# Synchronous Concerted Bond Heterolyses in the Solvolysis of Substituted Benzyl Azoxyarenesulphonates† and Characterization of the Transition State

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Hammett parameters [$\rho(\sigma_X^+) = -3.27$ and $\rho(\sigma_Y) = 1.07$] for the solvolysis of a range of substituted benzyl azoxyarenesulphonates in 1:1 (v/v) trifluoroethanol–water indicate that the rate-determining fragmentation is a synchronous concerted process.

Benzyl azoxytoluene-*p*-sulphonate (**1a**) has been shown to undergo solvolysis *via* a unimolecular fragmentation, equation (1).[1] We now present evidence that this rate-determining (r.d.) fragmentation involves concerted synchronous heterolysis of bonds (a) and (b) in (**1**), and that both bonds are between about one-half and three-quarters broken in the transition state.

$$(1) \xrightarrow{\text{r.d.s.}} \underset{(2)}{ArCH_2^+ N_2O\ ^-O_3SAr'} \xrightarrow[-N_2O]{ROH}$$

$$ArCH_2OR + Ar'SO_3H \quad (1)$$
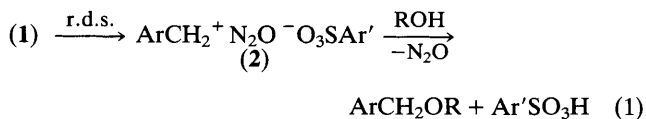
A standard molar free-energy reaction map[2] for the rate-determining production of the first-formed intermediate, the $N_2O$-separated ion-pair (**2**), is shown in Figure 1. Cleavage of bond (a) ahead of bond (b) to give initially a benzyl cation and a complex anion is represented by path (i). Alternatively, path (ii) describes the initial formation of a complex cation and the arenesulphonate nucleofuge through bond (b) under-

going heterolysis ahead of bond (a). Synchronous cleavage of bonds (a) and (b) leading directly to the $N_2O$-separated ion-pair is represented by the diagonal line (iii) in Figure 1.

Regardless of whether an intermediate intervenes in path (i) or in path (ii), cleavage of either the earlier or the later bond in either route could be the principal component of the reaction co-ordinate in the transition state. The alternatives for both routes (i) and (ii) are shown as the first two conventional
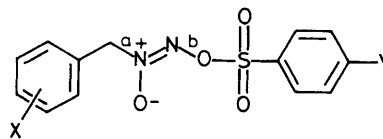


(1)

|   | 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 |

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† *N*-Benzyl-*N′*-arylsulphonyloxydiazene *N*-oxides; for consistency with previous publications the less systematic azoxyarenesulphonate-type nomenclature is retained in this Communication.

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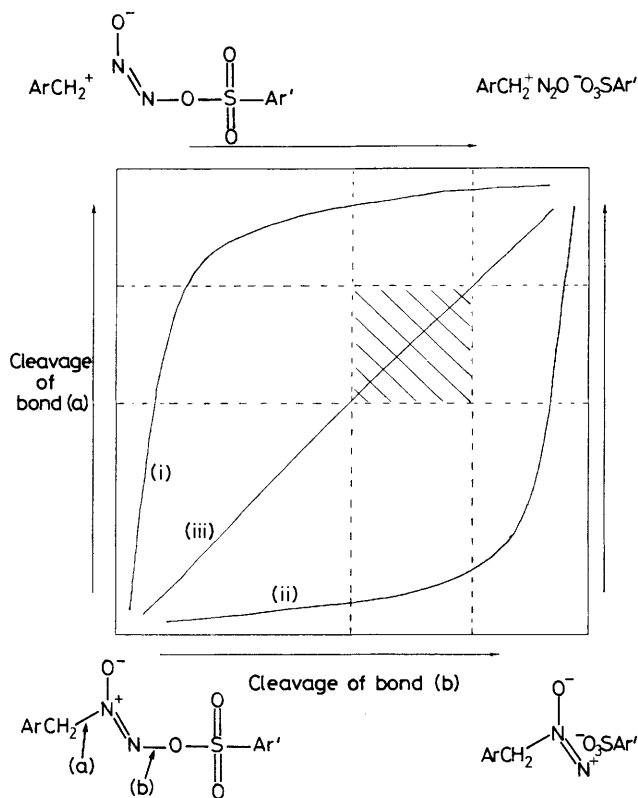
**Figure 1.** Standard molar free-energy reaction map for the conversion of (1) into the $N_2O$-separated ion-pair (2).
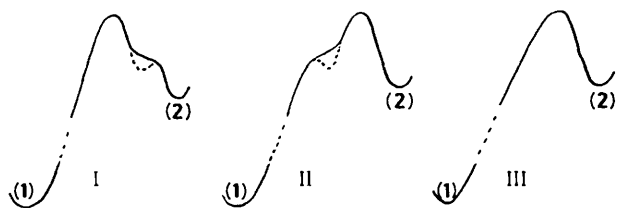


**Figure 2.** Reaction profiles for the conversion of (1) into the $N_2O$-separated ion-pair (2) by the routes across the reaction map in Figure 1. I, either route (i) or route (ii); II, either route (i) or route (ii); III, route (iii).
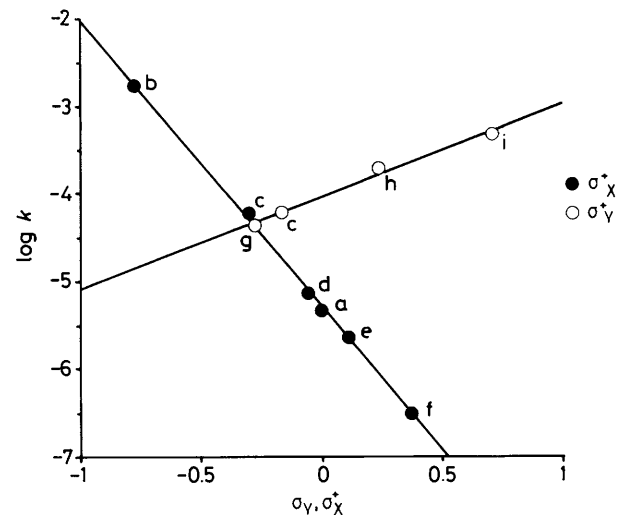


