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The Hammett equation applied to the nucleophilic displacement of ions and ion pairs on substituted benzenesulphonates

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epoc ABSTRACT: Nucleophilic substitution on *meta-* and *para*-substituted methyl benzenesulphonates was studied with two chloride salts with different structures: NBu_4Cl or KCl-Kryptofix 2,2,2. Treating the results with the Acree equation shows that the reaction proceeds by two reaction paths, one involving the chloride ion and the other, slower one, involving the ion pairs. Treating the results with the Hammett equation gives consistent data, and shows that ρ is positive and nearly the same for the two reaction paths ($\rho \approx +2$). The reactivity of methyl *p*-nitrobenzenesulphonate was compared with that of the corresponding ethyl derivative, and it is shown that the methyl derivative reacts faster than the ethyl derivative in both paths. The results are interpreted based on the assumption that in both paths a negative charge is developed on the leaving group in the transition state, and that the activated complex is linear. Copyright © 2001 John Wiley and Sons, Ltd.
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KEYWORDS: Hammett equation; ions; ion pairs; nucleophilic displacement

INTRODUCTION

The importance of ion pairs in chemistry is well known.[1] Several properties of a process, such as reactivity and stereochemistry, can depend on the reacting species, ion or ion pair.[1] Studies to estimate the relative reactivities of free ions and ion pairs have been reported in the literature and the data were treated with the classical Acree equation.[2] Recently, we studied the reactivity of ions and ion pairs in CH_2Cl_2 on a classical organic substrate (methyl *p*-nitrobenzenesulphonate) by applying the Acree equation. We used a series of chloride salts with different requirements, and found that the ion reactivity was always the same, and that the reactivity of the ion pairs was lower than that of the ion and variable as a function of the dissociation constants of the salts.[3] We also studied the reactivity of ions and ion pairs on an organometallic substrate,[4] obtaining similar results. The aim of this research was to study how the reactivity of ions and ion pairs varies upon changing the substituents in the aromatic ring, determine if there is a Hammett correlation and if the ρ value is different or similar for ions and ion pairs. Moreover, we checked how the reactivity is influenced when an ethyl group is substituted for the methyl group of the substrate.

RESULTS AND DISCUSSION

Pseudo-first-order rate costants (k_{obs}) were measured for the nucleophilic substitution reactions on methyl *para-* or *meta*-substituted benzenesulfonates induced by tetrabutylammonium chloride or KCl-Kryptofix 2,2,2 (KCl-Krypto) salts at 22 °C in CH_2Cl_2; the nucleophile can be both the free ion (Cl^-) and the ion pair (A^+Cl^-). We used the solvent dichloromethane, as in previous studies,[3,4] owing to its very low permittivity ($\varepsilon = 9.08$),[5] low donor number ($DN = 2$) and good acceptor number ($AN = 20.04$).[6] We chose Bu_4NCl because it has a very low interionic distance[7] with partial interpenetration between the ions[8] and KCl-Krypto because the distance between K^+ and Cl^- is fairly high. Their dissociation constants are 1.6×10^{-5} and 26.1×10^{-5} mol dm^{-3}, respectively, at 22 °C.[9] In one case bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) was used ($K_{DISS} = 34.1 \times 10^{-5}$ mol dm^{-3}); it has a large interionic distance (11.3 Å) because some solvent molecules are interposed between the ions.[7] The substituents used were *p*-CH_3 (**1**), *m*-NO_2 (**2**), *p*-H (**3**), *p*-Cl (**4**) and *p*-Br (**5**), and the data for *p*-NO_2 were available from previous work.[3] The processes involving competition between nucleophiles ions and ion pairs are shown in Scheme **1**.

