SECTION A Inorganic, Physical, and Theoretical Chemistry

Mechanism of Substitution at a Boron Atom. Part II.¹ Kinetics of Reaction of *o*-Nitroamines with Boron Halides

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The reaction of 2,4-dinitronaphthylamine with phenylboron dichloride and related reactions have been studied kinetically. Substitution by an $S_{s}2$ pattern, or *via* an unstable intermediate is a possible mechanism. The energetics of boronium ion formation are discussed in relation to these mechanisms.

Possible mechanisms of substitution at boron have been considered.¹ Kinetic results for the reaction of the very weak nucleophile 2,4-dinitronaphthylamine (DNN) with phenylboron dichloride ² in several solvents, in some of which the dihalide is present as a complex with the solvent are now presented and discussed. Reactions of 2,4dinitroaniline (DNA) with phenylboron dichloride, and of dinitronaphthylamine with phenylboron dibromide and butoxyphenylboron chloride, have also been briefly studied. Analysis was by spectrophotometry, whereby

$$RNH_{2} + PhBCI_{2} \longrightarrow RNH \cdot BPhCI + HCI$$
 (I)

the appearance of the red or violet substitution product 2 and/or the disappearance of the yellow amine could be followed.

EXPERIMENTAL

Reagents were prepared by standard routes. It was difficult to get reproducible kinetic results by spectrophotometry since the low concentration $(10^{-5}M)$ of amine heightened the effect of solvent impurity. A single batch of solvent had to be used for all determinations in a series, for rate constants varied from batch to batch. Fresh solutions of boron halide in solvent were made up every three days since they gave erratic results when kept longer.

Stoicheiometry.—In default of definite evidence ² the stoicheiometry of the reactions studied is assumed to be that given in equation (1). Whether a second molecule of amine is required to remove hydrogen chloride is arguable, but irrelevant to the kinetics which were run with a large excess of phenylboron dichloride so as to be of first order in amine.

Kinetics.—Reactions were run in a 1 cm. path-length silica cell with ground-glass stopper. Aliquot portions of stock solutions of amine and boron compound were mixed in the cell in a dry-box, and the cell removed to a spectrophotometer (Unicam S.P. 500) for readings (time required 2 min.). The cell carriage was a thermostatted block (Adkins type A). Cell temperatures became constant within 3 min. (this being taken as zero time) for a typical run above room temperature and were then subject to variations not greater than $\pm 0.03^{\circ}$ during a run. Reactions were run with boron halide in great excess ($\geq 0.125M$) to give firstorder kinetics, and amine at a suitable concentration to give an optical density of around unity for the initial longwavelength absorption maximum of amine around 390 mµ. Amine concentration throughout the run could be followed by means of this absorption. The product absorbed at about 500 m μ and the maximum in this region was used to estimate its concentration. Any intermediate in this reaction would be expected to have the form PhBX₂·NH₂R'. The nitrogen cannot in this form conjugate with the aromatic residue R' and hence the long-wavelength band typical of free amine will not be present. (The spectrum is expected to resemble the known spectra of R'H or $R'NH_3^+$.) Neither can the four-co-ordinate boron interact electronically with the o-nitro-group of the aromatic residue to produce a charge-transfer band like that of the product. Essentially, any intermediate would not absorb in the critical spectral regions employed for analysis. Typical plots for the determination of rate constants using the rate of disappearance of amine (73Y) and rate of appearance of product (73R) are shown in Figure 1.



FIGURE 1 Determination of rate constant for amine disappearance (73Y) and for product appearance (73R) at 30° in methyl cyanide. DNN, 0.0001m; PhBCl₂, 0.4M

Isosbestic Points.—For reactions of phenylboron dichloride with 2,4-dinitronaphthylamine in acetonitrile and in benzene, a series of spectra were taken at intervals during a run on a Perkin-Elmer Uvicord. The spectral changes occurring are typified in Figure 2. Isosbestic points occurred at 442 and 351 m μ for benzene solutions and 441 and 350 m μ for acetonitrile solutions.

Acetonitrile-Phenylboron Dichloride Adduct.—Acetonitrile (0.35 ml.) was added to a solution of phenylboron dichloride (0.96 g.) in pentane (5 ml.) at 0° . The white precipitate,

- ¹ Part I, J. C. Lockhart, J. Chem. Soc., 1962, 1197.
- ² J. C. Lockhart, J. Chem. Soc., 1962, 3737.

