Relative Nucleophilicities of Arenesulphonate Anions Towards Methyl Trifluoromethanesulphonate in Acetonitrile and Reactions of the Silver Salts with Methyl Iodide

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Summary Reactions of arenesulphonate anions with an acetonitrile solution of methyl trifluoromethanesulphonate exhibit a negative Hammett ρ value of slightly greater than unity, indicating substantial bonding to the anion within the transition state of the rate-determining step; reactions of the silver salts with methyl iodide exhibit an identical value and a classical S_N2Ag^+ mechanism is postulated.

Although arenesulphonate anions are considered as weak nucleophiles and good leaving groups, several related anions are considerably more nucleofugic. For example, in acetolysis of methyl derivatives, trifluoromethanesulphonate is about 10^4 times more nucleofugic than toluene-*p*-sulphonate.[1] The use of methyl trifluoromethanesulphonate as the substrate allows one to determine the relative nucleophilicities of arenesulphonate anions contained within a relatively inert solvent, such as acetonitrile.

$$ArSO_3^- + MeOSO_2CF_3 \xrightarrow{MeCN} CF_3SO_3^- + MeOSO_2Ar$$

Portions of the reactants were analysed in methanol. The unchanged substrate quantitatively produced acid during a time period in which the product was essentially unchanged.

For these same five temperatures and for concentrations of added tetra-n-butylammonium arenesulphonate within the range 0·015 to 0·15M, the accompanying solvolysis reaction was negligibly slow compared to the rates of anionic attack and, also, the second-order rate coefficients at any given temperature were constant, and independent of the salt concentration. Average values for reactions of a series of arenesulphonate salts are given, for two of the temperatures, in Table 1, together with the activation parameters and extrapolated values for 25·0 °C. Using the rate coefficient data and literature values for the ρ coefficients,[2] Hammett $\rho\sigma$ plots can be constructed and the calculated slopes (ρ values) are also given in Table 1.

The negative ρ values are similar in absolute magnitude to the positive values which have been observed for solvolyses of methyl arenesulphonates.[2,3] The significant selectivity shown by the substrate towards the arenesulphonate anions is difficult to reconcile with the ion-pair mechanism which has been proposed for substitution at a methyl carbon.[4] An ion pair containing a methyl carbonium ion has a high standard free energy change[5] and, on the basis of the Hammond postulate[6] and stability–selectivity[7] considerations, reactions in which it is present as an intermediate should show little differentiation between various attacking nucleophiles but a large differentiation with differing leaving groups. The observations are best rationalized in terms of a conventional S_N2 mechanism.

Table 1. Second-order rate coefficients[a] (k_2) for the reaction of a series of tetra-n-butylammonium arenesulphonates ($XC_6H_4SO_3^-Bu^n{}_4N^+$) with methyl trifluoromethanesulphonate in acetonitrile and enthalpies ($\Delta H^{\ddagger}$, kcal mol^{-1}) and entropies ($\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}) of activation (at 298 °C).[b]

Arene substituent X	10^2k_2/l mol^{-1} s^{-1}			$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	−23·6 °C	−0·1 °C	+25·0 °C[c]		
p-MeO	1·143	13·95	128·3	13·9 ± 0·3	−11·5 ± 0·8
p-Me	0·955	12·71	111·5	14·1 ± 0·2	−10·9 ± 0·6
H	0·681	8·57	81·7	14·2 ± 0·1	−11·4 ± 0·4
p-F	0·383	5·19	50·6	14·4 ± 0·1	−11·5 ± 0·4
p-Cl	0·300	3·99	38·3	14·3 ± 0·2	−12·4 ± 0·6
p-Br	0·287	3·53	34·2	14·1 ± 0·3	−13·5 ± 1·0
p-NO_2	0·081	1·11	11·6	14·7 ± 0·2	−13·5 ± 0·5
m-NO_2	0·071	1·06	11·3	14·9 ± 0·3	−12·8 ± 0·9
ρ Values[b,d]	−1·180 ± 0·065	−1·140 ± 0·055	−1·063 ± 0·056		
r[e]	0·991	0·991	0·991		

[a] Standard deviations, determined for each run, usually within range of 1—4% of value. [b] With associated standard deviations. [c] Extrapolated values, using measurements at five lower temperatures. [d] Using σ values from ref. 2. [e] Correlation coefficient.

