# Internal Return in the Solvolysis of Secondary Alkyl Arenesulphonates

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*Summary* In highly ionizing solvolytic media, such as hexafluoropropan-2-ol, 2-adamantyl azoxytoluene-*p*-sulphonate gives only solvent-derived products, while in a solvent less conducive to carbonium ions such as ethanol, 2-admantyl toluene-*p*-sulphonate may be detected among the solvolysis products; this demonstrates that the 2-adamantyl cation may be captured by the very weakly nucleophilic toluene-*p*-sulphonate anion even in a strongly nucleophilic medium and, with other results, establishes that internal return accompanies the solvolysis of 2-adamantyl toluene-*p*-sulphonate.

A central question in mechanistic organic chemistry is whether the ionization of simple secondary alkyl arenesulphonates and halides in solvolysis reactions is reversible (equation 1). Recombination of the first-formed ion-pair

$$\mathrm{R{-}X} \underset{?}{\rightleftharpoons} [\mathrm{R^+X^-}] \rightarrow\rightarrow \text{Products} \qquad (1)$$

(internal return) has been established when the secondary alkyl cation is stabilized in some way as in norbornyl[1] or bicyclo-octyl[2] derivatives, but evidence of internal return in simpler secondary systems[3] has been less widely accepted and some of it has been disputed.[4] Our approach to this problem has been to develop an independent method of generating the carbonium ion–arenesulphonate ion-pair and establish whether or not this gives any covalent alkyl arenesulphonate.

We now report the formation of 2-adamantyl toluene-*p*-sulphonate (**1**) by mutual capture of the ion-pair formed by heterolytic fragmentation of 2-adamantyl azoxytoluene-*p*-sulphonate (**2**) with liberation of nitrous oxide.

Investigation of the solvolytic decomposition of alkyl azoxytosylates *e.g.* (**2**) is a new method of studying carbonium ion intermediates.[5] In highly ionizing solvents such as hexafluoropropan-2-ol, trifluorethanol, and 50% aqueous ethanol, the adamantyl products from (**2**) are exclusively solvent-derived. However, (**1**) was detected by t.l.c. (silica, ethyl acetate–light petroleum) in the reaction of (**2**) in ethanol at 60—62 °C. It was isolated in low yield after reaction for 4 days and identified by i.r., n.m.r., and (after recrystallization) by m.p. In non-nucleophilic solvents with very poor ion-pair stabilizing properties such as chloroform and toluene, (**2**) gives (**1**) exclusively.

The Scheme illustrates our mechanism which accommodates these results. It involves an ion-pair (**3**) as the intermediate at which mechanistic bifurcation occurs,[†] which may either undergo ion-pair combination to give (**1**) or, depending upon the solvent, give solvolysis products directly. Compound (**1**) may be stable or, again depending upon the solvent, itself give solvolysis products *via* another ion-pair, (**4**). The formation of (**1**) from ion-pair (**3**) comprising the 2-adamantyl cation and toluene-*p*-sulphonate anion generated up to several bond lengths apart and perhaps separated by the $N_2O$ molecule in a medium as nucleophilic as ethanol requires that (**1**) should also be

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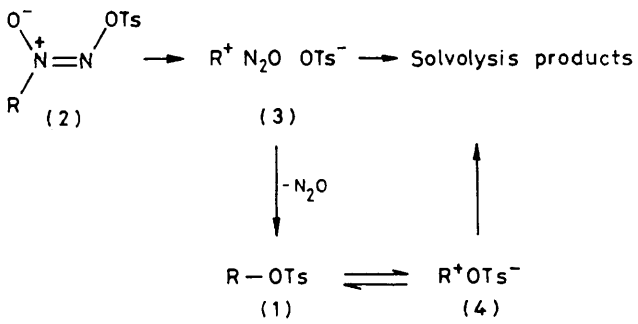
[†] An alternative non-ion-pair mechanism for the formation of (**1**) from (**2**) involving $Z \rightarrow E$ isomerization followed by a concerted cyclic reaction with the elimination of $N_2O$ was also considered. The enthalpy of activation [$\Delta H^\ddagger = 110(\mp 10)$ kJ mol$^{-1}$, deuteriotoluene, 60—100 °C] is too high for a cyclic substitution mechanism involving concerted bond-making and -breaking in the activated complex; $\Delta H^\ddagger$ for intermolecular $S_N2$ reactions and their intramolecular analogues *via* six-membered cyclic activated complexes are typically 65—90 kJ mol$^{-1}$ (D. F. Detar, F. D. McMullen, and N. P. Luthra, *J. Am. Chem. Soc.*, 1978, **100**, 2484; D. F. Detar and N. P. Luthra, *ibid.*, 1980, **102**, 4505). Furthermore, the analogous reaction of the less sterically congested cyclohexyl azoxytoluene-*p*-sulphonate → cyclohexyl toluene-*p*-sulphonate + $N_2O$ is slower than (**2**) → (**1**) at 70 °C. This is the expected order of reactivity in an unassisted ionization mechanism (ref. 4) whereas the cyclohexyl compound would be faster if the reactions involved a cyclic non-ion-pair mechanism. We thank Dr. F. G. Riddell for the n.m.r. experiments involved in this aspect of the investigation.