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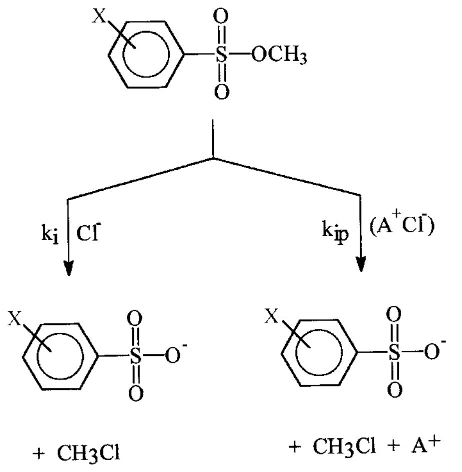

X = p-CH_3, p-H, p-Cl, p-Br, m-NO_2, p-NO_2

Scheme 1. Nucleophilic substitution reaction paths for alkyl benzenesulphonates induced by the free chloride (Cl^-) or the ion pair (A^+Cl^-)

Kinetics with the *m*-NO_2 derivative were followed by monitoring the increase in absorbance at $\lambda = 280$ nm, while the decrease of absorbance was followed in all the other substrates at $\lambda = 266$ nm. In every case, good pseudo-first-order plots were obtained. It should be considered that the dissociation constants (K_{DISS}) are measured at low concentration (10^{-5}–10^{-4} mol dm^{-3}), while the kinetic studies are carried out at higher concentrations (10^{-3}–10^{-2} mol dm^{-3}). In order to evaluate the ion and ion pair activities, the degree of dissociation of the salt (α) and the activity coefficients ($f_\pm$) of the free ion were calculated by the method of successive approximations using the Debye-Hückel equation.[10] In this treatment the activity coefficient of the ion pairs is taken equal to one, owing to their neutral nature.

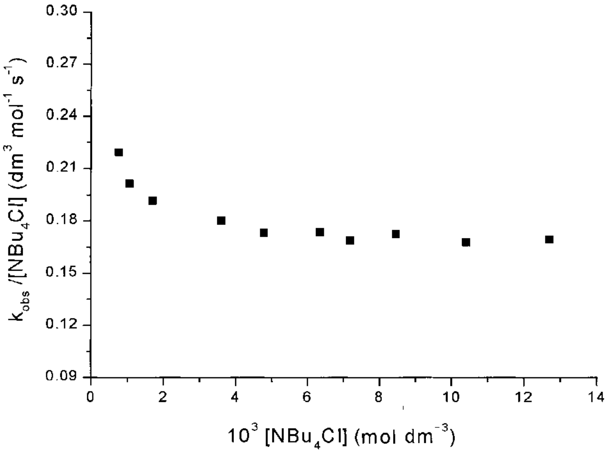

Figure 1. Plot of k_{obs}/[NBu$_4$Cl] versus [NBu$_4$Cl] for the reaction with methyl *m*-nitrobenzenesulphonate

Table 1. Observed first-order rate constants of methyl *m*-nitrobenzenesulphonate with NBu$_4$Cl in CH_2Cl_2 at 22 °C

[NBu$_4$Cl] (10^{-3} mol dm^{-3})	α	$f_\pm$	k_{obs}(10^{-3} s^{-1})
12.7	0.078	0.431	2.15
10.4	0.082	0.456	1.74
8.45	0.086	0.481	1.46
7.18	0.089	0.500	1.21
6.34	0.092	0.514	1.10
4.78	0.100	0.545	0.829
3.59	0.109	0.575	0.647
1.69	0.139	0.646	0.324
1.06	0.163	0.685	0.213
0.761	0.183	0.710	0.167

We observed a decrease in the k_{obs}/[salt] versus [salt] plots (see Fig. 1); this is an indication that the reaction proceeds through two parallel paths involving both the free ions and the ion pairs, as shown in Scheme 1. As an example, in Fig. 1 is reported this plot for the reaction of methyl *m*-nitrobenzenesulphonate with NBu$_4$Cl.

