Reactivity of ions and ion pairs in the nucleophilic substitution reaction on methyl *p*-nitrobenzenesulfonate

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Nucleophilic substitution on methyl *p*-nitrobenzenesulfonate has been studied with a series of chloride salts with different structures and solvations: Bu_4NCl, PPNCl or KCl complexed by 18-crown-6 or Kryptofix 2,2,2 as well as with a bromide salt (PPNBr) for comparison purposes. The rate constants and the activation parameters are in accordance with an S_N2 mechanism. The treatment of the data, following the Acree equation, shows that the process takes place by way of two reaction paths: the first, due to the chloride ion, has the same rate for all the salts, while the second slower path, involving the ion pair, has a rate related to the dissociation constant of the salts.

The importance of ion pairs in chemistry is well recognized.[1] Depending on the reacting species, free ions or ion pairs, several properties of a process are affected, such as reactivity, selectivity and stereoselectivity. To check the relative reactivity of ions and ion pairs, we studied the nucleophilic substitution reaction on a common substrate,[2] methyl *p*-nitrobenzenesulfonate (**1**) in CH_2Cl_2 with a series of salts with the same anion, but with cations differing in structure and solvation, in order to assess the kinetic behaviour of a series of ion pairs. Studies to assess the relative reactivities of free ions and ion pairs in S_N2 reactions have been reported in the literature,[3] but, to our knowledge, no systematic analysis of the reactivity of ion pairs with different structures is available.

The salts we used were tetrabutylammonium chloride, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), KCl–18-crown-6 (KCl–crown) or KCl–Kryptofix 2,2,2 (KCl–Krypto). In order to compare the reactivity of a different anion, PPNBr was also used. The kinetic data were treated with the classical Acree equation.[4]

Results and discussion

Pseudo-first-order rate constants (k_{obs}/s^{-1}) were measured for the nucleophilic substitution reactions on methyl *p*-nitrobenzenesulfonate induced by various chloride salts, in which the nucleophile can be both the free ion (Cl^-) and the ion pair (A^+Cl^-), at 22 °C in CH_2Cl_2. The relative data are reported in Tables 1–4.

The persistence of isosbestic points at 266 nm for two to three half lives suggests that no intermediates of spectrally significant concentration accumulated under these conditions. The process is shown in Scheme 1.

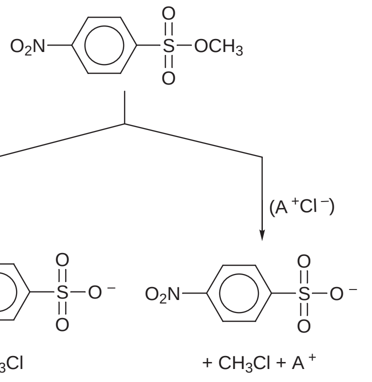
All the reactions were followed in dichloromethane, a very good solvent for organic and organometallic compounds because of its very low permittivity ($\varepsilon = 9.08$),[5] very low donor number (DN = 2) and good acceptor number (AN = 20.4).[6] While alkali halides and Me_4NCl are insoluble in this solvent, salts with large aliphatic or aromatic cations are soluble, but a large fraction will exist as ion pairs.[7,8]

Of the four salts used as a source of chloride, Bu_4NCl was chosen because it is a simple aliphatic salt whose interionic distance (*ca.* 4.9 Å) is smaller than the Stokes radius (*ca.* 5.6 Å)[9] and is supposed to form tight ion pairs with a partial compenetration of the anion between the aliphatic chains.[10] The dissociation constants are 1.6 (±0.2) × 10^{-5}, 1.7 (±0.9) × 10^{-5} and

Table 1 Observed first order rate constants for Bu_4NCl in CH_2Cl_2 at 22 °C, unless otherwise stated

