Concurrent Solvolytic and Non-solvolytic Reactions of Benzyl Azoxytoluene-*p*-sulphonate in Aqueous Trifluoroethanol containing Bases: An Unprecedented Mechanistic Duality

H. Maskill

Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland, U.K.

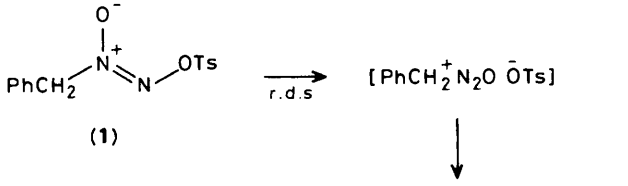
Benzyl azoxytoluene-*p*-sulphonate (**1**) undergoes heterolytic fragmentation on solvolysis with the anticipated electron flow from benzyl towards the toluene-*p*-sulphonate leaving group, but suffers concurrent nucleophilic attack by basic solutes at the sulphur atom of the toluene-*p*-sulphonate moiety with consequent heterolysis and electron flow in the opposite sense, the benzylazoxy group now being the nucleofuge.

Compounds which are capable of yielding (relatively) stable carbonium ion intermediates react under solvolytic conditions in ionizing media *via* the S_N1 range of mechanisms. Aryl-substituted-methyl or tertiary alkyl halides are classic examples.[1] In contrast, primary alkyl halides and other analogues which would give carbonium ions too unstable to exist under the particular solvolytic conditions react with nucleophilic solutes and the solvent *via* the S_N2 mechanism.[1,2] Compounds at the mechanistic borderline react either by both mechanisms concurrently or by a single mechanism which shows characteristics of both; investigations of such reactions are still a very active area of current research.[3] The leaving group in these

reactions departs following heterolysis in the same sense regardless of the uni- or bi-molecular character of the reaction of the electrophile, or of other mechanistic details.

In other reactions of electrophiles, nucleophilic attack may be at alternative sites according to the nature of the nucleophile and the experimental conditions.[4] For example, conjugated enones may undergo addition of a nucleophile at the carbonyl (1,2-addition) or at the activated β-position of the double bond (1,4-addition). These alternative mechanistic modes may take place concurrently, but both are always bimolecular.

In the course of our investigations of the reactions of the electrophile benzyl azoxytoluene-*p*-sulphonate (**1**) and its derivatives, we have identified a rare if not unique coexistence of heterolytic mechanisms. Compound (**1**) has been shown to undergo a solvolytic reaction in highly ionizing media *via* the initial rate-determining fragmentation shown in equation 1. Thiocyanate, a powerful nucleophile, gave rise to substantial yields of benzyl thiocyanate, and a second-order kinetic term corresponding to bimolecular nucleophilic attack at the benzylic carbon was sought. If found, such a reaction would have corresponded to an S_N2 mechanism with N_2O and toluene-*p*-sulphonate as leaving groups departing in concert and was the anticipated nucleophilic displacement reaction competing with the S_N1 reaction of equation 1. No such kinetic term was found, evidence which led to the formulation of a bifurcated solvolytic mechanism involving two product-forming routes.[5] However, reaction of (**1**) in the same solvent containing bases which are much weaker nucleophiles than thiocyanate towards carbon did show higher order kinetic terms (Table 1) and led to the formation of new products (Table 2) which were isolated and identified by comparison with authentic synthetic samples. But the new products did *not* correspond to nucleophilic attack at the benzylic carbon *i.e.* we still had no evidence of the expected S_N2 companion to the established S_N1 mechanism for (**1**).



Ts = tosyl = toluene-*p*-sulphonyl

Table 1. Rates of reaction of benzyl azoxytoluene-*p*-sulphonate (**1**) in 1:1 (v/v), trifluoroethanol : water containing basic solutes, 42 °C.