The data were then treated with the Acree equation,[2]

$$k_{obs} = k_i[\text{ion}] + k_{ip}[\text{ion pair}] \qquad (1)$$

$$k_{obs}/c\alpha f_\pm = k_i + k_{ip}(1-\alpha)/\alpha f_\pm \qquad (2)$$

where α is the degree of dissociation, $f_\pm$ is the activity coefficient, evaluated as reported previously,[3,4] and c is the total concentration of the salt. A plot of $k_{obs}/c\alpha f_\pm$ versus $(1-\alpha)/\alpha f_\pm$ is expected to give a straight line, with intercept k_i and slope k_{ip}. The contribution of the free ion to the total reactivity is small; nevertheless, the consistency of the data obtained for three salts both in this paper and in the preceding one[3] confirms the significance of the data. The k_{obs} values for the various substrates are given as supplementary material at the epoc website at http://www.wiley.com/epoc. Tables 1 and 2 report the data with X = *m*-NO_2 (**2**), as an example, and the related Acree plots are shown in Figs 2 and 3.

Table 2. Observed first-order rate constants of methyl *m*-nitrobenzenesulphonate with KCl-Krypto in CH_2Cl_2 at 22 °C

[KCl] (10^{-3} mol dm^{-3})	α	$f_\pm$	k_{obs}(10^{-3} s^{-1})
17.8	0.524	0.160	6.78
15.1	0.518	0.176	5.87
12.0	0.513	0.201	4.87
8.88	0.509	0.236	3.64
6.22	0.511	0.280	2.60
3.56	0.527	0.353	1.57
2.67	0.541	0.391	1.07
1.78	0.567	0.445	0.815
0.889	0.623	0.534	0.414

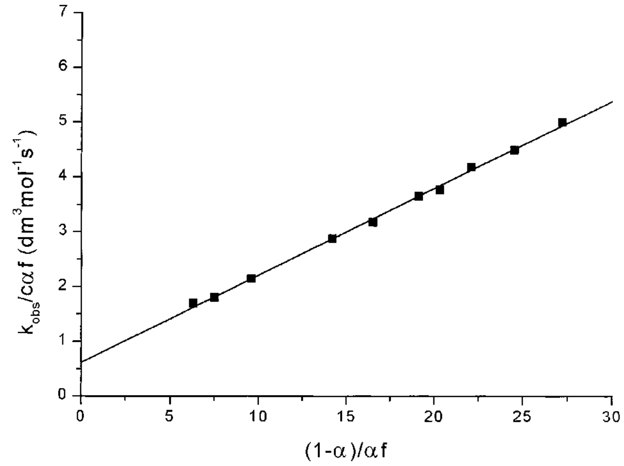

Figure 2. Using the Acree equation [Eqn. (2)] to determine k_i and k_{ip} for the substrate (**2**) with the salt NBu_4Cl

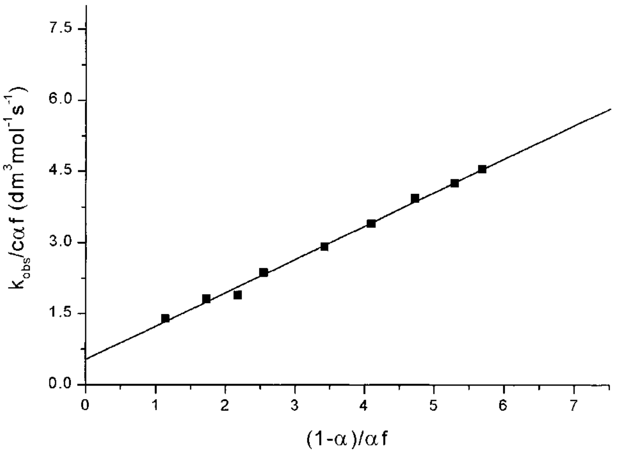

Figure 3. Using the Acree equation [Eqn. (2)] to determine k_i and k_{ip} for the substrate (**2**) with the salt KCl-Krypto

Table 3 and Table 4 report the rate constants obtained from the Acree equation for all the substrates with NBu_4Cl and KCl-Krypto, respectively.