$[Bu_4NCl]/10^{-3}$ M	α	$f_\pm$	$k_{obs}/10^{-3}\ s^{-1}$
0.83	0.178	0.703	0.19
2.90	0.116	0.596	0.54
3.97	0.106	0.565	0.66
5.80	0.095	0.524	0.97
6.54	0.092	0.511	1.097
7.53	0.088	0.495	1.10
10.2	0.082	0.459	1.51
11.6	0.080	0.443	1.75
21.5	0.072	0.362	3.03
41.8	0.070	0.269	5.50
2.11[a]	0.135	0.620	0.16
4.67[a]	0.106	0.541	0.29
7.00[a]	0.095	0.495	0.38
12.7[a]	0.083	0.423	0.71
19.8[a]	0.077	0.364	0.95
28.1[a]	0.075	0.316	1.49
35.0[a]	0.075	0.284	1.59
42.2[a]	0.075	0.257	2.05
2.11[b]	0.169	0.588	0.61
4.22[b]	0.139	0.514	0.95
7.00[b]	0.123	0.454	1.13
12.7[b]	0.111	0.378	1.72
14.00[b]	0.110	0.364	2.14
19.80[b]	0.106	0.316	2.78
28.10[b]	0.106	0.265	4.04
35.00[b]	0.108	0.233	4.59
42.20[b]	0.111	0.206	5.10

[a] At 12 °C. [b] At 1 °C.



Scheme 1 Nucleophilic substitution reaction paths for methyl *p*-nitrobenzenesulfonate induced by the free chloride ion (Cl^-) or the ion pair (A^+Cl^-)

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Table 2 Observed first order rate constants for PPNCl in CH_2Cl_2 at 22 °C

[PPNCl]/10^{-3} M	a	$f_{\pm}$	$k_{obs}/10^{-3}$ s^{-1}
0.30	0.767	0.672	0.16
0.30	0.767	0.672	0.16
0.59	0.695	0.601	0.38
0.65	0.686	0.592	0.38
0.89	0.654	0.558	0.60
1.28	0.617	0.518	0.70
3.18	0.533	0.420	1.56
3.18	0.533	0.420	1.52
6.37	0.478	0.349	2.72
6.47	0.477	0.348	2.92
7.03	0.471	0.340	2.90
8.80	0.455	0.319	4.10
9.42	0.451	0.313	3.87
11.67	0.436	0.294	4.77
14.90	0.421	0.274	6.07
17.80	0.409	0.260	7.59

Table 3 Observed first order rate constants for KCl–crown[a] in CH_2Cl_2 at 22 °C

[KCl]/10^{-3} M	a	$f_{\pm}$	$k_{obs}/10^{-3}$ s^{-1}
1.46	0.163	0.637	0.21
1.62	0.157	0.627	0.21
3.07	0.129	0.562	0.36
4.04	0.120	0.531	0.49
4.09	0.120	0.530	0.49
4.47	0.117	0.520	0.56
7.20	0.105	0.460	0.76
7.30	0.105	0.458	0.83
8.07	0.103	0.445	0.92
12.00	0.096	0.389	1.25
13.40	0.095	0.373	1.38
13.80	0.095	0.368	1.51
15.40	0.094	0.351	1.59
16.00	0.094	0.345	1.58
20.20	0.094	0.308	1.84
22.00	0.094	0.294	1.95
22.67	0.095	0.289	1.98
28.00	0.097	0.253	2.50
30.40	0.099	0.238	2.53
30.80	0.099	0.236	2.86

[a] The ratio crown : KCl was 1.7/1, see Experimental section.

Table 4 Observed first order rate constants for KCl–Krypto[a] in CH_2Cl_2 at 22 °C

[KCl]/10^{-3} M	a	$f_{\pm}$	$k_{obs}/10^{-3}$ s^{-1}
0.36	0.713	0.641	0.21
0.37	0.711	0.639	0.20
0.72	0.643	0.560	0.33
1.11	0.603	0.506	0.61
3.72	0.526	0.347	1.67
5.21	0.515	0.303	2.15
5.55	0.513	0.295	2.45
7.47	0.509	0.257	2.80
11.1	0.511	0.210	4.39
14.9	0.518	0.178	4.81
22.4	0.533	0.138	6.69

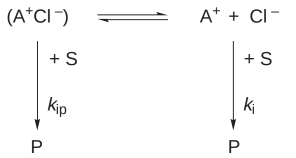
[a] The ratio Krypto : KCl was 1.7/1, see Experimental section.

