66	0.59
	66	2.550 ± 0.019	66	4.574 ± 0.065	25	0.86
	56	0.990 ± 0.044	56	1.514 ± 0.018		
83H	76	6.162 ± 0.028	76	42.99 ± 0.09	66	0.14
	56	0.824 ± 0.038	56	6.493 ± 0.22	25	0.11
90H	76	4.444 ± 0.081	76	47.06 ± 0.25	66	0.080
	56	0.605 ± 0.011	56	9.11 ± 0.11	25	0.035

[a] Rate constants represent the average of those obtained from 5—9 experiments followed to 15—85% completion. Uncertainties are standard errors. [b] Ratios based on rate constants obtained by extrapolation of all the individual rate constants, the averages of which are given in the Table.

One can also note in the present results that in all media the effect for the internal $\beta\text{-}{}^{2}\mathrm{H}_{2}$ is considerably larger than for the terminal $\beta\text{-}{}^{2}\mathrm{H}_{3}$. This has been observed in other media and systems and has been attributed to conformational influence,[1a] although we have argued that elimination may be the major cause.[4]

Except for the γ-effects in trifluoroethanol which are unity or very slightly inverse, all other observed values are ' normal '. An increase in the latter in the order 65E < 88T < 83H (Table 2) is the general trend and it parallels the decrease of the nucleophilicity of these solvents in the same order (Table 3). This agrees with the increase in α- and β-effects usually associated with more limiting solvolytic behaviour such as that believed to accompany a change from aqueous ethanol to trifluoroethanol.[1a] This behaviour is most pronounced for the $\beta\text{-}{}^{2}\mathrm{H}_{2}$ effect and least for the $\alpha\text{-}{}^{2}\mathrm{H}_{1}$ effect.

It is interesting to note also that in all cases the increase is larger from 65E to 88T than from 88T to 83H, corresponding to the irregular decrease in the nucleophilic ability of these media which is larger from 65E to 88T than from the latter to 83H. This and other features of the solvent nucleophilic properties discussed in this paper are based on the values of *k*(propan-2-yl)/*k*(2-adamantyl) (for sulphonates), a rate ratio used as a measure of the ability of a medium to provide nucleophilic assistance.[8] Pertinent rate constants and such ratios for the present solvents are given in Table 3, in addition to or further refinement of the values reported earlier.[6] Thus, this ratio for the *p*-bromobenzenesulphonates at 25 °C * is 48, 0.86, and 0.11 in 65E, 88T, and 83H, respectively, corresponding to a *ca.* 56-fold decrease from 65E to 88T as compared to a *ca.* eight-fold decrease from the latter to 83H. The same ratio in TFA is 0.028 [13] (for the toluene-*p*-sulphonates at 25 °C) which is smaller than 0.11, the value in 83H, but comparable to the value in 90H which is 0.035 (Table 3).† Less aqueous mixtures of hexafluoroisopropyl alcohol should give still smaller ratios and become less nucleophilic than even TFA, as has been found to be the case.[9,§]

Using the information available from our α-, β-, and γ-isotope effects one can proceed to propose mechanisms. Thus, by using as a probe the percentage of the maximum α-isotope effect of *ca.* 1.22, specific and

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* At 66 °C, the temperature at which the present isotope effects are reported, this ratio is 18, 0.59, and 0.14 in 65E, 88T, and 83H, respectively (Table 3).

† Our earlier comparison [6] of the values of the *k*(propan-2-yl)/*k*(2-adamantyl) ratio in 90H and TFA was based on the incorrect value of 0.0054 reported [8] for this ratio in TFA which has since been revised [13] to the above value of 0.028.

§ Compared with 90H where at 56 °C a ratio of 0.069 is obtained (Table 3), the respective values in 95, 98, and 99.5% w/w hexafluoroisopropyl alcohol are 0.032, 0.021, and 0.018.[9] The last value is some four times smaller than in 90H, and thus also in TFA which gives a ratio similar to 90H.