From the data of Tables 3 and 4, it can be seen that the rate constants for the ion, k_i, obtained with the two salts are in good agreement, taking into account that such data are not very precise since they are obtained from the small value of the intercept of the straight line. We also applied the Acree equation to the m-NO_2 derivative (**2**) with bis(triphenylphosphoranylidene)ammonium chloride (PPNCl)[7] and obtained consistent $k_i = 0.52$ (0.06) $dm^3\ mol^{-1}\ s^{-1}$ and $k_{ip} = 0.63$ (0.02) $dm^3\ mol^{-1}\ s^{-1}$ values. The data in Table 3 and Table 4 show that with NBu_4Cl the reactivity of the free Cl^-, k_i, is always larger than that of the ion pair, k_{ip}; this can be explained by the lower nucleophilicity of the ion pair with respect to the

Table 3. Calculated values of k_i and k_{ip} for the reaction of methyl-substituted benzenesulphonates with NBu_4Cl in CH_2Cl_2 at 22 °C (the dissociation constant of NBu_4Cl in CH_2Cl_2 is 1.58×10^{-5} mol dm^{-3} at 22 °C)

X	k_i[a]($dm^3\ mol^{-1}\ s^{-1}$)	k_{ip}[a]($dm^3 mol^{-1}\ s^{-1}$)	σ[b]	r[c]
p-NO_2[d]	1.07 (0.07)	0.12 (0.003)	+0.78	0.998
m-NO_2	0.62 (0.04)	0.159 (0.002)	+0.74	0.999
p-Br	0.072 (0.033)	0.0167 (0.0011)	+0.22	0.978
p-Cl	0.083 (0.034)	0.0137 (0.0012)	+0.22	0.965
p-H	0.018 (0.006)	0.0053 (0.0002)	0	0.994
p-CH_3	0.011 (0.008)	0.0027 (0.0003)	−0.16	0.936

[a] Standard deviations in parentheses.
[b] Substituent constant from Ref. 11.
[c] Correlation coefficient for the Acree plot.
[d] From Ref. 3.

Table 4. Calculated values of k_i and k_{ip} for the reaction of methyl-substituted benzenesulphonates with KCl-Krypto in CH_2Cl_2 at 22 °C. (the dissociation constant of KCl-Krypto in CH_2Cl_2 is 26.1×10^{-5} mol dm^{-3} at 22 °C.)

X	k_i[a]($dm^3\ mol^{-1}\ s^{-1}$)	k_{ip}[a]($dm^3\ mol^{-1}\ s^{-1}$)	σ[b]	r[c]
p-NO_2[d]	0.98 (0.12)	0.52 (0.03)	+0.78	0.982
m-NO_2	0.54 (0.06)	0.70 (0.02)	+0.74	0.998
p-Br	0.065 (0.020)	0.059 (0.005)	+0.22	0.970
p-Cl	0.071 (0.025)	0.049 (0.006)	+0.22	0.934
p-H	0.016 (0.004)	0.0179 (0.0008)	0	0.990
p-CH_3	0.010 (0.002)	0.0068 (0.0004)	−0.16	0.983

[a] Standard deviations in parentheses.
[b] Substituent constant from Ref. 11.
[c] Correlation coefficient for the Acree plot.
[d] From Ref. 3.

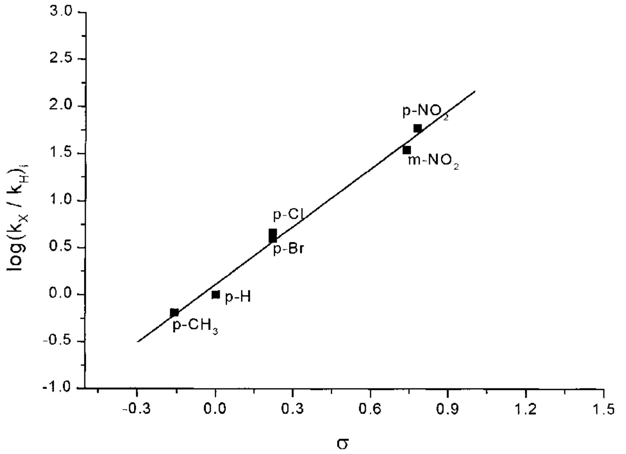

Figure 4. Hammett equation [Eqn. (3)] for the ion rate constants, k_i, with NBu_4Cl