Methyl trifluoromethanesulphonate slowly solvolyses in acetonitrile and the kinetics of this process can be followed by quenching portions in acetone at −78 °C and titrating the *N*-methylacetonitrilium cation against sodium methoxide in methanol. A study at five temperatures within the range −24 to +6 °C led to an extrapolated first-order rate coefficient at 25·0 °C of $2{\cdot}03 \times 10^{-4}$ s^{-1}, an enthalpy of activation of 16·3 ± 0·2 kcal mol^{-1}, and an entropy of activation of −20·7 ± 0·5 cal K^{-1} mol^{-1}.

An analysis of the kinetic data obtained, in acetonitrile at 25·0 °C, for the reactions of a series of silver arenesulphonates with methyl iodide is presented as an example of the use of the results from this study. The silver salts will be only partially dissociated within the concentration range (0·005—0·16M) used and complications due to differences in the degree of dissociation were avoided by extrapolation

TABLE 2. The 2½-order rate coefficients[a], $k_{5/2}$ h, for the reaction of a series of silver arenesulphonates ($XC_6H_4SO_3^-Ag^+$) with methyl iodide in acetonitrile at 25·0 °C and, for each concentration, the associated Hammett ρ value

Arene substituent X	$10^3k_{5/2}$/mol$^{-3/2}$ s^{-1} for series of [$AgOSO_2Ar$].					
	0·16M	0·08M	0·04M	0·02M	0·01M	0·005M
p-MeO	1·515	1·304	1·170	1·066	1·019	0·829
p-Me	1·290	1·079	0·995	0·913	0·869	0·765
H	0·950	0·819	0·719	0·654	0·608	0·568
p-F	0·640	0·538	0·466	0·417	0·386	0·342
p-Cl	0·511	0·408	0·357	0·320	0·288	0·257
p-Br	0·474	0·394	0·356	0·316	0·288	0·249
p-NO_2	0·162	0·131	0·111	0·099	0·084	0·073
m-NO_2	0·157	0·128	0·112	0·099	0·083	0·073
ρ Values[b]	−0·976	−0·999	−1·021	−1·033	−1·087	−1·085
r[c]	0·994	0·994	0·994	0·994	0·994	0·992

[a] Each value is average of several determinations; standard deviations, determined for each run, usually within range of 1 to 6% of value. [b] Using σ values of ref. 2; standard deviations of 0·041, 0·043, 0·042, 0·045, 0·046, and 0·053, respectively. [c] Correlation coefficient.

of the data to very low concentrations. The observed kinetics were close to the 2½-order previously observed for reaction of silver nitrate with a wide variety of organic halides.[8]

Values for the 2½-order rate coefficients, measured at six concentrations, are given in Table 2. For each concentration, using Hammett σ values from the literature,[2] Hammett ρ values were calculated. At low concentrations, a limiting value of −1·09 ± 0·05 was obtained. This value is essentially the same as that obtained at 25·0 °C for the reaction of tetra-n-butylammonium salts with methyl trifluoromethanesulphonate (−1·06 ± 0·06). The reported standard deviations arise from systematic rather than random effects and the correlation is best seen from a direct logarithmic plot of the respective second-order and 2½-order (at 0·005M) rate coefficients; the slope of this plot is 0·980 ± 0·019, with a correlation coefficient of 0·9989. This correlation indicates that the decrease in charge at the transition state within the arenesulphonate anion, and hence the degree of bonding to the methyl carbon, is virtually identical for attack upon either a methyl iodide-silver ion complex or a methyl trifluoromethanesulphonate molecule. If the latter is considered as a S_N2 reaction, then the former should be formulated as a S_N2Ag^+ reaction. Further, it appears that I^-Ag^+ and $SO_3CF_3^-$ are equally nucleofugic or, alternatively, the degree of bonding to a given nucleophile is independent of the nature of the leaving group.[9]

(*Received*, 9*th April* 1976; *Com.* 388.)

[1] R. L. Hansen, *J. Org. Chem.*, 1965, **30**, 4322.
[2] H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.
[3] R. E. Robertson, *Canad. J. Chem.*, 1953, **31**, 589; D. N. Kevill, K. C. Kolwyck, D. M. Shold, and C. B. Kim, *J. Amer. Chem. Soc.*, 1973, **95**, 6022.
[4] J. M. Scott, *Canad. J. Chem.*, 1970, **48**, 3807; J. Koskikallio, *Acta Chem. Scand.*, 1972, **26**, 1201.
[5] M. H. Abraham, *J.C.S. Chem. Comm.*, 1973, 51.
[6] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.
[7] R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, 1966, **88**, 2594; D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4821.
[8] D. N. Kevill and L. Held, *J. Org. Chem.*, 1973, **38**, 4445.
[9] For a recent discussion, see C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755.