# Solvolysis of substituted benzyl azoxyarenesulfonates: † characterisation of the transition state and the selectivity of benzylic intermediates in 50% aqueous 2,2,2-trifluoroethanol ‡

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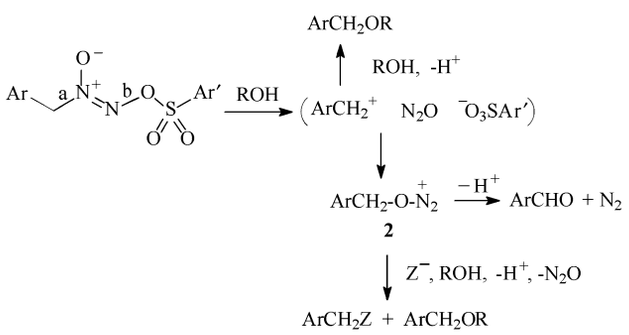
Thirteen substituted benzyl azoxyarenesulfonates have been prepared and rate constants for solvolysis of twelve have been measured in 50% (v/v) aqueous 2,2,2-trifluoroethanol over a range of temperatures from which activation parameters and rate constants at 25 °C have been determined. A six-point Hammett correlation for substituents in the benzylic electrofuge, with azoxytoluene-*p*-sulfonate as the common nucleofuge, gives $\rho(\sigma^+) = -3.27$. With 4-methylbenzyl as a common electrofuge, four substituents in the azoxybenzenesulfonate nucleofuge give $\rho(\sigma) = 1.07$. Comparison with model reactions indicates a synchronous concerted rate-limiting fragmentation for these substrates. With the less reactive 3-chlorobenzyl as electrofuge, $\rho$ for substituents in the nucleofuge is only *ca.* 0.7 which indicates a lower degree of charge development in the arenesulfonate in the transition state for these reactions. Product analyses have been carried out for compounds of high, intermediate, and low reactivity. These indicate a reactivity–selectivity relationship for capture of the substituted benzylic electrophiles by water and 2,2,2-trifluoroethanol. Substituted benzaldehydes are formed from the less reactive substrates, indicating trapping of the first-formed benzylic carbenium ion by nitrous oxide and subsequent elimination of nitrogen and a proton; but yields are low and decrease as the substituted benzyl cation becomes increasingly stable.

## Introduction

Whether the various changes which constitute a chemical reaction are concerted or step-wise is a fundamental question which continues to be investigated for reactions newly discovered and ones long known.[1] Mechanisms of solvolyses of alkyl halides and arenesulfonates were amongst the earliest to be investigated; they provided much of the technical vocabulary of the subject still in current use ($S_N1$, $S_N2$, E1, E2, *etc.*) and illustrate well the issues involved.[2] $S_N2$ and E2 mechanisms are concerted and $S_N1$ and E1 mechanisms are step-wise proceeding through carbenium ion intermediates. The degree to which a concerted mechanism is synchronous is an issue which has been appreciated only relatively recently.[1] Benzyl arenesulfonates were first thought to react simply *via* step-wise $S_N1$ mechanisms on the grounds that nucleophilic solutes had no effect upon rates but led to substitution products, and electron-donating substituents in the electrofuge lead to appreciably greater reactivity.[3] More recent work indicated that substituted benzyl arenesulfonates may be $S_N1$ or $S_N2$ according to the nature of the substituents and experimental conditions.[4] The parent benzyl toluene-*p*-sulfonate and analogues with electron-withdrawing substituents react by solvent-induced $S_N2$ mechanisms in 1 : 1 (v/v) aqueous 2,2,2-trifluoroethanol, and coupling between the departure of the nucleofuge and the bonding of the nucleophile depends upon the substituent in the electrofuge.[5] The mechanistic characterisation of a solvolytic reaction of a benzylic arenesulfonate, for example, as $S_N1$, $S_N2$, or both concurrently, remains a difficult area.

