Nucleophilicity of Halide Ions in Molten Quaternary Ammonium Salts

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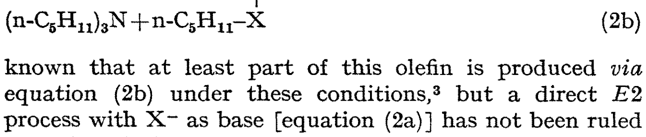
Summary The relative rates of nucleophilic displacement by halide ions from tetra-n-pentylammonium cations in the molten tetrapentylammonium salts at 180° ($Cl^-:Br^-:I^- = 620:7{\cdot}7:1$) reflect the enhanced nucleophilicity expected for unsolvated, unassociated halide ions.

IN molten quaternary ammonium salt media, where deactivation by ion solvation and ion association[1] are absent,[2] halide ions should show a nucleophilic reactivity in the order: $F^- > Cl^- > Br^- > I^-$. This proposition has not been rigorously tested. The reverse Menschutkin reaction (1) is qualitatively more rapid for X = Br than for X = I in studies in sealed ampoules,[3] but the reaction is accompanied by formation of olefin [equation (2)]. It is known that at least part of this olefin is produced *via* equation (2b) under these conditions,[3] but a direct $E2$ process with X^- as base [equation (2a)] has not been ruled out. Pyrolysis of some alkaloid methohalides under the high-vacuum conditions obtaining in the ionization chamber of a mass spectrometer gives predominantly elimination;[4] since secondary $RX–R_3N$ reaction is unlikely under these conditions, the $E2$ path (2a) must be the source.

$$(n\text{-}C_5H_{11})_4N^+X^- \longrightarrow (n\text{-}C_5H_{11})_3N + n\text{-}C_5H_{11}\text{–}X \qquad (1)$$



$$(n\text{-}C_5H_{11})_4N^+X^- \searrow Me\text{-}[CH_2]_2\text{-}CH{=}CH_2 + (n\text{-}C_5H_{11})_3NH^+X^- \qquad (2a)$$

$$(n\text{-}C_5H_{11})_3N + n\text{-}C_5H_{11}\text{–}X \uparrow \qquad (2b)$$

We have now established conditions (180°; 10^{-3} Torr) under which the tetra-n-pentylammonium halides decompose entirely *via* equation (1), allowing determination of the relative rates of displacement by competition experiments. The results in the Table yield the relative rates: $Cl^-:Br^-:I^- = 620:7{\cdot}7:1$, in accord with the theory of medium effects on X^- nucleophilicity which identifies the inversion of the nucleophilicity order $I^- > Br^- > Cl^-$, observed in hydroxylic solvents, to $Cl^- > Br^- > I^-$ in dipolar aprotic solvents with the structural change: $X^- \cdots H\text{–}O\text{–}R \longrightarrow X^-$.[1,5,6] The poorly solvated X^- in dipolar aprotic solvents are more reactive than their $X^- \cdots H\text{–}O\text{–}R$ counterparts by factors ranging from 10^4 for I^- to 10^7 for the more strongly solvated Cl^-. The observed order of second-order rate constants for the S_N2 reaction of unassociated X^- with primary alkyl toluene-*p*-sulphonates is $Cl^-:Br^-:I^- = 8:3:1$ (Me_2SO; 25°),[6] 9:3:1 ($HCONMe_2$; 0°),[7] 18:4:1 (Me_2CO; 25°).[5] The much greater ratios observed in the molten $R_4N^+X^-$ show that this medium represents a further increase in dispersion of X^- nucleophilicity, presumably both because there is some residual anion solvation (and deactivation) in dipolar aprotic solvents,[8] and because

TABLE

Pyrolysis of $(\text{n-C}_5\text{H}_{11})_4\text{N}/\text{X}^1,\text{X}^2)$ *mixtures at* 180 ± 10°

		Reactants (mmol)		Products (mmol)[a]			Products (%)			Relative rate[b]	
X^1	X^2	$n°(R_4NX^1)$	$n°(R_4NX^2)$	$n(RX^2)$	$n(RX^2)$	$n(R_3N)$	RX^1	RX^2	R_3N	$k(X^2)/k(X^1)$	
I^-	—	0·101	—	0·096	—	0·100	95[c]	—	100[c]	—	
Cl^-	—	0·110	—	0·111	—	0·119	101[d]	—	108[d]	—	
I^-	Br^-	0·105	0·102	0·0034	0·022	—	3·3	22	—	7·3	7·7 ± 0·4
I^-	Br^-	1·005	0·101	0·068	0·044	—	6·8	44	—	8·1	
Br^-	Cl^-	1·27	0·141	0·0243	0·109	—	1·9	77	—	76	81 ± 4
Br^-	Cl^-	1·03	0·110	0·0027	0·025	—	0·26	23	—	85	

[a] Trapped at −196° and determined by gas chromatography: all analyses in duplicate, precision ±2%. [b] Calculated from the expression $k(X^2)/k(X^1) = \log\{n°(R_4NX^2)/[n°(R_4NX^2) - n(RX^2)]\}/\log\{n°(R_4NX^1)/[n°(R_4NX^1) - n(RX^1)]\}$, which follows from the integrated first-order rate law. This assumes constant volume of the reacting melt; consequently we arranged the experiments to keep the decrease in volume during reaction {as judged from $[n°(R_4NX^1) - n(RX^1) + n°(R_4NX^2) - n(RX^2)]/[n°(R_4NX^1) + n°(R_4NX^2)]$} less than *ca* 10%. [c] Trace of pent-1-ene detected. [d] No pent-1-ene detected.

the less reactive substrate, R_4N^+, causes a lower decrease in selectivity. We suggest that the fused-salt results provide the best model for the intrinsic relative nucleophilicities of the X^- toward saturated carbon.

The ratios of substitution [equation (1)] to elimination [equation (2)]† products observed in mass-spectrometrically monitored pyrolyses of alkaloid methohalides were interpreted in terms of diminishing S_N2 and increasing $E2$ reactivity in the order I^-, Br^-, Cl^-, F,[4,9] but the present results show that, instead, it is due to a greater increase in the $E2$ rate constants in the order $I^- < Br^- < Cl^- < F^-$ than that for the S_N2 rate constants. Comparison of the data for the strychnine methohalides at 330—360° with those in the Table indicates the following relative $E2$ rates (temperature difference being ignored): $Cl^-:Br^-:I^- = 2400:15:1$. These ratios are again much greater than those typical (*e.g.* 6:2:1 for X^- dehydrobromination in acetone at 69·9°)[10] of dipolar aprotic solvents; they are perhaps more in line with the probably larger differences in basicity of X^-.[11]

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† Elimination competes with substitution in many of these alkaloid methohalide pyrolyses in contrast to our results; whether this is due to the structural difference in R_4N^+, the temperature difference (350—400° *vs.* 180°), or both, is not known.

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