2.5 (±0.5) × 10^{-5} M at 22, 12 and 1 °C respectively. The corresponding thermodynamic parameters ($\Delta H_0 = 14.9 \pm 3.9$ kJ mol^{-1} and $\Delta S_0 = 142.7 \pm 14.0$ J mol^{-1} K^{-1}) are similar to those determined by Song and Trogler.[11] The low enthalpic factor and the high negative entropy are in accord with a substantial intervention of CH_2Cl_2 in solvating the separated ions. In PPNCl, the cation has two structures, one linear and the other bent, with the positive charge being delocalized on nitrogen, on phosphorus and on the aromatic rings.[12] In CH_2Cl_2 the interionic distance is great (11.3 Å),[9] so that the salt is supposed to form solvent-separated ion pairs. Some authors claim that the salt is 'highly dissociated';[13] but they did not report the dissociation constant; we measured it and found $K_{diss} = 34.1 \times 10^{-5}$ M, which corresponds to a degree of dissociation of about 0.40 at a concentration of 0.01 M. Thus this salt, too, gives both ions and ion pairs.

The adduct KCl–18-crown-6 was used on the assumption that the anion, in the presence of the crown ether, is 'naked' and unencumbered by strong solvation forces, and is therefore very reactive.[14] Even though the potassium is surrounded by the receptor, it is still accessible from above and below the crown ether plane.[4d,15] It is then tightly connected to the chloride anion with a very short interionic distance (even shorter than in crystalline KBr);[16] the dissociation constant is rather low (1.87×10^{-5} M). Consequently, in this case too, the salt is mainly in the form of tight ion pairs. With the hope of obtaining a naked anion, the Kryptofix 2,2,2 was used, because it surrounds the potassium ion with two cycles (like a football),[17] which should leave the anion completely free. In fact, the distance between K^+ and Cl^- is rather high (*ca.* 6.5 Å)[1f,4d,18,19] but they still form ion pairs with a dissociation constant of 26.1×10^{-5} M.

A problem arising with such salts in low permittivity solvents is that the dissociation constants (K_{diss}) are measured at low concentration (10^{-5}–10^{-4} M), while the kinetics are carried out at higher concentrations (10^{-3}–10^{-2} M). To obtain an accurate value of the ion and ion pair activities, the degree of dissociation of the salt (alpha) and the activity coefficients ($f_{\pm}$) of the free ion were calculated at each concentration by the method of successive approximations using the extended Debye Huckel expression.[20] This treatment assumes that the activity coefficient of the ion pairs is equal to one, owing to its neutral nature.

Since we observed a decrease in the k_{obs}/[salt] *versus* [salt] plot, we assumed that the reaction takes place through two different paths: one due to the free ion and the other due to the ion pair (Scheme 2). So, the kinetic data were treated following the Acree equation [eqn. (1)].[4] We chose to use the equation in the



Scheme 2 Representation of reaction paths, one due to free ion at rate k_i, the other due to the ion pair at rate k_{ip}

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

form shown in eqn. (2), where c is the total salt concentration,

$$k_{obs}/caf_{\pm} = k_i + k_{ip}(1 - a)/af_{\pm} \qquad (2)$$

a is the dissociation degree and $f_{\pm}$ is the activity coefficient, evaluated as previously discussed.

The data for the various salts are reported in Fig. 1. The fit by linear regression analysis is very good and the four straight lines have the same intercept (within experimental error) and different slopes.

The calculated rate constants of the free ions (k_i) and of the ion pairs (k_{ip}) are reported in Table 5, together with the dissociation constants (K_{diss}) of the related salts.