Some years ago, we reported that secondary alkyl azoxyarenesulfonates undergo unimolecular solvolysis uncomplicated by parallel bimolecular reactions,[6] and that these reactions represent a mechanistic link between alkyl arenesulfonate solvolysis and alkylamine deamination.[7] We established that they involve an initial rate-determining concerted fragmentation of the alkyl azoxyarenesulfonate, followed by capture of the carbenium ion intermediate by the solvent. In other words, these are unambiguously step-wise reactions involving intermediate carbenium ions generated in an initial rate-limiting concerted fragmentation. The benzyl carbenium ion, generated along with nitrous oxide and the nucleofuge within the same solvent cage, from the parent benzyl azoxytoluene-*p*-sulfonate (structure **1a**) was shown to be too short-lived to be captured by dilute nucleophiles.[8] But about half is trapped by the proximate nitrous oxide molecule generated in the initial fragmentation (a form of internal return) in competition with capture by the solvent, aqueous TFE (Scheme 1,




**Scheme 1**

Ar = Ph, Ar′ = 4-tolyl). The product of trapping by nitrous oxide itself then undergoes further reaction, mainly nucleophilic capture.

For substituted benzyl azoxyarenesulfonates **1a**–**i**, we also reported preliminary kinetic effects of substituents X (in the

† The IUPAC name for benzyl azoxyarenesulfonate is *N*-benzyl-*N*′-arylsulfonyloxydiazene *N*-oxide.
‡ Electronic supplementary information (ESI) available: synthesis and analytical data of azoxyarenesulfonates. See http://www.rsc.org/suppdata/p2/b1/b106887n

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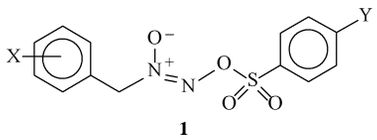

**1**

| | X | Y |
|---|---|---|
| **a**, | H | Me |
| **b**, | 4-MeO | Me |
| **c**, | 4-Me | Me |
| **d**, | 3-Me | Me |
| **e**, | 4-Cl | Me |
| **f**, | 3-Cl | Me |
| **g**, | 4-Me | MeO |
| **h**, | 4-Me | Br |
| **i**, | 4-Me | CN |
| **j**, | 3-Cl | MeO |
| **k**, | 3-Cl | Br |
| **l**, | 3-Cl | CN |
| **m**, | 4-CN | Me |

electrofuge) and Y (in the nucleofuge) which indicated that the initial concerted fragmentation is essentially synchronous.[9] We now present details of that study and product analysis results for solvolysis of **1b**, **1c**, and **1f** in 50% (v/v) aqueous 2,2,2-trifluoroethanol (50TFE, molar ratio $H_2O$ : TFE = 4 : 1). We have also investigated substituent effects upon the kinetics of four 3-chlorobenzyl azoxyarenesulfonates (**1f** and **1j**–**l**) to learn how $\rho(\sigma_Y)$ depends upon the nature of the electrofuge, *i.e.* to investigate the second-order effect of substituents in the electrofuge upon the $\rho$-value for substituents in the nucleofuge on the rate-limiting initial fragmentation. Finally, we report activation parameters for solvolyses of all compounds **1a**–**l** in 50TFE which complement results based upon product analysis and substituent effects upon rate constants at a single temperature in this overall mechanistic investigation.

