

TRIFLUOROACETOLYSIS KINETICS OF 3,3-DIMETHYL-2-BUTYL TOSYLATE.¹ THE QUESTION OF NUCLEOPHILICALLY UNASSISTED SOLVOLYSIS IN SELECT SECONDARY ALKYL SUBSTRATES

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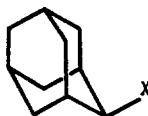
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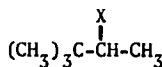
Two structures have recently been independently advanced^{4,5} as secondary alkyl substrates whose solvolyses proceed with neither neighboring group (k_{Δ})^{4c} nor solvent nucleophilic (k_s)^{4c} assistance. Such models are sought as a basis for evaluating rate enhancements in k_s and k_{Δ} pathways for other reactants.

Schleyer and coworkers⁴ have adduced broad evidence for nucleophilically unassisted (k_c)^{4c} solvolyses of 2-adamantyl halides and tosylate, 1. Combined rate comparisons with isopropyl tosylate in trifluoroacetic acid (for minimum nucleophilicity) and other solvents have been taken to provide lower-limit values of k_s/k_c for this substrate in the more nucleophilic media.^{4c} Ion-pair partitioning effects were not explicitly considered in this treatment.

Shiner *et al.*⁵ have presented data for 3,3-dimethyl-2-butyl (pinacoyl) brosylate, 2b, in support of a mechanism of rate-determining ionization, where ion-pair return is precluded by rapid methyl migration.



1a, X = OTs
b, X = Br, Cl



2a, X = OTs
b, X = OBs

A test for the mutual validity of models 1 and 2 as idealized k_c reactants is their comparative rate response to solvent change. In the absence of differential ion-pair phenomena, the relative k_c rates of two substrates should be independent of solvent.^{4c,6} Particularly instructive in such an assessment should be trifluoroacetic acid (TFA), which is considerably less nucleophilic and more highly ionizing than other common solvents producing displacement products.^{1,4,5,7} Based on this medium the degree of parallel k_c behavior for 1a and 2a may be described by the closeness to unity of the expression in eq 1.

$$\frac{(k_{\text{solvent}}/k_{\text{TFA}})_{\text{PinOTs}}}{(k_{\text{solvent}}/k_{\text{TFA}})_{\text{2-AdOTs}}} = 1 \quad (1)$$

We have measured the trifluoroacetylolysis kinetics of pinacolyl tosylate and applied the results together with those published for other solvents to eq 1. The relatively rapid rate at 26.2° (half-life 147 sec) was measured by a new technique for continuous photometric observation after rapid mixing,⁸ while at lower temperatures series of reactions conducted in a thermostatted bath were quenched after programmed intervals with -70° 95% ethanol and assayed spectrophotometrically.⁹ The data are listed in Table I; the linear least-squares Eyring plot gave $\Delta H^\ddagger = 18.8$ kcal/mole and $\Delta S^\ddagger = -6.5$ cal/deg-mole, with a mean deviation of the experimental rate constants from those on the line of 0.58%.

Table I. Trifluoroacetylolysis^a Rate Data^b for 3,3-Dimethyl-2-butyl Tosylate (2a).

Temp, °C	26.2	25.0	15.1	10.2	5.6
10 ⁴ k, sec ⁻¹	47.1	40.9 ^c	13.2	7.34	4.26

^aIn the presence of 0.06 M sodium trifluoroacetate and 1 wt% trifluoroacetic anhydride. ^bSee text for measurement techniques. ^cInterpolated from the data at other temperatures.

Table II presents the solvent-effect ratio of eq 1 for five solvents. In all these media significant upward departures from unity are observed, ranging to 16 in 80% ethanol. A correlation of increasing solvent-effect ratio with decreasing Y value¹⁰ is found within the aqueous ethanol and the carboxylic acid solvent groups. In view of the much larger values of this ratio¹¹ associated with substrates more open to solvent nucleophilic assistance^{4c,12}, the present results indicate similar but non-identical rate-determining processes for systems 1 and 2.

It seems most reasonable that the solvent-effect distinctions reflect differences in ion-pair chemistry, with return to reactant in the pinacolyl case being preempted by rearrangement as proposed.^{5a} Partitioning of 2-adamantyl tosylate ion pairs should be a complex function of solvent, involving solvent-separated as well as contact species.¹³ Within solvent groups of similar nucleophilicity,¹⁴ however, one might anticipate increasing return with decreasing solvent Y values, in accordance with the relationships of Table II. If the tight ion pairs sterically resemble the covalent ground state sufficiently to be substantially protected from backside attack, then product formation will follow tight ion-pair dissociation^{4i,2} and net solvolysis should become a decreasing fraction of ionization as solvent dissociating (ionizing) power decreases.

An alternative explanation of the data might be sought in solvent-dependent methyl

Table II. Solvent Rate Effects on 3,3-Dimethyl-2-butyl (Pin) Tosylate^a (2a) Relative to 2-Adamantyl (2-Ad) Tosylate^b (1b) at 25.0°.

Solvent	$\frac{k_{\text{Pin}}}{k_{\text{2-Ad}}}$	$\frac{(k_{\text{solvent}}/k_{\text{TFA}})_{\text{Pin}}}{(k_{\text{solvent}}/k_{\text{TFA}})_{\text{2-Ad}}}$	Y_{solvent}^c
80% aq. CH ₃ CH ₂ OH ^d	72.5	16	0.000
50% aq. CH ₃ CH ₂ OH ^d	36.1	7.9	1.655
97% aq. CF ₃ CH ₂ OH ^d	11.4	2.5	1.148
CH ₃ CO ₂ H	32.2	7.1	-1.639
HCO ₂ H ^d	20.3	4.5	2.054

^aComplementary data from S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952); S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956); and refs 5a and 10a. ^bData from refs 4c and 4d, except for a revised trifluoroacetylolysis rate constant communicated personally by Professor Schleyer, $k = 8.98 \times 10^{-4} \text{ sec}^{-1}$. ^cRef 10. ^dThe pinacolyl tosylate/brosylate rate ratio in acetic acid, 0.275, was assumed to hold in the other solvents.

assistance in pinacolyl solvolysis. By consideration of the Hammond Postulate,¹⁵ such participation if operative should assume increasing kinetic importance (in the absence of k_s processes) as solvent ionizing power decreases from trifluoroacetic acid.^{5a,d} Closely similar and minor γ -d₉ isotope effects, however, have been reported for pinacolyl brosylate in 50% aqueous ethanol and 97% trifluoroethanol^{5a} and in 43% ethanol and 95% trifluoroacetic acid,^{5c} implying negligible methyl-group participation throughout.

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