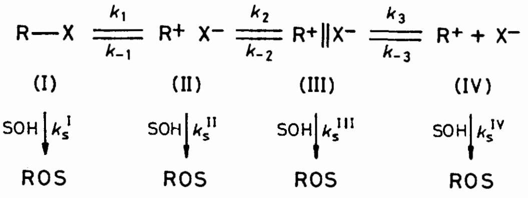
different mechanisms within Winstein's ion pair scheme have been assigned to the solvolysis of such secondary alkyl sulphonates depending on the choice of solvent.[1a] Thus, as many as four different steps within this scheme have been argued, although this is not universally accepted,[2] to be rate controlling when changing the solvent from aqueous mixtures of ethanol to trifluoroethanol, and to trifluoroacetic acid.[1a] However, our long held views, based on the unified theory and mechanistic model, suggest the operation of one and the same mechanism.[4,14,15] One of the several features of this model as applied to the present system is the *generality* suggested for nucleophilic solvent assistance plus neighbouring group nucleophilic assistance (participation–hyperconjugation [14a]) to C_α, coupled with electrophilic solvent assistance to the leaving group. These interactions and their generality hold all along the reaction co-ordinate and in all solvolytic media.* Only quantitative and not qualitative differences are anticipated between the above interactions, hence between the resultant reaction features as well, as the medium is varied. The object of mechanistic studies becomes the study of these interactions and of their quantitative trends rather than the assignment of different mechanisms and qualitative differences in general.

The above generality of interactions leads to the expectation that each of the three reaction types, substitution, elimination, and rearrangement, will involve features of the other two. It also suggests the simultaneous, complementary, and competitive operation of these reactions, as well as their being reflected in the overall reaction rate, namely their rate-determining participation in the overall process.[4]

Although our data can be interpreted in terms of Winstein's scheme for nucleophilic substitution, as has been done for analogous observations before,[1a,3] we nevertheless feel that they are best explained in terms of the above features. These two different positions are discussed below.

According to the interpretation based on Winstein's scheme, the increase in the isotope effects in the sequence 65E ⟶ 88T ⟶ 83H, particularly the increase in the α-effects (from 1.118 to 1.174), is associated with a change in mechanism within Winstein's scheme in the sense used to explain such trends in the solvolysis of *e.g.* isopropyl brosylate.[1a] The increase of the α-isotope effect for isopropyl brosylate in going from aqueous ethanol to aqueous trifluoroethanol and to trifluoroacetic acid (from 1.10 in 80% v/v aqueous ethanol to 1.14 in 70T to 1.16 in 97T and to 1.22 in TFA at 25 °C) has been attributed by Shiner to a change over four mechanisms with the sequence k_S^{I} to k_1 to k_S^{II} and k_2 of Winstein's scheme becoming progressively the rate-controlling steps (Scheme).[1a] This assignment is based on the reasoning [1a] that higher isotope effects should be observed when (a) bonding (of C_α) with the solvent is not involved in the rate-determining step, as when k_1 or k_2 determine the rate, and (b) when this step occurs late in the sequence of Winstein's scheme [(I) ⟶ (II) ⟶ (III) ⟶ (IV)], namely when the extent of the rupture of the C_α–leaving group bond is greater.

There are divergent views on the above interpretation,[2] but the latter is nevertheless representative and illustrative of fundamental elements of Winstein's scheme and of related ideas about solvolytic mechanisms.



SCHEME

According to the aforementioned features of our model on the other hand, steps like k_1 and k_2 which do not involve any bonding with the solvent, and limiting nucleophilic substitution in general, are not allowed, nor is there any change in mechanism and rate-determining step expected to occur in this system as the medium is changed along the present or other solvolytic media [4,14,15] even including trifluoroacetic acid.[17] The increasing recognition of the role of nucleophilic solvent assistance [2] supports this position.

Our model suggests rate-determining reaction of a unified ' intermediate complex ',[14a, 15a–c] involving competitive substitution, elimination, and rearrangement.[4]

Based on the above model, the trends observed in the isotope effects in the sequence 65E ⟶ 88T ⟶ 83H can be explained in terms of the following two kinds of factors both of which should contribute to an increase in the isotope effects.

(a) One factor is an expected increase in electrophilic solvent assistance to the leaving group accompanied by a decrease, but not extinction, of nucleophilic solvent assistance to C_α, which should raise the α-effect, plus an increase in nucleophilic assistance by neighbouring groups, which should raise the β-effect. The parallelism observed between the trends in the isotope effects and the change in the nucleophilicities along the series of media is in line with this position.