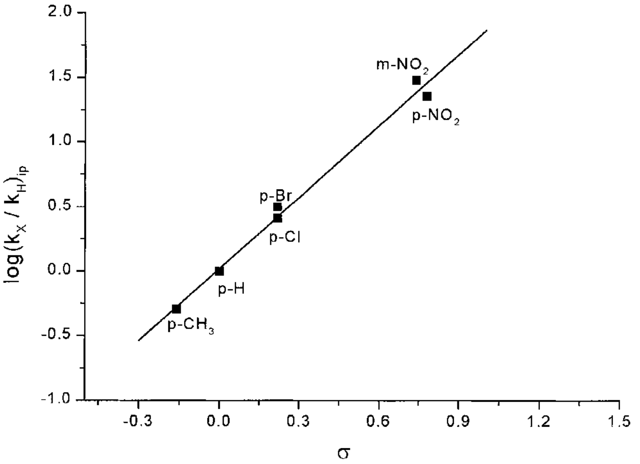

Figure 5. Hammett equation [Eqn. (3)] for the ion pair rate constants, k_{ip}, with NBu_4Cl

free ion, due to the bond strength between the ion and the counterion, which are very close to each other, as previously discussed.[3]

With KCl-Krypto, k_i is similar to that found with NBu_4Cl and the reactivities of free Cl^- and the ion pair are similar to each other: this is due to the weakness of the bond of the ion pair in this system. In fact, the distance between the ion and the counterion is larger than in NBu_4Cl. Comparison between the k_{ip} values of the two salts shows that the rate constant for the KCl-Krypto ion pair is always larger than that of the NBu_4Cl ion pair; this result can also be explained by the different bond strengths between the ion and the counterion.

Application of the Hammett equation[11] [Eqn. (3)] to the data in Table 3 and Table 4, i.e.

$$\log(k_X/k_H) = \rho\sigma \tag{3}$$

gives information about the structure of the transition state for the process involving either the ion or the ion pair. The Hammett plots for the free ion and the ion pair with NBu_4Cl are shown in Figs 4 and 5, respectively.

Good correlations were also obtained with the KCl-Krypto system. The Hammett constants are reported in Table 5, which shows that the ρ values are positive (ca +2). This is in agreement with the development of a negative charge on the leaving group in the transition state of the nucleophilic substitution reaction. Very similar ρ values were obtained for the free ion and ion pair in both salts. This is evidence that the two processes are very similar and, even though the cation in the ion pair influences the rate, it does not influence the distribution of the charge developed in in the leaving group in the transition state.

To our knowledge, only one group has studied the influence of some *para* and *meta* substituents on the rate constants k_i and k_{ip}.[2b] Cayzergues *et al.*[2b] studied the nucleophilic substitution of some benzylic chlorides with EtO^-Na^+ in EtOH and applied the Hammett equation to it. They only examined four substrates and one (the unsubstituted one) deviated from linearity. They found two different mechanistic pathways with different ρ values: +2.2 for the free ion and −0.6 for the ion pair, but they did not explain this fact. However, it has to be considered that their system is different; in fact, the effect of the substituents is on the benzylic carbon atom, whereas in our case the effect of the substituents is on the leaving group.

Another relevant paper is that of Lee *et al.*,[12] who studied the reaction of substituted benzenesulphonates with anilines, and they also found a positive ρ value of about +1 in CH_3OH and CH_3CN. This result compares well with our results. Moreover, they found that 'the S_N2 reactions of ethyl derivatives occur 10–30 times less readily than those of methyl compounds', and attributed this fact to the bulkiness of the reaction centre, in agreement with our results (see below).

Reaction of ethyl *p*-nitrobenzenesulphonate (6) with NBu_4Cl or KCl-Krypto salts

In order to obtain some information about the steric effects of the ion or ion pair nucleophile, the k_i and k_{ip} values for ethyl *p*-nitrobenzenesulphonate (**6**) with NBu_4Cl or KCl-Krypto were determined (Table 6).