## Methods and results

Syntheses of substituted benzyl azoxyarenesulfonates followed our previous route starting from substituted benzaldehydes which react with hydroxylammonium chloride and sodium ethanoate in aqueous methanol to give oximes in high yields.[6,8] The oximes were then reduced with sodium cyanoborohydride under controlled acidic conditions in methanol;[10] the hydroxylamine products had to be purified to ensure good yields in the subsequent nitrosation with sodium nitrite in aqueous hydrochloric acid containing methylated spirit. **CAUTION:** The nitrosated products, actually substituted *N*-benzyl-*N*′-hydroxydiazene oxides, were treated as potent carcinogens. Six substituted benzyl azoxytoluene-*p*-sulfonates (and 4-methylbenzyl azoxy(4-bromo)benzenesulfonate) were prepared by the Tipson method from the substituted *N*-benzyl-*N*′-hydroxydiazene oxides and tosyl (or 4-bromobenzenesulfonyl) chloride.[11] 4-Dimethylaminobenzyl azoxytoluene-*p*-sulfonate proved too reactive to allow isolation (effervescence in the reaction mixture indicated that it had formed but decomposed with the evolution of nitrous oxide). The Tipson method proved less successful for the preparation of other azoxyarenesulfonates and an aqueous method was used.[12] The azoxyarenesulfonates were isolated as crystalline products and purified by trituration with ether–pentane mixtures for kinetics; the three compounds used for product analytical studies were further purified by recrystallisation at low temperatures from ether and/or pentane. All preparative experimental details are available as electronic supplementary information. ‡

### Kinetics

Average rate constants for solvolysis in 50TFE at four temperatures were determined by our usual computer-controlled UV method,[6] from which values at 25.0 °C and activation parameters were determined using the Eyring equation.[13] Results for six azoxytoluene-*p*-sulfonates (**1a**–**f**), *i.e.* with a common nucleofuge, are shown in Table 1. Rate constants at 25 °C lead to an excellent 6-point Hammett correlation and $\rho(\sigma_X^+) = -3.27$ ($r > 0.999$);[9] 4-cyanobenzyl azoxytoluene-*p*-sulfonate (**1m**) did not give reproducible rate constants for solvolysis. The enthalpies of activation decrease regularly as the electron-supplying ability of the substituent in the benzyl residue increases, but no trend in the small negative entropies of activation is evident. Results for 4-methylbenzyl azoxyarenesulfonates (**1c**,**g**–**i**), *i.e.* reactants with the same reactive electrofuge, are also included in Table 1 and lead to a simple linear Hammett correlation, $\rho(\sigma_Y) = 1.07$ ($r = 0.996$). Again, a trend in $\Delta H^‡$ is evident; values decrease as the substituents in the nucleofuge become more electron-withdrawing, but the $\Delta S^‡$ values are similarly small and negative. Additionally, results for four 3-chlorobenzyl azoxyarenesulfonates (**1f**,**j**–**l**), *i.e.* reactants with the same unreactive electrofuge, were determined and are also included in Table 1; no trends are evident in either $\Delta H^‡$ or $\Delta S^‡$. For these reactants, the Hammett plot using all four points and the normal $\sigma$ constants is curved, but a linear correlation is obtained using $\sigma^+$ parameters (Fig. 1) $\rho(\sigma_Y^+) = 0.71$ ($r = 0.99$).

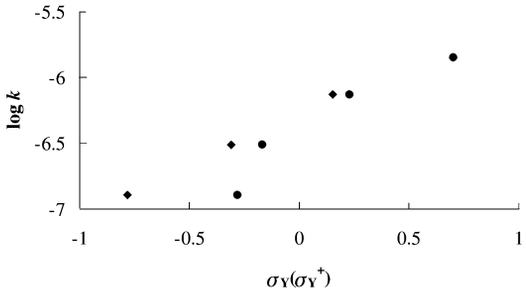


**Fig. 1** Hammett plots for substituents Y in 3-chlorobenzyl azoxy-(4-Y)benzenesulfonates: ◆ for $\sigma^+$ parameters and ● for $\sigma$ parameters.