SCHEME. R = 2-adamantyl.

formed by internal return from the intimate ion-pair (**4**) implicated in the solvolysis of 2-adamantyl toluene-*p*-sulphonate itself. The question mark can, therefore, be removed from equation (1): solvolysis of (**1**) is accompanied by internal return from an intimate ion-pair.

This is in accord with our conclusions based upon solvolytic results in the bicyclo[3.2.1]octane system,[6] with the views of Winstein,[1,3a] Shiner,[3b,7] and others,[3c,8] concerning solvolysis generally. In establishing that the ionization of (**1**) is reversible even in a strongly nucleophilic medium, we have effectively demonstrated that the standard free energy barrier for the forward reaction of the ion-pair (**4**) cannot be lower than that for internal return (Scheme). The general principle of microscopic reversibility requires, therefore, that initial ionization of (**1**) cannot be the solvolytic rate-determining step (the one with the highest standard free energy barrier). Because of the central position of 2-adamantyl substrates among secondary alkyl derivatives in solvolytic studies,[4] our results have extensive ramifications and may require drastic revision of some current solvolytic mechanisms.

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[1] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 1952, **74**, 1154; H. Maskill, *ibid.*, 1976 **98**, 8482.

[2] H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, 1968, **90**, 2848, 2856, 2862; H. Maskill, *J. Chem. Soc. Perkin* 2, 1975, 1850.

[3] (a) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, 1968, **90**, 1904; S. Winstein, B. Appel, R. Baker, and A. Diaz, 'Symposium on Organic Reaction Mechanisms' Spec. Publ., No. 19, The Chemical Society, London, 1965, 109; (b) V. J. Shiner and W. Dowd, *J. Am. Chem. Soc.*, 1969, **91**, 6528; V. J. Shiner, R. D. Fisher, and W. Dowd, *ibid.*, p. 7748; (c) M. Gillard, F. Metras, S. Tellier, and J. J. Dannenberg, *J. Org. Chem.*, 1976, **41**, 3920; K. Okamoto, S. Saito, and H. Shingu, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3008; A. Streitweiser, T. D. Walsh, and J. R. Wolfe, *J. Am. Chem. Soc.*, 1965, **87**, 3682, 3686; C. Paradisi and J. F. Bunnett, *ibid.*, 1981, **103**, 946.

[4] T. W. Bentley, S. H. Liggrto, M. A. Imhoff, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1974, **96**, 1970; F. L. Schadt, T. W. Bentley, and P. von R. Schleyer, *ibid.*, 1976, **98**. 7667; T. W. Bentley and P. von R. Schleyer, *ibid.*, p. 7658; *Adv. Phys. Org. Chem.*, 1977, **14**, 1.

[5] H. Maskill, P. Murray-Rust, J. T. Thompson, and A. A. Wilson, *J. Chem Soc., Chem. Commun.*, 1980, 788.

[6] R. M. Banks and H. Maskill, *J. Chem. Soc., Perkin Trans.* 2, 1977, 1506, 1991; R. M. Banks, H. Maskill, R. Natarajan, and A. A. Wilson, *ibid.*, 1980, 427.

[7] R. D. Fisher, R. C. Seib, V. J. Shiner, I. Szele, M. Tomic, and D. E. Sunko, *J. Am. Chem. Soc.*, 1975, **97**, 2408; V. J. Shiner and W. Dowd, *ibid.*, 1971, **93**, 1029; V. J. Shiner, D. A. Nollen, and K. Humski, *J. Org. Chem.*, 1979, **44**, 2108; V. J. Shiner, S. R. Hartshorn, and P. C. Vogel, *ibid.*, 1973, **38**, 3604.

[8] J. M. Harris, D. C. Clark, A. Becker, and J. F. Fagan, *J. Am. Chem. Soc.*, 1974, **96**, 4478; J. J. Dannenberg, *ibid.*, 1976, **98**, 6261; D. G. Graczyk, J. W. Taylor, and C. R. Turnquist, *ibid.*, 1978, **100**, 7333; M. L. Sinnott and M. C. Whiting, *J. Chem. Soc., Perkin Trans.* 2, 1975, 1446; J. A. Bone, J. R. Pritt, and M. C. Whiting, *ibid.*, p. 1447; H. J. Storesund and M. C. Whiting, *ibid.*, p. 1452; Y. Karton and A. Pross, *ibid.*, 1978, 595.