Table 5. Hammett ρ values for ions and ion pairs

Salt	ρ (ion)[a]	ρ(ion pair)[a]	r^b	r^c
NBu_4Cl	+2.05(0.11)	+1.85(0.09)	0.993	0.995
KCl-Krypto	+2.06(0.11)	+2.06(0.11)	0.994	0.994

[a] Standard deviations in parentheses.
[b] Correlation coefficient of the Hammett plot for the ion.
[c] Correlation coefficient of the Hammett plot for the ion pair.

Table 6. Rate constants, k_i and k_{ip}, for methyl and ethyl *p*-nitrobenzenesulphonates

Salt	k_i[a] ($dm^3\ mol^{-1}\ s^{-1}$)	k_{ip}[a] ($dm^3\ mol^{-1}\ s^{-1}$)	*R*
NBu_4Cl[b]	1.07 (0.07)	0.12 (0.003)	CH_3
KCl-Krypto[b]	0.98 (0.07)	0.52 (0.03)	CH_3
NBu_4Cl	0.021 (0.002)	0.00624 (0.00012)	CH_2CH_3
KCl-Krypto	0.023 (0.008)	0.027 (0.002)	CH_2CH_3

[a] Standard deviations in parentheses.
[b] Data from Ref. 3.

It can be seen that there is good agreement between the reactivity of the ion, k_i, determined with the two salt solutions (0.021 vs 0.023 $dm^3\ mol^{-1}\ s^{-1}$). The reactivity of the ion pair, k_{ip}, with KCl-Krypto is higher than that obtained with NBu_4Cl, in agreement with the data for the methyl derivatives. The average $k_i(CH_3)/k_i(CH_2CH_3)$ ratio is 48. The $k_{ip}(CH_3)/k_{ip}(CH_2CH_3)$ ratio is 19.3 for both salts. Steric effects in the S_N2 process are relevant for both ions and ion pairs . However, the steric hindrance of the ethyl group as compared with the methyl group is higher for the ion than for the ion pair. An explanation of this fact can be that the ion approaches the centre of the nucleophilic attack more than the ion pair, and so it is more influenced by the bulkiness of the alkyl group. Moreover, the fact that the k_{ip} ratio is the same for both salts can be attributed to the fact that the activated complex is linear and that the influence of the cation on it is very low.

If we compare our results with the theoretical results obtained by Streitwieser[13] for the reaction of alkyl chlorides with chlorides, it can be seen that in his case the ions react faster than the ion pairs and that in the ion pair path the bulkier alkyl groups react faster than the smaller groups. He interpreted these results by saying that the activated complex for the ion pair is cyclic and influenced by the bulkiness of the reacting substrates. The differences between our experimental results and the theoretical studies by Streitwieser can be explained considering that our processes occur in solution and solvation energies play a role. Moreover, the large difference in the structure and size of our ion pairs can favour the conditions for a linear transition state.

EXPERIMENTAL

Materials. The solvent and salts were purified as described previously.[3] Methyl *p*-methylbenzenesulphonate (**1**) was a commercial product (Aldrich). All the other substituted benzenesulphonate derivatives were synthesized from the corresponding benzenesulphonyl chloride (commercial) by a common procedure which is described here for methyl *m*-nitrobenzenesulphonate (**2**).

