NEIGHBORING GROUP PARTICIPATION EFFECTS IN THE SOLVOLYSIS OF ISOBUTYL AND NEOPENTYL SULFONATE ESTERS

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The solvolysis of neopentyl sulfonate esters yields, nearly exclusively, products of rearranged carbon skeletal structure.[1] Considerable controversy still centers around the question of whether in this rearrangement methyl migration occurs during or after the ionization of the carbon-oxygen bond.[1-3] In a study of the trifluoroacetolysis of some γ-deuterated neopentyl 2,4-dinitrobenzenesulfonates, Schubert and Henson[3] observed that the label positions in the products indicated that a CD_3 group migrated, in intramolecular competition, about 1.20–1.30 times more slowly than a CH_3 group. Nevertheless, the γ-$\underline{d}_9$ ester solvolyzed only 3% more slowly than the unlabelled ester. They concluded, therefore, that methyl migration probably occurs after the rate-determining step. The results could be explained alternatively by a synchronous rather than a stepwise occurrence of ionization and migration only if the two non-migrating methyl-$\underline{d}_3$ groups caused an inverse isotope effect of sufficient magnitude to nearly cancel the expected normal isotope effect on migration.[4] This possibility was considered by these authors and rejected because β-deuterium substitution generally shows a normal isotope effect, slowing the formation of a carbon cationic center. However, it now appears from several examples that γ-deuterium substitution on non-migrating carbon generally slightly accelerates the solvolysis of compounds undergoing Wagner-Meerwein rearrangement synchronous with ionization.[5] We have therefore studied the α-$\underline{d}$ rate effects for several neopentyl and isobutyl sulfonate ester solvolyses in the hope of shedding more light on this mechanistic problem.

Alpha deuterium rate effects were recently determined for the solvolysis of some structurally closely related neophyl sulfonate esters[6] for which neighboring phenyl participation (synchronous with ionization) has been clearly established.[7] The α-$\underline{d}$ effects were found to vary with phenyl ring substituent, leaving group and solvent in the range 1.10–1.13 and are therefore significantly lower than the value of 1.15–1.16 associated with unassisted rate-determining ionization in the solvolysis of 3,3-dimethyl-2-butyl (pinacolyl) sulfonates.[8] The lower α-$\underline{d}$ effects for the neophyl esters were attributed to partial transition state phenyl-C_α bonding, which partially compensates for the loss of H-C_α-O bending force constant on ionization of the C_α-O bond. If neopentyl reacts with methyl participation, a comparable reduction in the α-d effect would be expected.

The solvolysis rate data for neopentyl and isobutyl sulfonate esters are summarized in the Table. Aqueous ethanolysis and trifluoroethanolysis of neopentyl trifluoromethanesulfonate-(triflate) yields α-$\underline{d}$ effects of 1.120–1.125 which are remarkably solvent independent and comparable to those found in the phenyl assisted solvolysis of neophyl sulfonate esters.[6] In neither 80E nor 97T does the ^{2}H nmr spectrum of the reaction mixture product of solvolysis of

Table.   Solvolysis Rate Constants and Secondary Deuterium Isotope Effects for Isobutyl and Neopentyl Trifluoromethanesulfonates at 25°C.[a]

	Isobutyl					Neopentyl		
	$k \times 10^{-5}$ sec^{-1}	$k_H/k_{\beta\text{-}d}$	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\gamma\text{-}d_6}$	$k/k_{neopentyl}$	$k \times 10^{-5}$ sec^{-1}	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\gamma\text{-}d_9}$
80E	123.73	1.208	1.050		16.7	7.4121	1.123	
50E						76.08	1.124	
70T	46.928	1.871			1.4	32.799	1.125	1.026[b]
97T	11.334	2.093	1.129	0.983	.88	12.946	1.120	
98TFA	2.02[c]	1.92±0.06[d]	1.12		.51	3.68[c]	1.11	1.03[e]

[a]Rates determined conductometrically using trifluoromethanesulfonate esters prepared from the corresponding alcohol and trifluoromethanesulfonic acid anhydrides unless otherwise noted. 80E and 50E refer to 80 and 50 vol. % ethanol in water. 70T and 97T, and 98TFA are wt. % 2,2,2-trifluoroethanol and trifluoroacetic acid, respectively, in water. [b]R. D. Fisher, Ph.D. thesis, Indiana University. Neopentyl perfluorobenzenesulfonate in 50T at 45°C. [c]Alkyl perfluorobenzenesulfonate, rates determined spectrophotometrically with a reproducibility in the rate of ±0.5%. [d]Ref. 1. Isobutyl tosylate in 100TFA at 100°C. [e]Ref. 3. 2,4-Dinitrobenzenesulfonate at 40°C in buffered 97.3TFA.

the α-$\underline{d}_2$ ester show any detectable unrearranged product; a yield as high as 2% would have been detected. The slightly lower α-$\underline{d}$ rate effect for the trifluoroacetolysis of neopentyl perfluorobenzenesulfonate(perflate) is also in agreement with the lower α-$\underline{d}$ effects found with poorer leaving groups in the neophyl ester solvolyses.[6] We feel that this 3-4% reduction in the α-$\underline{d}$ effect relative to that observed for unassisted ionization is due to the influence of methyl participation in the rate-determining transition state. The γ-$\underline{d}_9$ rate effect of 1.026 in 50T is in excellent agreement with that observed by Schubert and Henson in 97TFA;[3] the significance of this value is discussed below.