(b) A second factor is an anticipated change in the relative contributions of the three reactions to the overall process, and thus to the observed rates and isotope effects (as a result of their suggested rate-determining involvement and different isotope effects). An increase in the proportion of elimination coupled with higher isotope effects for this reaction over substitution could contribute to raising the observed isotope effects. This suggestion is also supported by the earlier observation that the elimination fraction in the solvolysis of (1) increases from 65E to 88T, and that this reaction gives higher isotope effects than does substitution.[4]

Although Shiner's alternative interpretation [1a] can

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* The recently introduced S_N2(intermediate) or ion sandwich mechanism [13,16] has been an implicit part of the unified mechanism (see *e.g.* refs. 14*a*,*b*, and 15*a*).

explain the results, definite answers to the question of isotope effects and mechanism in this system and in nucleophilic substitution in general require in our opinion an extensive and many-sided treatment of the subject. This treatment will be the subject of forthcoming publications.

In conclusion, the present study gives a complete and accurate α- to γ-deuterium isotope effect spectrum in the solvolysis of a model secondary straight chain alkyl system in aqueous hexafluoroisopropyl alcohol and in a group of solvents covering a wide spectrum of nucleophilic powers. Some features and the usefulness of this solvent system, which has been proposed as a model for the study of solvolytic reactions, have also been illustrated. The observed isotope effects and their trends with the medium which follow closely the nucleophilic properties of the medium are used to propose that they do not have to be interpreted in terms of Winstein's mechanistic scheme and the operation of different mechanisms of nucleophilic substitution but can also be explained in terms of some features of our unified mechanism including the operation of a single mechanism.

EXPERIMENTAL

N.m.r. spectra were obtained on a Varian A-60 spectrometer. G.l.c. analyses were carried out on a Hewlett–Packard 5720A gas chromatograph, and preparative g.l.c. separations were carried out using a Varian Aerograph A-700 Autoprep. Distillations were carried out on a Nester–Faust spinning-band apparatus. B.p.s and m.p.s are uncorrected. Microanalyses were performed by the Analytical Laboratory of the Department of Chemistry of N.R.C. ' Demokritos '.

Rate measurements by the pH-stat technique were made using a Radiometer automatic titration assembly consisting of an autoburette ABU-13, a titrator TTT-2, and a titrigraph SBR-2c. Karl Fisher water titrations were done on a Radiometer titration assembly TTA-1c also using a TTT-1c titrator and an ABU-13 autoburette.

Materials.—Lithium aluminium deuteride and trideuterioiodomethane (Merck) used had a degree of deuteration not less than 98 and 99%, respectively.

Commercially available octan-2-ol was purified to better than 99.9% purity by preparative g.l.c. The deuteriated octan-2-ols were prepared as follows and purified to better than 99.5% by preparative g.l.c. Their n.m.r. spectra gave no discernible signal for ^{1}H at the position of deuteriation. Had here been more than 5% deuteriation it would have been detected.

[1,1,1-$^{2}H_{3}$]*Octan*-2-*ol*.—Heptanal and the Grignard reagent from trideuterioiodomethane gave the alcohol by a conventional Grignard reaction.

[2-$^{2}H_{1}$]*Octan*-2-*ol*.—Reduction of octan-2-one with lithium aluminium deuteride in refluxing dry ether gave the title compound. The n.m.r. spectrum of the purified product indicated no signal for ^{1}H at C-2.

[3,3-$^{2}H_{2}$]*Octan*-2-*ol*.—Reduction of ethyl caproate (14.4 g) with lithium aluminium deuteride in refluxing dry ethyl ether gave after the usual work-up and fractional distillation [1,1-$^{2}H_{2}$]hexan-1-ol (7.5 g, 74%). This alcohol was converted to [1,1-$^{2}H_{2}$]-1-bromohexane (7.3 g, 61%) by reaction with phosphorus tribromide (23.4 g) at 0 °C for 75 min in a manner similar to that used earlier in an analogous reaction (conversion of [1,1,1,3,3-$^{2}H_{5}$]pentan-2-ol to the bromide).[18] The n.m.r. spectra of both the alcohol and the bromide products showed no discernible signal for ^{1}H at C-1. Reverse addition of the Grignard reagent prepared from [1,1-$^{2}H_{2}$]-1-bromohexane (4.5 g) to an ethyl ether solution of acetaldehyde (2.0 g) followed by the usual work-up and removal of the solvent by fractional distillation gave, after preparative g.l.c. purification of the residue, pure [3,3-$^{2}H_{2}$]octan-2-ol (1.5 g, 42%).