### Product analyses

The products from three reactants (**1b**, **c**, and **f**) which span a range in reactivity of $5.5 \times 10^3$ at 25 °C in 50TFE were investigated. For **1c** and **1f**, absolute yields of alcohols in the completed reaction mixtures were analysed by direct injection HPLC using calibration curves constructed from pure authentic samples of the alcohols. Absolute yields of 2,2,2-trifluoroethyl ethers and aldehydes from **1c** and **1f** were analysed using molar response factors with respect to the alcohols for the HPLC UV detector.[8] A low yield (<1%) of *N*-(3-chlorobenzyl)-hydroxydiazene oxide was obtained (using an estimated value for the molar response factor) from the reaction of **1f**. Thus, absolute yields for all products were obtained for the reactions of **1c** and **1f** (Table 2). 4-Methoxybenzyl azoxytoluene-*p*-sulfonate (**1b**) was too reactive and unstable to obtain pure, so accurate absolute yields could not be determined. However, no *N*-(4-methoxybenzyl)hydroxydiazene oxide was detected amongst the products, and there was only a trace of the aldehyde (<0.01%). Consequently, relative yields of the alcohol and 2,2,2-trifluoroethyl (TFEt) ether were obtained from direct HPLC analysis using the molar response factor for the alcohol and ether (Table 2). We observe that the ratio of alcohol : ether from (**1f**) is smaller (3.2) than the ratio of water : TFE in the solvent (4 : 1), but it increases with increasing reactivity of the substrate (4.0 for **1c** and 8.1 for **1b**). The yield of aldehyde from **1f** is very low and decreases further as the reactivity of the substrate increases.

## Discussion

The Hammett results based upon (i) different substituents in the benzyl residue and a constant azoxytoluene-*p*-sulfonate

**Table 1** Rate constants at 25 °C and activation parameters for solvolysis of X-benzyl azoxy(4-Y)benzenesulfonates (**1a–l**) in 1 : 1 (v/v) 2,2,2-trifluorothanol–water

| Substituent X | 4-Substituent Y | Compound | $10^5 k$/s$^{-1}$ (25 °C) | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 3-Cl | MeO | (**1j**) | 0.013 | 114 | 4 |
| 3-Cl | Me | (**1f**) | 0.031 | 107 | −11 |
| 3-Cl | Br | (**1k**) | 0.074 | 109 | 4 |
| 3-Cl | CN | (**1l**) | 0.14 | 114 | 26 |
| 4-Cl | Me | (**1e**) | 0.232 | 103 | −6 |
| H | Me | (**1a**) | 0.467 | 100 | −12 |
| 3-Me | Me | (**1d**) | 0.764 | 101 | −6 |
| 4-Me | MeO | (**1g**) | 4.24 | 95 | −11 |
| 4-Me | Me | (**1c**) | 5.95 | 92 | −17 |
| 4-Me | Br | (**1h**) | 19.1 | 87 | −25 |
| 4-Me | CN | (**1i**) | 46.5 | 89 | −9 |
| 4-MeO | Me | (**1b**) | 174 | 86 | −9 |

**Table 2** Products of solvolysis of X-substituted benzyl azoxytoluene-*p*-sulfonates in 1 : 1 (v/v) trifluoroethanol–water[a]

| Substituent X (Compound) | $XC_6H_4CH_2OH$ (%) | $XC_6H_4CH_2OTFEt$ (%) | $XC_6H_4CHO$ (%) | $XC_6H_4CH_2N(O)NOH$ (%) |
|---|---|---|---|---|
| 3-Cl (**1f**)[b] | 74 | 23 | 0.12 | 0.84 |
| 4-Me (**1c**)[c] | 80 | 20 | 0.01 | <0.01[d] |
| 4-MeO (**1b**)[e] | 89 | 11 | <0.01[f] | <0.01[d] |

[a] Estimated errors for alcohols and 2,2,2-trifluoroethyl ethers, ±3%. [b] Normalised absolute values; total recovery = 98%. [c] Normalised absolute values; total recovery = 93%. [d] Not detected. [e] Average relative yields from four reactions each analysed five times. [f] A trace was detected.