In contrast to the apparent constancy of the solvolytic mechanism for neopentyl esters, the mechanism for isobutyl triflate varies systematically with solvent nucleophilicity. As the solvent nucleophilicity decreases, the internal nucleophile, neighboring hydrogen, competes more favorably with the solvent at the reacting carbon as reflected in the large changes in the amount of rearranged product and in the β-$\underline{d}$-isotope effect. From ^{2}H nmr analysis, products derived from the $\underline{t}$-butyl cation were determined to be 10%, 62%, and 96% in 80E, 70T, and 97T, respectively, while trifluoroacetolysis yields only rearranged products.[1] Paralleling this change in neighboring hydrogen migration is the β-$\underline{d}$ effect which has a minimum value of 1.208 in 80E and a maximum of 2.093 in 97T. Winstein and coworkers observed a somewhat lower value of 1.92 in the trifluoroacetolysis of isobutyl tosylate, a difference which is not unexpected since they detected as much as 20% 2-butyl trifluoroacetate which is formed by methyl rather than hydrogen migration.[1] Beta deuterium effects of the magnitude observed in 97T and TFA coupled with the lack of direct elimination product are consistent only with hydrogen migration in the rate-determining transition state.

The α-$\underline{d}$ effect is also sensitive to these mechanistic changes. In 80E the α-$\underline{d}$ effect of 1.050 for isobutyl triflate is comparable to the value of 1.06 observed for $\underline{n}$-propyl triflate in 100T, which was explained as being due to a predominantly S_N2 reaction combined with a small fraction of competing limiting solvolysis indicated by a 13% yield of $\underline{i}$-propyl product.[9] In addition to the low α-$\underline{d}$ effect in this solvent, a further indication of the extent of nucleophilic solvent involvement is the relatively high isobutyl/neopentyl rate ratio of 17, which decreases as solvent nucleophilicity decreases. The maximum α-$\underline{d}$ effect of 1.129 in 97T and the slightly lower value of 1.12 in 98TFA are very similar to those observed in neopentyl and neophyl ester solvolyses, and it shows a similar leaving group dependence. From the large, primary β-$\underline{d}$ effects, α-$\underline{d}$ effects similar to those for neophyl ester solvolyses and the large yields of rearranged products, we conclude that the isobutyl ester solvolyzes in 97T and 98TFA with dominant neighboring hydrogen participation. Nucleophilic solvent attack is competitive with neighboring hydrogen participation in the more nucleophilic solvent 70T (62% $\underline{t}$-butyl products, and lower β-$\underline{d}$ and α-$\underline{d}$ effects than in 97T) and dominates in 80E (only 10% $\underline{t}$-butyl products, low β-$\underline{d}$ and α-$\underline{d}$ effects).

It is now interesting to compare the γ-$\underline{d}$ rate effects in the neighboring group assisted solvolyses of isobutyl- and neopentyl triflates. In the solvolysis of isobutyl triflate the non-migrating CD_3's cause a rate acceleration of ~2%, but γ-$\underline{d}_9$ neopentyl triflate, in which one of the CD_3's must migrate, shows an overall rate retardation of ~3%. We feel that the γ-$\underline{d}_9$ rate effect is low, in comparison with the relative intramolecular migratory ability of CD_3 vs. CH_3, because of the near cancellation of the inverse effects from the non-migrating CD_3 groups and the normal effect from the migrating CD_3 group. This appears to us as the only explanation which is consistent with the observed α- and γ-deuterium effects as well as with the α-^{14}C effect of 1.05 observed by Ando and coworkers in the acetolysis of neopentyl p-nitrobenzenesulfonate.[10] We will report in a subsequent paper the results of experiments which allow a more quantitative test of the postulate of cancelling γ-$\underline{d}$ effects.

Although it now seems clear that neopentyl esters solvolyze with methyl participation, it is difficult to assess just how much rate acceleration this participation entails. For example, Winstein found that neopentyl tosylate undergoes trifluoroacetolysis ~450 times faster than ethyl tosylate at 75°C.[1] If both rates are assumed to represent unimolecular ionization, an inductive effect of about 8−10 would be expected to accelerate neopentyl. In addition, internal return, which is prevented in neopentyl solvolysis by methyl migration, could be significant for the ethyl tosylate ion pair. Both of these effects would tend to make neopentyl solvolysis faster than ethyl. On the other hand, ethyl must be accelerated relative to neopentyl by an S_N2 component even in trifluoroacetolysis, as indicated by the low α-$\underline{d}$ effect (1.06),[9] a pathway denied neopentyl for steric reasons. Although ethyl is not accelerated by neighboring group participation[1] and neopentyl may be, the difficulty in this comparison is the estimation of the importance of return and S_N2 attack. Nordlander $\underline{et}$ $\underline{al}$. proposed adamantyl carbinyl sulfonate esters as models for rate comparisons[2b] since a neopentyl-like rearrangement in this compound to form the 3-homoadamantyl cation would be accompanied by a considerable increase in strain, which would favor a stepwise ionization-rearrangement process. Even though neopentyl esters undergo ionization with methyl participation, adamantyl carbinyl esters acetolyze approximately twice as fast.[2b] Thus, either carbon participation is little subject to steric retardation or the

rate effect of methyl participation in neopentyl sulfonate solvolyses must be less than the presumably small inductive and/or steric effects which might operate to accelerate the solvolysis of adamantyl carbinyl esters. Further work concerning these relative rates in model systems for neopentyl solvolysis will be published at a later date. At this time, it would appear that neighboring methyl or hydrogen participation does not greatly accelerate solvolysis rates in neopentyl or isobutyl sulfonate esters, although the kinetic isotope effect evidence is overwhelmingly in accord with participation in the rate-determining step.

References

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