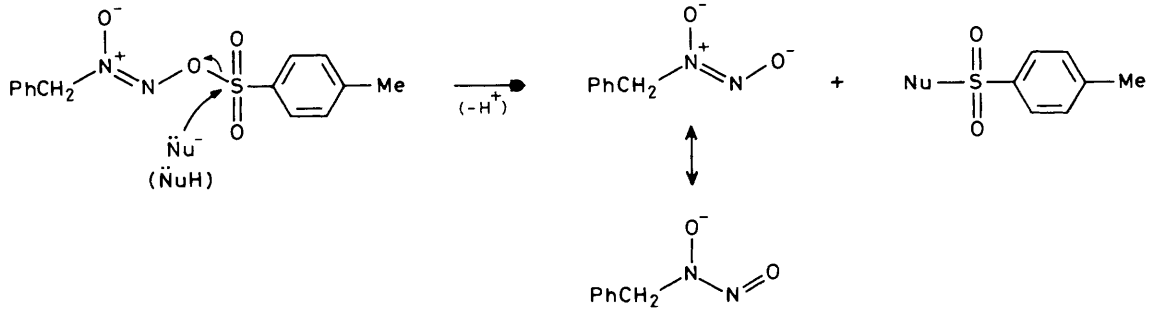
Solute	Concentration/mol dm^{-3}	10^5k/s^{-1}
None	0[a]	4.6
NaOAc	0.2[a]	27
	0.3[a]	29
	0.3[b]	6.5
	0.5	57
	0.5[b]	6.7
	1.0	105
	1.0[b]	8.0
	1.0[c]	11
Imidazole[d]	0.4	29
	0.74	49
	1.0	61

[a] Ionic strength made up to 0.5 mol dm^{-3} with $NaClO_4$. [b] Buffered with $MeCO_2H$, $[AcO^-]/[MeCO_2H] = 29$. [c] Buffered with $MeCO_2H$, $[AcO^-]/[MeCO_2H] = 57$. [d] Buffered with perchloric acid, $[Im]/[ImH^+] \sim 0.8$.

Table 2. Products from reactions of benzyl azoxytoluene-*p*-sulphonate (**1**) in 1:1 (v/v), trifluoroethanol : water containing basic solutes, 42 °C.

Solute	Concentration/ mol dm^{-3}	Solvolysis product[a]	CF_3CH_2OTs	ImTs
None	0[b]	100	—	—
NaOAc	0.05[b]	60	40	—
	0.05[c]	86	14	—
	0.10[b]	53	47	—
	0.10[c]	82	18	—
	0.25[b]	25	75	—
	0.25[c]	79	21	—
	0.50	20	80	—
	0.50[c]	73	27	—
	1.0	11	89	—
	1.0[c]	67	33	—
Imidazole[d]	0.05	59	30	11
	0.25	33	53	14
	0.50	14	63	23

[a] $PhCH_2OH + PhCH_2OCH_2CF_3 + PhCHO$. [b] Ionic strength maintained at 0.5 mol dm^{-3} with $NaClO_4$. [c] Buffered with $MeCO_2H$, $[MeCO_2^-]/[MeCO_2H] = 17$. [d] Buffered with perchloric acid, $[Im]/[ImH^+] \sim 0.8$. In the absence of the acid buffer at $[Im] = 0.5$ mol dm^{-3}, virtually no solvolysis product was detected.



a; $Nu^- = CF_3CH_2O^-$
b; NuH = imidazole

Scheme 1

The formation of *N*-tosylimidazole (ImTs) from reactions containing imidazole, and of trifluoroethyl toluene-*p*-sulphonate from reactions containing either imidazole or sodium acetate require nucleophilic attack at the sulphur of (**1**) by the low concentration of the conjugate base of the solvent system, principally $CF_3CH_2O^-$ and, in the case of imidazole, by the basic solute itself. Thus, in addition to unimolecular fragmentation, (**1**) also suffers bimolecular nucleophilic attack; the electrophilic site of this bimolecular reaction is not the benzylic carbon, but the sulphur at the other end of the extended sequence of hetero-atoms.[6] The electronic redistribution associated with this bimolecular reaction is in the *opposite* sense from that of the concurrent unimolecular fragmentation (equation 1), and the nucleofuge of the bimolecular displacement is the *N*-benzylazoxy anion (perhaps assisted by hydrogen-bonding), Scheme 1. The processes characterized by the mechanisms of equation 1 and Scheme 1 take place concurrently in proportions determined by the relative magnitudes of their rate constants (first and second order respectively) and the concentration of the nucleophilic species.[7] In the absence of a base, the bimolecular reaction is inoperative, and we have shown that, even at modest concentrations of unbuffered imidazole, the solvolytic reaction is virtually completely prevented by the parallel bimolecular options forming CF_3CH_2OTs and *N*-tosylimidazole.

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