J. Chem. Soc. (A), 1966

m. p. 118·5—120° (decomp.), analysed as the 1:1 complex (Found: B, 5·3; Cl, 35·0. $C_8H_8BCl_2N$ requires B, 5·4; Cl, 35·5%) and had infrared absorption (Nujol mull) quite distinct from that of the components, with the expected shift ³ of $\nu(C=N)$ (to near 2330 cm.⁻¹) and of the B–Cl stretching frequencies from 900 cm.^{-1.4}

Ether-Phenylboron Dichloride Adduct.—This was similarly prepared, but proved very unstable, the crystals becoming



FIGURE 2 Isosbestic points in spectra of the dinitronaphthylamine-phenylboron dichloride reaction in acetonitrile. Curve 1, 3 min. after mixing, 2, 22 min., 3, 55 min., 4, 88 min., 5, 201 min.

brown and liquefying at room temperature within 30 min. (cf. nature of decomposition ⁵). However, by rapid filtration and collection at $<18^{\circ}$, the adduct was obtained for immediate analysis (Found: B, 4.7; Cl, 30.5. C₁₀H₁₅BCl₂O requires B, 4.65; Cl 30.5%).

Acetonitrile-Phenylboron Dibromide Adduct.—Dibromide (2 g.) and nitrile (0.4 ml.) gave 2.2 g. (95%) of complex, m. p. 145—149° (decomp.), ν (C=N) near 2330 cm.⁻¹ (±10 cm.⁻¹) (Found: B, 3.7; Br, 53.0. C₈H₈BBr₂N requires B, 3.75; Br, 55.3%). Phenylboron dichloride did not apparently form a complex with benzene, anisole, or chlorobenzene; nor butoxyphenylboron chloride with ether or acetonitrile. Equimolar mixtures of the solvent and halide had the summed infrared spectra of the two components, with very little shift in the B-Cl stretching frequencies near 900 cm.⁻¹.

Competitive Reaction.—Phenylboron dichloride (3 mmoles) was added at 0° to an equimolar mixture of diethyl ether (3 mmoles) and acetonitrile (3 mmoles). There was a vigorous reaction and white crystals of phenylboron dichloride-acetonitrile were precipitated. The mother-liquor did not contain free acetonitrile (infrared evidence).

RESULTS AND DISCUSSION

Reactions were run with a large excess of boron halide, being effectively of first order overall. The rate of disappearance of the amine as measured spectrophoto-

³ W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, J. Chem. Soc., 1960, 2182.

metrically gave rate constants first-order in amine (labelled Y in Table 1) in all solvents. The rate of appearance of product measured spectrophotometrically was also represented by a first-order equation and was equal to the rate of disappearance of amine. Rate of appearance of product (R in Table 1) was generally measured in the same run as rate of disappearance of amine. Rate constants showing the effect of changing concentration, temperature, substrate, nucleophile, or solvent, are in Table 1. These were reproducible within 15%.

TABLE 1*

Reaction	\mathbf{of}	$2, 4\mbox{-}dinitron a phthylamine$	with	$PhBCl_2$	in
		CH ₂ CN			

		DNN	$k_{\mathbf{Y}}$	$k_{\mathbf{R}}$	$k_{(Av)}$
Temp.	$PhBCl_2(M)$	(10-4м)	(min1)	(min1)	(min1)
30.38°	0.2	4.7 - 7.7	0.0293	0.0290	0.0291
40.40	0.125	7.3	0.0283	0.0292	0.0288
40.40	0.2	9.4	0.0516	0.0541	0.0529
40.40	0.2	$7 \cdot 3$	0.0463	0.0479	0.0471
40.40	0.4	9.4	0.1009	0.0944	0.0977

Reaction of PhBXY (0.25M) with 8.0×10^{-4} M-DNN in CH₃CN

Temp.	PhBXY	ky (min. ⁻¹)	k _R (min.⁻¹)	k _(Av) (min. ⁻¹)
27°	PhBCl,			0.0335 †
27	PhBBr,	0.280	0.300	0.290
30	Ph(BuÕ)BCl	0.0233	0.0224	0.0228

Reaction of PhBCl₂ (0.125_M) with different amines

Гетр. 20·0°	Amine o-NA	(10 ⁻⁴ м) 9·0	Solvent Et ₂ O	$k_{\rm R}$ (min. ⁻¹) over in
$22 \cdot 5 \\ 25 \cdot 0 \\ 26 \cdot 3$	DNA DNN DNN	8·8 9·4 9·4	Et ₂ O Et ₂ O C ₆ H ₆	$\begin{array}{c} 0.0677 \\ 0.0027 \\ 0.269 \end{array}$

* Rate constants are average of two or more runs. DNN = 2,4-dinitronaphthylamine, DNA = 2,4-dinitroaniline *o*-NA = *o*-nitroaniline. † Extrapolated.