From the data of Table 5 and from Fig. 1 several considerations can be made. First of all it can be seen that applying Acree's model gave consistent results: the plots of the data gave four straight lines for the four chlorides, with a common intercept and positive slopes. It follows that both the free ions and

Table 5 Second order rate constants[a] and dissociation constants in CH_2Cl_2 at 22 °C, unless otherwise stated

Salt	$k_i/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$k_{ip}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$K_{diss}/10^{-5}\ \mathrm{M}$
Bu_4NCl	1.07 (0.07)	0.12 (0.003)	1.58
KCl–crown	0.83 (0.09)	0.077 (0.004)	1.87
KCl–Krypto	0.98 (0.12)	0.52 (0.03)	26.1
PPNCl	1.04 (0.07)	0.51 (0.02)	34.1
PPNBr	0.46 (0.1)	0.42 (0.03)	25.8
Bu_4NCl[b]	0.402 (0.094)	0.043 (0.003)	1.7
Bu_4NCl[c]	0.177 (0.03)	0.009 (0.001)	2.5

[a] Standard deviations in parentheses. [b] At 12 °C. [c] At 1 °C.

Table 6 Observed first order rate constants for PPNBr in CH_2Cl_2 at 22 °C

$[PPNBr]/10^{-3}\ \mathrm{M}$	α	$f_\pm$	$k_{obs}/10^{-3}\ \mathrm{s}^{-1}$
0.48	0.663	0.642	0.14
0.58	0.641	0.623	0.19
1.10	0.568	0.561	0.36
1.22	0.556	0.551	0.49
2.75	0.472	0.471	0.91
4.45	0.428	0.426	1.41
6.60	0.394	0.390	1.99
8.35	0.375	0.370	2.63
10.00	0.361	0.355	3.56

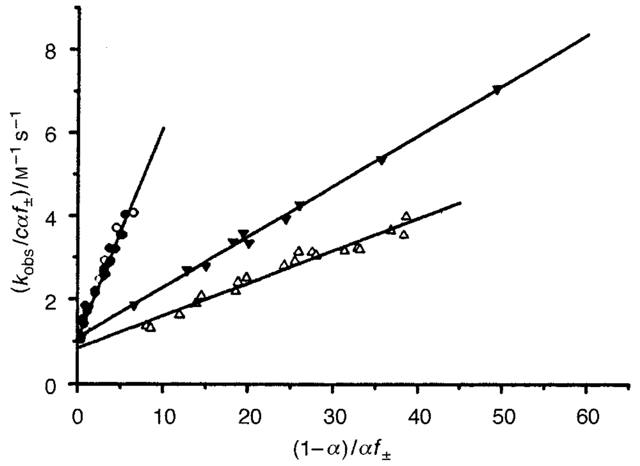


Fig. 1 Using the Acree eqn. [eqn. (2)] to determine k_i and k_{ip}. Plot of $(k_{obs}/c\alpha f_\pm)$ *vs.* $(1-\alpha)/\alpha f_\pm$, where α is the dissociation degree and $f_\pm$ is the activity coefficient. k_i is given by the intercept, k_{ip} by the slope. ●, PPNCl; ○, KCl–Krypto; ▼, Bu_4NCl; △, KCl–crown.

the ion pairs are reactive species and compete (Fig. 1) to carry out the nucleophilic substitution reaction on the sulfonate. The mechanism of the reaction is assumed to be the classical S_N2 process, as found in several other studies on similar substrates.[2] The k_i values, calculated from the intercept of the straight lines in Fig. 1, are constant (within experimental error) for all four chlorides, and the average value for the second-order rate constant for the free chloride is $k_i = 0.98 \pm 0.1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. The second-order rate constants (k_{ip}) of the ion pairs (calculated from the slopes) are different for all the salts, and always smaller than the rate constant of the free ion, but for PPNCl and KCl–Krypto it is just half the rate of the free ion. The lower reactivity of the ion pairs (k_{ip}) as compared to that of the free ion can be explained by the fact that the reacting chloride is bound to the counterion, and then the nucleophilicity of the chloride within the ion pair is lower than that of the free ion because the negative charge is partially neutralized, and because this bond must be broken during the reaction. It can be noticed that there is a substantial correlation between the dissociation constant (K_{diss}) and the rate constant (k_{ip}) (see Table 5). The effect of steric hindrance does not appear to be significant, or else it is masked by the importance of the bond between anion and cation of the ion pair. It is reasonable to think that the counterion is far from the reaction center and not interacting with it. The lower reactivity of the ion pair as compared to the free ion is reported in the literature,[3,4] but studies with a large variety of counterion are not available.