nucleofuge, and (ii) different substituents in the nucleofuge and a constant 4-methylbenzyl electrofuge, have already been discussed in a preliminary communication, and indicate a synchronous concerted rate-determining fragmentation.[9,14] The rigorous method of investigating how the $\rho$-value for substituents in the nucleofuge is affected by substituents in the electrofuge, and *vice versa*, is to determine the cross interaction coefficients championed by Lee.[15] However, this would have required the non-trivial synthesis of a wider range of substrates than was practicable, so we restricted this aspect of our study to a second $\rho(\sigma_Y)$-value determination using 3-chlorobenzyl as the common electrofuge in place of 4-methylbenzyl. The simple Hammett plot shown in Fig. 1 for four 3-chlorobenzyl azoxyarenesulfonates is curved principally because **1j** is less reactive than its simple $\sigma_Y$-value predicts. If that single result is omitted, a fair three point correlation is obtained ($\rho_Y = 0.75$, $r = 0.99$). However, the reduced reactivity of **1j** and, to decreasing extents, **1f** and **1k** (compared with **1c** and **1g–i**) could be due to stabilisation of the initial state by resonance interaction between the 4-substituents in the nucleofuge and the sulfonyl group whose electron deficiency in **1f** and **1j–l** is enhanced by the 3-chloro-substituent in the electrofuge. If so, use of $\sigma^+$ substituent parameters in the nucleofuge is justified for **1f** and **1j–l** which leads to a good four-point linear correlation, $\rho(\sigma_Y^+) = 0.71$, $r = 0.99$. Regardless of which correlation is better justified, however (and we did not have sufficient data to justify use of a proper Yukawa–Tsuno treatment),[16] the $\rho$-values for substituents in the nucleofuge of these less reactive 3-chlorobenzyl azoxyarenesulfonates are much the same (0.71 or 0.75) and smaller than that obtained for the corresponding reactions of the more reactive 4-methylbenzyl analogues where $\rho(\sigma_Y) = 1.07$ for **1c** and **1g–i**. This indicates a lower development of negative charge in the incipient nucleofuge in the transition structures from **1f** and **1j–l** than from **1c** and **1g–i**. This cannot be due to an earlier transition state in a fully synchronous concerted fragmentation in the less reactive substrates (a violation of the Hammond principle),[17] but could be due to a decrease in the synchronicity of the concerted fragmentation. Thus, cleavage of bond (a) begins before cleavage of bond (b) in **1** with deactivating substituents in the electrofuge, and the reaction path in Fig. 1 of our earlier report is curved towards the upper left for such reactants, *i.e.* towards route (i).[9]

The activation parameters for the solvolysis of substituted benzyl azoxyarenesulfonates shown in Table 1 in 50TFE are generally similar to those reported earlier for 2-adamantyl azoxytoluene-*p*-sulfonate in a range of solvents,[6] *i.e.* large $\Delta H^{\ddagger}$ values and small mostly negative $\Delta S^{\ddagger}$ values. The former are as expected for reactions in which bond breaking is unassisted by appreciable bond making. The increase in entropy due to conversion of the reactant into a loosely bonded transition structure on the verge of fragmenting into three species is just about balanced by the loss of entropy associated with the increased solvation expected as covalent substrate becomes dipolar transition structure. We also see clearly that the change in reactivity along the two Hammett series previously reported, for which $\rho(\sigma_X^+) = -3.27$ and $\rho(\sigma_Y) = 1.07$, is due entirely to the trends in $\Delta H^{\ddagger}$. For the new Hammett series, $\sigma_Y$ *ca.* 0.7 for the 3-chlorobenzyl azoxyarenesulfonates, the trend in reactivity does not seem quite so easily attributable to enthalpy or entropy components of $\Delta G^{\ddagger}$. The same was observed with 3-chlorobenzyl arenesulfonates where a satisfactory linear free energy relationship did not allow dissection into interpretable enthalpy and entropy components.[5]