**Figure 3.** Hammett plots for the solvolysis of (1) in 1:1 (v/v) $CF_3CH_2OH$–$H_2O$ at 25 °C.

**Table 1.**

| Mechanism, Figure 1, Figure 2 | Bond status in transition state | Predicted reaction parameters | |
|---|---|---|---|
| | | $-\rho(\sigma_X^+)$ | $\rho(\sigma_Y)$ |
| Route (i), Profile I | (a) attenuated (b) intact | Large | Small |
| Route (i), Profile II | (a) broken (b) attenuated | V. large | Large |
| Route (ii), Profile I | (a) intact (b) attenuated | Small | Large |
| Route (ii), Profile II | (a) attenuated (b) broken | Large | V. Large |
| Route (iii), Profile III | (a) attenuated (b) attenuated | Large | Large |

reaction profiles in Figure 2. If the bond cleavages are synchronous as well as concerted, then the reaction profile is the section through Figure 1 along route (iii) represented as the single smooth curve III in Figure 2.

The five mechanistic alternatives can, in principle, be distinguished experimentally by a Hammett-type analysis.[2] Heterolysis of bond (a) leads to development of positive charge at the benzylic carbon which would be conjugated with a potential electron-supplying group at the *para*-position of the benzylic ring. Consequently, the correlation with substituents X should be with $\sigma_X^+$ (rather than $\sigma_X$) and, qualitatively, electron-withdrawing substituents will retard the reaction, therefore $\rho(\sigma_X^+)$ will be negative. At the other end of the molecule, electron-withdrawing substituents Y will facilitate the departure of the nucleofuge following cleavage of bond (b), but they cannot interact conjugatively with the build-up of negative charge in the sulphonate residue. Consequently, the correlation will be with $\sigma_Y$ (rather than $\sigma_Y^-$) and $\rho(\sigma_Y)$ will be positive. A more complete analysis of the reaction is given in Table 1.

Rate constants were obtained§ for the solvolysis in 1:1 (v/v) trifluoroethanol–water over a range of temperatures for six X-substituted benzyl azoxytosylates (1a—f) (Y = Me). From the derived rate constants at 25 °C, an excellent linear Hammett plot (correlation coefficient >0.999) was obtained with $\rho(\sigma_X^+)$ = −3.27, Figure 3. Similarly, the correlation for the *p*-Me-substituted benzyl Y-substituted azoxybenzenesulphonates, (1c), (1g—i), was obtained, Figure 3. This correlation is less extensive (only four compounds) and has a lower correlation coefficient (>0.99) but the result is unambiguous: an appreciable positive gradient with $\rho(\sigma_Y)$ = 1.07.

Ideally, the $\rho$-value for a kinetic process should be normalised by comparison with the $\rho$-value of the overall reaction, *i.e.* its maximum possible value, in order to estimate the position of the transition state along the reaction co-ordinate.[3] This is not possible in the present case. However, model reactions are available which allow us to conclude that these $\rho(\sigma_X^+)$ and $\rho(\sigma_Y)$ values, although large, are not maximal. The acetolysis of substituted benzyl tosylates at 40 °C has $\rho(\sigma_X^+)$ = −5.58 for the very reactive members of the series which probably react *via* an $S_N1$ mechanism or a

§ Rate constants were measured by monitoring the decrease in u.v. absorbance with time of a solution of reactants in 1:1 (v/v) trifluoroethanol–water in the thermostatted cell compartment of a conventional u.v. spectrophotometer.

strongly uncoupled $S_N2$ process with a very substantial (if not complete) degree of positive charge development at the benzylic carbon in the transition state.[4] For the less reactive members of the series, which almost certainly react with a solvent-induced $S_N2$ mechanism, $\rho(\sigma_X{}^+) = -2.81$ indicating a lower (though still significant) degree of benzylic positive charge development in the transition state.[4] The present result of $\rho(\sigma_X{}^+) = -3.27$, therefore, indicates that bond (a) is between about one-half and three-quarters broken in the transition state for fragmentation of (1). 2-Adamantyl arenesulphonates undergo ethanolysis at 25 °C with $\rho(\sigma_Y) = 1.86$.[5] The transition state in this reaction is between the intimate and the solvent-separated ion-pair in a limiting $S_N1$ mechanism[6] and, consequently, involves a fully developed negative charge on the nucleofuge and, therefore, the maximal $\rho(\sigma_Y)$. [A smaller result of $\rho(\sigma_Y) = 1.37$ was obtained for the solvent-induced $S_N2$ displacement reaction of $m$-chlorobenzyl arenesulphonates in 1:1 (v/v) trifluoroethanol–water at 25 °C indicating a less fully developed negative charge on the nucleofuge in the transition state.[7]] Again, therefore, we see that the $\rho(\sigma_Y)$ result for the solvolysis of (1) is between about one-half and three-quarters of the maximum possible value.

Taken together, the results of our present double-Hammett investigation of the solvolysis of (1) establish that there is substantial though not complete charge development at both the benzyl carbon and the oxygen of the arenesulphonate nucleofuge in the transition state for the fragmentation. This requires that the heterolyses are not only concerted, but also synchronous, and suggests that the transition state is located within the shaded area of the reaction map of Figure 1.

## References

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