Methyl m-nitrobenzenesulphonate (2). *m*-Nitrobenzenesulphonyl chloride, 2.4 g (11.5 mmol), was added in small aliquots to a stirred solution of 1.6 ml (11.5 mmol) of triethylammine in 100 ml of CH_3OH at 0 °C. The solution was left with stirring for 2 h at room temperature. The solvent was then removed by rotary evaporation and H_2O and Et_2O were added to the solid residue. The ether phase was washed with water up to neutrality. Evaporation of the Et_2O gave a yellow solid. Recrystallizing twice with Et_2O–*n*-hexane at 0 °C yielded the sulphonate (1.06 g, 42%), purity by vapour-phase chromatography (VPC) always >99%, m.p. 87–89 °C. Found: C, 38.87; H, 3.26; N, 6.94. $C_7H_7NO_5S$ requires C, 38.71; H, 3.25; N, 6.45%. NMR: δ_H (200 MHz, $CDCl_3$) 3.8 (3 H, s, Me), 7.8 (1 H, t), 8.23–8.27 (1 H, m) 8.51–8.52 (1 H, m), 8.76–8.78 (1 H, m). MS: *m/z* 217 (M^+, 100%), 186 (34), 171 (68), 123 (88), 75 (84), 50 (83).

*Methyl benzenesulphonate (**3**).* VPC always showed purity >99%. Found: C, 48.82; H, 4.66. $C_7H_8O_3S$ requires C, 48.83; H 4.68%. NMR: δ_H(200 MHz; $CDCl_3$) 3.8 (3 H, s, Me), 7.5–7.95 (5 H, m, Ph).

Methyl p-chlorobenzenesulphonate (4). VPC always showed purity >99%; m.p. 51–52 °C. Found: C, 40.73; H, 3.5. $C_7H_7ClO_3S$ requires C, 40.69; H, 3.41%. NMR:δ_H(200 MHz; $CDCl_3$) 3.8 (3 H, s, Me), 7.51–7.89 (4 H, AaBb system, m, Ar).

Methyl p-bromobenzenesulphonate (5). VPC always showed purity >99%; m.p. 59– 60 °C. Found: C, 33.51; H, 2.73. $C_7H_7BrO_3S$ requires C, 33.48; H, 2.81%. NMR:δ_H(200 MHz; $CDCl_3$) 3.8 (3 H, s, Me), 7.68–7.80 (4 H, AaBb system, m, Ar).

Ethyl p-nitrobenzenesulphonate (6). M.p. 89–91 °C. Found: C, 41.35; H, 4.06; N, 6.01. $C_8H_9NO_5S$ requires C, 41.56; H, 3.92; N, 6.06%. NMR: δ_H (200 MHz; $CDCl_3$) 1.4 (3 H, t, Me), 4.25 (2 H, q, CH_2), 8.1–8.5 (4 H, AaBb system, m, Ar).

Kinetic measurements. All kinetic measurements were carried out on a Kontron Uvikon 923 double-beam spectrophotometer. The path length of the quartz cell was 1 cm. The reaction was started by adding with a microsyringe the appropriate amount of substrate solution to the thermostatted salt solution in the cuvette. The rate constants (k_{obs}/s^{-1}) were determined for Bu_4NCl or KCl-Krypto solutions by following the decrease in absorbance at 266 nm due to the disappearance of the reagent with *p*-CH_3 (**1**), *p*-H (**3**), *p*-Cl (**4**) and *p*-Br benzenesulphonate (**5**); with methyl *m*-nitrobenzenesulphonate (**2**) and ethyl *p*-nitrobenzenesulphonate (**6**) the increase in absorbance due to the formation of the *m*- or *p*-nitrobenzenesulphonate anion product was monitored at 280 nm. For the reaction of methyl *m*-nitrobenzenesulphonate (**2**) with PPNCl the increase in absorbance was followed at 290 nm.

The classical equation $\ln [(A_{\infty}-A_0)/(A_{\infty}-A_t)] = k_{obs}t$ or $\ln [(A_0-A_{\infty})/(A_t-A_{\infty})] = k_{obs}t$ was used. Linearity was observed up to 80% of the reaction. Duplicate runs showed that the reproducibility was within 6%. To obtain a pseudo-first-order condition, there was always an excess of salt (at least 10-fold). Most of the reactions were followed to completion. The slower reactions were followed up to ≈70% and the A_{∞} value was calculated from the data for the faster reactions. The same final absorbance value was obtained even with different excesses of nucleophile, which shows that the reactions are not an equilibrium but go to completion. Blank experiments showed that the substrates and salts were stable under the kinetic experiment conditions.

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