Change in amine concentration within a limited range (dictated by the method of following the reaction) did not alter the rate constants, but gross changes in the concentration of phenylboron halide did, indicating that the reaction was of first order in boron halide also. Rates were higher for more basic amines. Phenylboron dibromide in acetonitrile was substituted more rapidly than the dichloride. Butoxyphenylboron chloride reacted at the same rate as the dichloride in acetonitrile, but more slowly in ether.

The most important conclusion with regard to mechanism is that for the reaction of phenylboron dichloride with dinitronaphthylamine an $S_N 2$ process probably operates. This arises from the information that -d[amine]/dt = d[product]/dt (that is $k_{\rm T} = k_{\rm R}$) within experimental error, and the supporting information in Figure 2. The existence of the isosbestic points implies that no intermediate is present to an extent greater than 2% at any time under observation in the reaction of

⁴ L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, J. Chem. Soc., 1958, 2412; F. K. Butcher, W. Gerrard, M. Howarth, E. F. Mooney, and H. A. Willis, Spectrochim. Acta, 1963, 19, 905.

⁵ S. H. Dandegaonker, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1957, 2872, 2893.

811

phenylboron dichloride and dinitronaphthylamine. It had been supposed that attack of amine on a boron halide (N-B bond formation) would require little activation energy,^{1,6} and that the rate-determining step would be a boron-halogen bond-fission from a rapidly formed donor-acceptor adduct: however bond-formation and bond-fission in this reaction are effectively synchronous to our kinetic probing. This does not entirely rule out a short-lived intermediate and the $S_{\rm N}2$ intermediate mechanism (see, e.g., equation 2), but it does suggest that the ratio k_2/k_1 must be in the region of 100 instead of the inverse as might have been expected.

$$RNH_2 + PhBCI_2 \xrightarrow{k_1} RNH_2 \cdot BPhCI_2 \xrightarrow{k_2} \\ \xrightarrow{k_1} intermediate \\ RNH \cdot BPhCI + HCI (2)$$

Substituent Effects.—The observed effects (Table 1) can be rationalised in terms of current concepts although it is not possible to determine from them the relative importance of bond-fission and bond-formation in the mechanism. The acceptor strength of boron halides towards certain amines and nitriles as reference bases and the basicity of the amines used in this work towards the proton as reference acid are known. It is recognised that these are thermodynamic data, but the success of many linear free-energy relationships shows that for a series of closely related bases, with the same functional basic group (e.g., substituted o-nitroamines) the nucleophilicity and basicity (used in the sense of ref. 7, p. 91 and ref. 8, p. 24) are usually in the same relative order.^{8,9} The rate order (Table 1) o-nitroaniline > dinitroaniline > dinitronaphthylamine observed for the reaction of this series with phenylboron dichloride is in agreement with their known pK_{BH} +.² Relative acceptor strengths of the substrates PhBBr₂ > PhBCl₂ are assumed by analogy with the trihalides 10,11 to which they should be very similar ¹² and the order $PhBCl_2 >$ Ph(BuO)BCl was observed experimentally. The observed rate order parallels this (Table 1), with the strongest acceptor reacting most quickly.

The rate order $PhBBr_2 > PhBCl_2$ also reflects the gasphase ionisation energy sequence for boron-halogen bonds in the sense

$$>$$
B - X \rightarrow >B⁺ + X⁻

The ionisation energy can be calculated from massspectrometric ionisation potentials (with the usual limitations as to the accuracy of the value) by use of Stevenson's formulæ: 13

$$D(R^{+} X^{-}) = D(R^{-}X) + I(R) + E(X)$$
(3)

$$= A(R^+) + E(X) \tag{4}$$

⁶ G. B. Kistiakowsky and C. E. Klots, J. Chem. Phys.,

TABLE 2

obtained using either (3) or (4) are given in Table 2 for

some boron-halogen compounds. These extremely

Bond ionisation energies (kcal. mole⁻¹)

$D(\mathrm{R^+X^-}) = D(\mathrm{RX})^a + I(\mathrm{R})^b$ -	$- I(\mathbf{X}^{-})^{c} = A(\mathbf{R}^{+})^{d}$	I(X-)
$R-X D(R^+ - X^-)$	R-X I	$D(R^{+} - X^{-})$
F ₂ B-F 290-295 •	H,B-H	2631
$CI_{2}B-CI$ 186 \pm 5 °	Bu ₂ B-Cl	160 ¹
$Br_{2}B-Br$ 166 \pm 5 °	Bu ₂ B-Br	149
$I_2 B - I \dots I_5 I \pm 5^{e}$	Bu ₂ B-I	1377