[4,4-$^{2}H_{2}$]*Octan*-2-*ol*.—Reduction of ethyl valerate with lithium aluminium deuteride to yield [1,1-$^{2}H_{2}$]pentan-1-ol, followed by treatment of the purified alcohol with phosphorus tribromide by the above procedure yielded [1,1-$^{2}H_{2}$]-1-bromopentane. The n.m.r. spectra of both the alcohol and the g.l.c.-purified bromide products gave no discernible signal for ^{1}H at C-1. Reaction of [1,1-$^{2}H_{2}$]-1-bromopentane (4.5 g) with potassium carbonate (6 g) and acetylacetone (4.5 g) in absolute ethanol (25 ml) by a method used for the preparation of undeuteriated heptan-2-one [19] yielded after purification by g.l.c. [4,4-$^{2}H_{2}$]octan-2-one (1.1 g, 29%). Reduction with lithium aluminium hydride and g.l.c. purification gave pure [4,4-$^{2}H_{2}$]octan-2-ol.

Octan-2-yl p-*Bromobenzenesulphonate* (1).—The ester was prepared from octan-2-ol and *p*-bromobenzenesulphonyl chloride in pyridine by the usual procedure, and was recrystallized from benzene–hexane (1 : 10 v/v) giving the pure brosylate (1), m.p. 38—40° (lit.,[20] 40—41°) (Found: C, 48.15; H, 6.0. Calc. for $C_{14}H_{21}BrO_{3}S$: C, 48.15; H, 6.05%).

Deuteriated Derivatives of (1). These derivatives, *i.e.* α-$^{2}H_{1}$, β-$^{2}H_{3}$, β-$^{2}H_{2}$, and γ-$^{2}H_{2}$, were prepared from the respective alcohols by the same method used for the preparation of the unlabelled ester (1). The m.p.s for all derivatives were between 37.5 and 39.5°.

Propan-2-yl p-*Bromobenzenesulphonate*.—This ester, m.p. 30.5—32° (lit.,[21] 33—34°), was prepared from propan-2-ol by the usual procedure.

2-*Adamantyl* p-*Bromobenzenesulphonate*.—This ester, m.p. 113—114° (lit.,[22] 112.8—113.6°), was prepared as previously reported.[22]

Solvents.—The aqueous alcoholic solvents used were prepared gravimetrically from the respective alcohols and triple distilled water. Their water content was checked and exactly adjusted following Karl Fisher titration. Ethanol (analytical grade) and hexafluoroisopropyl alcohol (Eastman–Kodak) were used without further purification. 2,2,2-Trifluoroethanol (Halocarbon Products Corp., Hackensack) was used without further purification or purified as described previously [21] (purification of these solvents does not affect the kinetic results). Impurities in these solvents detectable by g.l.c. analysis were lower than 0.05, 0.14, and 0.09%, respectively, for the aqueous ethanol, 2,2,2-trifluoroethanol, and hexafluoroisopropyl alcohol solvents used.

Kinetic Experiments.—Titrimetric rates were measured by continuously titrating the reacting solution to a pre-set constant pH, set near the initial pH reading of the solvolysis medium. A Radiometer (Copenhagen) automatic titration assembly (ABU 13–TTT 2–SBR-2c) was used along with a specially home-constructed double-jacketted cell equipped with a pair of glass and calomel electrodes. The solvent (25 ml) was allowed to stand in the reaction vessel for 20 min, the time required for temperature and pH stabilization, before the addition of ester (*ca.* 6 mg). The titrant was a 0.015M solution of sodium hydroxide in the same solvent, and its volume consumed *versus* time was continuously monitored, by the titrigraph SBR-2c recorder, and recorded at appropriate intervals. *Ca.* 80 readings were taken per experiment which was followed between 15 and 85% completion of the reaction. Pseudo-first-order rate constants were obtained by a least squares treatment of the data.

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