Only a very low yield of *N*-(3-chlorobenzyl)hydroxydiazene oxide (<1%) is obtained from **1f** indicating a very low extent of nucleophilic attack by solvent at the sulfonyl group in contrast to what would be observed under basic conditions.[8] There is no evidence of bimolecular reactions from **1c** and **1b**. As reactivity increases along the series **1f**, **1c**, and **1b**, fragmentation leads to increasingly stable benzyl carbenium ions. This series may be unique in that all three first-formed intermediate electrophiles are unambiguously benzylic carbocations. In previous investigations into the selectivity of benzylic electrophiles, it has not always been demonstrated that the products are derived from carbenium ions in step-wise reactions. Some benzyl arenesulfonates, for example, are now known to react by a solvent-induced $S_N2$ mechanism (in which rate-limiting and product-determining steps are one and the same)[5] rather than by an $S_N1$ mechanism involving benzyl carbenium ions.[3] The increasing stabilities of carbenium ions from the present series of substrates (**1f**, **1c**, and **1b**) appear to be reflected in increasing selectivities for reaction with water rather than TFE. The ratio of alcohol : ether ranges from 3.2 for **1f** (*i.e.* an apparent selectivity in favour of TFE) to 4.0 for **1c** and 8.1 for **1b**. For the first two,

the selectivities are lower than for the corresponding benzylic arenesulfonates (7.3 for 3-chlorobenzyl arenesulfonates and 4.9 for 4-methylbenzyl toluene-*p*-sulfonates). However, we know that about half of the initially formed benzyl carbenium ion from the parent benzyl azoxytoluene-*p*-sulfonate (**1a**) is trapped by the adjacent nitrous oxide molecule to give the benzyloxydiazonium ion, **2** in Scheme 1.[8] This then leads on to give principally a further solvent-derived substitution product and, in the absence of a base, only a very low yield of benzaldehyde. Thus, we are unable to ascribe the present overall ratio of alcohol to ether wholly to the selectivity of the benzylic carbenium ion, and we have insufficient data from the reactions of **1f**, **1c**, and **1b** to calculate the extents of involvement of the corresponding substituted benzyloxydiazonium ions (**2**).

## Experimental

TFE (Fluorochem) was refluxed over polyphosphoric acid for 1.5 h then fractionally distilled from molecular sieves (type 3A). Preparative details and structural assignments are available as electronic supplementary information. ‡

### Kinetics

Rates of solvolysis in 1 : 1 (v/v) TFE–$H_2O$ were measured by monitoring the decrease in UV absorbance at a suitable wavelength in the range 230–260 nm in the thermostatted cell compartment of a Pye-Unicam SP-800 spectrophotometer fitted with a platinum resistance thermometer and interfaced to an Apple microcomputer.[5,6] Initial substrate concentrations were usually *ca.* $10^{-5}$ mol $dm^{-3}$. Each reaction was monitored for 4–5 half-lives with the collection of 80–100 absorbance readings. First-order rate constants were calculated by a non-linear least squares programme; standard deviations on individual rate constants were generally <1% and reproducibility was normally ±3%. Activation parameters and rate constants at a common temperature of 25.0 °C were calculated by a computer version of the Eyring equation using average rate constants from triplicate determinations at each of four temperatures covering a 30 degree range.

### Product analysis[5,8]

HPLC was carried out using Gilson instrumentation and a UV detector connected to a Pye-Unicam PU 4810 computing integrator. Glass distilled water and HPLC grade methanol were filtered before use. The three substituted benzyl azoxytoluene-*p*-sulfonates were each solvolysed at least twice for at least 10 half-lives, and each reaction mixture was analysed directly at least 5 times to give averaged product analyses. Reverse phase (C-18 Spherisorb) HPLC was used with manual injections (Rheodyne valve with 20 μl loop), aqueous methanol flow rate = 1.5 $cm^3$ $min^{-1}$; the UV detector was set at 257 nm.


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