Mechanistic Crossover in Substitution Reactions of Acetonitrile–Boron Halide Adducts

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WE have observed a crossover in mechanism from S_N2 (equation 1) in substitution reactions of acetonitrile–boron trichloride with 2,4-dinitroaniline (DNA) and 2,4-dinitronaphthylamine (DNN) to S_N1 (equation 2 and 3), now demonstrated for the first time, in the corresponding reactions of acetonitrile–boron tribromide. The stoicheiometry of the reaction is given in reaction (1)

$$\mathrm{MeCN,BX_3} + \mathrm{RNH_2} \xrightarrow{\text{slow}} \mathrm{MeCN} + \mathrm{RNH,BX_2} + \mathrm{HX} \quad (1)$$

$$\mathrm{MeCN,BX_3\ (soln.)} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \mathrm{MeCN}\ (l) + \mathrm{BX_3}\ (l) \quad (2)$$

$$\mathrm{BX_3} + \mathrm{RNH_2} \xrightarrow{\text{fast}} \mathrm{RNH,BX_2} + \mathrm{HX} \quad (3)$$

$$(\mathrm{X} = \mathrm{Cl, Br})$$

Previous work on similar reactions was discussed in terms of an S_N2 process.[1] The startling discovery of the rate reversal Cl < Br for DNN but Br > Cl for DNA, led us to recognise the new mechanism. Our expectation was that for mechanism (1) reactions the B–Br bond should break more rapidly than B–Cl,[1] while for the process represented in (2) and (3), acetonitrile–boron tribromide, the stronger adduct, would dissociate more slowly. For the reactions discussed here, activation energies and entropies have been obtained and are compared in the Table with the heat of dissociation† (ΔH_2) for reaction (2). The telling feature of this Table is in the dramatic difference which exists between the bromide system and the chloride system with regard to activation energy: $E^{\ddagger}$ for the chloride system (with both amines) is very much less than the dissociation energy required for reaction (2) (ΔH_2), so that the associative process (1) is a reasonable mechanism, but not the dissociative (2) + (3). However, for the bromide system (again with both amines) $E^{\ddagger}$ is the same within experimental error as the dissociation energy for reaction (2), which suggests reaction (2) is the rate-determining step in the overall substitution. The negative entropies of activation $\Delta S^{\ddagger}$ for the chloride systems fit the associative (S_N2) interpretation, while the positive entropies for the bromide systems fit the dissociative interpretation. Although in the bromide system DNA is slightly more reactive than DNN (by a factor of merely 2, despite the difference in pK_{BH+} of 2 units[2]), the importance of reaction (3) in determining rate is still minor. The relative reactivity k_{DNA}/k_{DNN} (about 40) for the chloride system is consistent with the reactive boron entity being a considerably weaker electrophile than that in the bromide system. Since, in solution, ΔH_2 for chloride and bromide dissociation are the same, within experimental error (Table), free BCl_3 and BBr_3 have the

† Estimated from literature,[3,4] value for $\mathrm{MeCN.BX_3}(c) \longrightarrow \mathrm{MeCN}(l) + \mathrm{BX_3}(l)$ using new measurements on heat of solution of crystalline $\mathrm{MeCN,BX_3}$.

TABLE

		$MeCN,BCl_3$	$MeCN,BBr_3$
	ΔH_2(kcal./mole)	18·1 ± 0·4	19·6 ± 1·3
DNA	k*(min.$^{-1}$)	0·80	0·11
	E‡(kcal./mole)	10 ± 2	20 ± 2
	ΔS‡ (25°)(e.u.)	− 18 ± 5	10 ± 5
DNN	k*(min.$^{-1}$)	0·018	0·058
	E‡(kcal./mole)	10 ± 2	21 ± 2
	ΔS‡ (25°)(e.u.)	− 27 ± 5	12·5 ± 5

* The rate constants k are pseudo first-order, extrapolated to 25° and $[MeCN,BX_3] = 5 \times 10^{-2}$ M, and refer to rate of disappearance of amine.

same acceptor strength; the rate reversal mentioned already is not explicable if both mechanisms are S_N1, but is consistent with free BBr_3 and complexed BCl_3 as the substrates attacked by amine *i.e.* equation (1) is the mechanism for BCl_3 and equation (2) + (3) for BBr_3 systems.

Isosbestic points as in the earlier work[1] rule out any massive (>5%) accumulation of an intermediate between RNH_2 and $RNHBX_2$.

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