Phase-transfer Mechanism and Nucleophilicity of Halide Ions in an Aqueous–Organic Two-phase System

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Summary Nucleophilic substitution by halide ions in n-octyl methanesulphonate catalysed by hexadecyltributylphosphonium halides in a water–chlorobenzene two-phase system occurs in the organic phase; the reactivity range ($Cl^- : Br^- : I^- = 0{\cdot}6 : 1{\cdot}1 : 1$) is largely determined by the specific solvation of the anion by a limited number of water molecules.

It is generally accepted that aqueous–organic two-phase reactions catalysed by onium salts follow the mechanism proposed by Starks:[1] the anion, transferred from the aqueous to the organic phase by the lipophilic cation, reacts as a poorly associated and poorly solvated ion pair, and so as a highly reactive species. However, even if this mechanism accounts for the main experimental facts, it is supported by few kinetic data,[1,2] and no systematic investigation of the relative nucleophilicity of anions in two-phase systems has been carried out.

We now report on the kinetics of nucleophilic displacement of methanesulphonate from n-octyl methanesulphonate by Cl^-, Br^-, and I^-, catalysed by hexadecyltributylphosphonium halides in water–chlorobenzene [equation (1)].

$$n\text{-}C_8H_{17}OSO_2Me + KX \xrightarrow[H_2O\text{–}PhCl]{C_{16}H_{33}\overset{+}{P}Bu_3X^-} n\text{-}C_8H_{17}X + MeSO_3K \qquad (1)$$

$X = Cl, Br, I$

In blank experiments it was shown (Volhard titrimetric and ^1H n.m.r. analyses) that under the reaction conditions essentially all the phosphonium halide is in the organic phase, while methanesulphonate anion is quantitatively transferred to the aqueous phase. Equilibrium (2) is thus fully shifted to the right.

$$(C_{16}H_{33}\overset{+}{P}Bu_3MeSO_3^-)_{org} + (X^-)_{aq} \rightleftarrows (C_{16}H_{33}\overset{+}{P}Bu_3X^-)_{org} + (MeSO_3^-)_{aq} \qquad (2)$$

The reactions, carried out by stirring at 1000—1200 r.p.m.† a heterogeneous mixture of a chlorobenzene solution of the substrate and catalyst and an aqueous solution of potassium halide, follow a pseudo-first-order kinetic equation (3) up to at least 80% conversion. The observed

$$\text{rate} = k_{obs}\,[\text{substrate}] \qquad (3)$$

rate constants (k_{obs}) are linearly dependent on catalyst concentration in the range examined ($1{\cdot}8$—10×10^{-2}M). As shown in Table 1 the second-order rate constants for the three halide ions are very similar, the reactivity ratio being $Cl^-:Br^-:I^- = 0{\cdot}6:1{\cdot}1:1$.

TABLE 1

Nucleophilic substitution of methanesulphonate by halide ions in n-octyl methanesulphonate.[a]

X	Phase-transfer conditions[b]	Homogeneous conditions[c] Anhydrous PhCl[d]	Aqueous PhCl[e]	
	10^3k_{obs}/[cat] /(l mol^{-1} s^{-1})[f]	10^3k /(l mol^{-1} s^{-1})[f]	[H$_2$O] /(mol l^{-1})[g]	10^3k /(l mol^{-1} s^{-1})
Cl	1·8 (0·6)	19·7 (6·5)	0·27	2·2
Br	3·2 (1·1)	8·1 (2·5)	0·19	3·3
I	2·8 (1·0)	3·0 (1·0)	0·15	2·7

[a] At 60 °C. [b] 20 ml of a solution of substrate ($6{\cdot}0 \times 10^{-1}$ M) and of catalyst ($1{\cdot}8$—10×10^{-2} M) in chlorobenzene, and 15 ml of a water solution of potassium halide (4·2 M). Kinetics were measured by following the disappearance of the methanesulphonate and the appearance of alkyl halide (^{1}H n.m.r. analysis). [c] Kinetics were measured by following the disappearance of halide ions (Volhard test). [d] [substrate] = 2—6 $\times 10^{-2}$ M, [phosphonium halide] = 2—8 $\times 10^{-2}$ M. [e] [substrate] = $6{\cdot}0 \times 10^{-1}$ M, [phosphonium halide] = $4{\cdot}0 \times 10^{-2}$ M. [f] Relative rates in parentheses. [g] Corresponding to the water associated to the substrate and to the phosphonium halide in the organic phase under phase-transfer conditions.

In anhydrous chlorobenzene with comparable concentrations of phosphonium halide and substrate (Table 1) the second-order rate constant remains practically unaltered for I$^-$, but increases (3 and 1 fold) for Br$^-$ and Cl$^-$, respectively. The reactivity order, $Cl^-:Br^-:I^- = 6{\cdot}5:2{\cdot}5:1$, is similar to that normally found in aprotic dipolar solvents.[3]

TABLE 2

Activation parameters

X	Phase-transfer conditions[a] ΔH* /(kcal mol^{-1})[c]	ΔS*/(cal mol^{-1} K^{-1})[c]	Anhydrous PhCl[b] ΔH*/(kcal mol^{-1})[c]	ΔS*/(cal mol^{-1} K^{-1})[c]
Cl	20·2±0·2	−10·6±0·5	17·6±0·3	−15·7±0·8
Br	18·4±0·2	−14·8±0·5	19·2±0·1	−11·7±0·3
I	19·8	−11·0	20·9±0·4	−7·7±1·4

[a] From measurements at 50, 60, and 70 °C. [b] From measurements at 40, 50, and 60 °C. [c] The activation parameters and root mean square deviations are computer generated (CII 100800) values obtained by least squares.

^{1}H N.m.r. and Karl Fischer analyses showed that a certain amount of water accompanies each molecule of phosphonium halide in the transfer from water to chlorobenzene, the number of water molecules being about 3·4, 2·1, and 1·1 for Cl$^-$, Br$^-$, and I$^-$, respectively. Furthermore 0·15 mol of water per mol of octyl methanesulphonate are present in the organic phase. When the amount of water associated with the phosphonium salt and the substrate was added to chlorobenzene, the rate constants were practically equal to those found under two-phase conditions (Table 1).

Activation parameters, measured both in anhydrous chlorobenzene and under phase-transfer conditions, are reported in Table 2.

The data, as a whole, rigorously show that in the displacement of methanesulphonate group by halide ions under two-phase conditions the reaction takes place in the organic phase and that the rate is not diffusion-controlled. They point out the influence that the specific solvation of the anion by a limited number of water molecules exerts on the reaction rate.

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† The stirring speed was found to have no effect on the reaction rate in the range 350—2000 r.p.m.

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