The activation parameters determined for Bu_4NCl are in agreement with an S_N2 mechanism, where association between the reactants takes place.[21] In fact, the $\Delta H^\ddagger$ for the free ion is not large (54.4 ± 2.5 kJ mol^{-1}), and smaller than that for the ion pair (79.5 ± 2.9 kJ mol^{-1}), where the dissociation between ion and counterion must be taken into account. The $\Delta S^\ddagger$ for the free ion is negative (-58.6 ± 8.4 J mol^{-1}) as in most S_N2 reactions, due to an increase of order in the activated complex. The $\Delta S^\ddagger$ (7.9 ± 10 J mol^{-1}) for the ion pair (even though more difficult to explain) can be justified because the formation of the activated complex is coupled with a partial bond breaking of the reacting salt.

The salt PPNBr was also studied in order to compare the reactivities of two salts with different anions (Br^- *vs.* Cl^-). It can be seen from Table 5 that the reactivity of free bromide is lower than that of free chloride (0.46 *vs.* 1). This is consistent with the known lower nucleophilicity of Br^- *vs.* Cl^- in solvents in which these ions are not strongly solvated.[1b,22] It can also be noticed that the rate constant of the PPNBr ion pair is similar to the one of PPNCl (see Table 5).

Experimental

Spectral grade dichloromethane (Carlo Erba) was refluxed over P_2O_5 and distilled in the dark under a dry nitrogen atmosphere immediately before use. Bu_4NCl (Fluka) was crystallised from diethyl ether–ethanol and dried under vacuum before use. PPNCl (Strem) and KCl were crystallised from boiling water and dried under vacuum at 80 °C and 120 °C, respectively. The Kryptofix 2,2,2 (Fluka) was dried under vacuum before use. The 18-crown-6 (Fluka) was crystallised from *n*-hexane and dried under vacuum. The complexed KCl was prepared by Pedersen's method[23] using methanol to solubilize the KCl and crown ether or Kryptofix 2,2,2. The conductometric measurements were performed as described in ref. 11 and 24. While some dissociation constants can be found in the literature, we measured all of those used in the experiments in order to have homogeneous data.

All kinetic measurements were made on a Beckman DU 7500 diode array spectrophotometer. The path length of the glass cell was 1 cm. The temperature was monitored with a thermocouple. The reaction was started by adding with a microsyringe the appropriate amount of substrate solution to the thermostatted salt solution in the cuvette. Rate constants, k_{obs}/s^{-1}, were determined by following the increase in absorbance at 280 nm (or at 290 for PPNCl) due to the formation of the product *p*-nitrobenzenesulfonate ion (**2**), using the classical equation $\ln[(A_\infty - A_0)/(A_\infty - A_t)] = k_{obs}t$. Linearity was observed up to 90% of the reaction. Duplicate runs showed that the reproducibility was within 5%. The sulfonate and salt concentrations were 3×10^{-5} M and $(0.3–30) \times 10^{-3}$ M respectively; to obtain a pseudo-first-order condition, there was always an excess of salt. The reactions were followed to completion. The same final absorbance was obtained even with different excesses of nucleophile, showing that the reaction is not an equilibrium but goes to completion. For each salt the quality of the isosbestic points was checked (at 266 nm). Blank experiments showed that the substrate and the salts were stable in the conditions of the kinetic experiments. The *p*-nitrobenzenesulfonate product was also shown to be stable by the constancy of the A_∞ value. In some cases, the same rate constants were also obtained by following the decrease in the absorbance of (**1**) at 253 nm. Very good agreement was obtained by both methods (within 3%).

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