^a Absolute values were not available. Mean D(B-H) was used from H. A. Skinner and N. B. Smith, *Trans. Faraday Soc.*, 1955, **51**, 19. For Bu₂B-X, bond energies obtained by H. A. Skinner and T. F. S. Tees, J. Chem. Soc., 1953, 3378, corrected to comply with Skinner and Smith's new value for BCl_3 , (*loc. cit.*) were used. ${}^{b}I(BH_2)$ from W. S. Koski, J. J. Kaufman, and C. F. Pachuki, J. Amer. Chem. Soc., 1959, **81**, 1326. $I(\text{Et}_2\text{B})$ from the same Paper was used instead of $I(\text{Bu}_2\text{B})$, so $I(E_{3}E)$ from the same Paper was used instead of $I(Bu_2D)$, so that each Bu_2B-X value is probably slightly high, but the relative values will be correct. • Electron affinity of X from R. S. Berry and C. W. Riemann, J. Chem. Phys., 1963, **38**, 1540. • $A(R^+)$ from Koski *et al.* (loc. cit.) except for BF₃, F. C. Brinckman and F. G. A. Stone, J. Amer. Chem. Soc., 1960, **82**, 6235. • From equation (4). • From equation (3).

high figures would represent the activation energy for an $S_{\rm N}1$ reaction of R-X via R⁺ in the gas phase (cf. Maccoll 14). Homolytic dissociation would require less energy than heterolysis, thus it is unlikely that simple ionisation would occur. However, the energy required for heterolysis might be considerably lowered by concomitant or prior bond-formation in an $S_{\rm N}2$ or $S_{\rm N}2$ intermediate mechanism ¹⁵ and by stabilisation by solvation.¹⁴ By argument from Table 2, it seems likely that ionisation energies for B-X bonds run in the sequence B-F > B-Cl > B-Br > B-I, this being mainly the result of the same sequence for dissociation energies of these bonds, although the decrements differ in the two series.

Thus the substituent effects are all reasonable in terms of an $S_N 2$ or $S_N 2$ intermediate mechanism and jointly exclude the $S_{\rm N}$ mechanism. It is possible that data for a wider range of reagents would enable us to decide on the relative importance of bond-formation and -fission. Variation of the nucelophile may give information on bond-formation, but unfortunately changes in the leaving group on boron usually alter not only the strength of the broken bond, but also the electrophilicity of the

¹¹ J. M. Miller and M. Oyznszchuk, Canad. J. Chem., 1965, 43, 1877.

⁷ F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958.
⁸ J. O. Edwards, "Inorganic Reaction Mechanisms," Ben-

jamin, 1964.

¹⁰ J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 14. ¹⁰ N. N. Greenwood and P. G. Perkins, *J. Chem. Soc.*, 1960, 1141.

¹² P. G. Perkins, Chem. Eng. News, 1965, 43, 98.
¹³ D. P. Stevenson, Discuss. Far. Soc., 1951, 10, 35.
¹⁴ A. Maccoll, Chem. Soc. Spec. Publ., No. 16, 1962, "The Transition State," p. 159; A. Maccoll, in Adv. Phys. Org. Chem., ed. V. Gold, Academic Press, London and New York, 1965, vol. 3, p. 91. ¹⁵ M. G. Evans and M. Polanyi, Trans. Faraday Soc., 1938,

^{34, 11.}

boron substrate. Hence it may be difficult to ascribe any change in rate exclusively to either a change in rate of bond-fission or -formation.

Solvents.—Apart from the obvious inference that complexing solvents retard the reaction, the interpretation of solvent effects is difficult. Although acetonitrile was a stronger ligand than ether in a competitive reaction for dichloride (a like situation occurs for boron trichloride), the reaction of dinitronaphthylamine with phenylboron dichloride was much slower in diethyl ether, so that the solvent has some specific solvating role in addition to complex formation. For non-complexing solvents, the simple mechanism in equation (2) or the even simpler situation in which RNH_2 ·BPhCl₂ is the transition state rather than the intermediate, agrees with the facts. For complexing solvents, the equilibrium between free and complexed halide must be taken into account:

$$CH_{3}CN,PhBCl_{2} \xleftarrow{k_{7}}{CH_{3}CN} + PhBCl_{2}$$
(7)

Substitution on boron could occur directly on free

chloride [reaction (7) followed by (1)] or on the complexed chloride (equation 8).

$$CH_{3}CN,PhBCl_{2} + RNH_{2} \xrightarrow{k_{3}} RNH \cdot BPhCl + CH_{3}CN + HCl (8)$$

The first alternative can be ruled out for the dinitronaphthylamine reaction, since the Arrhenius activation energy calculated from Table 1 is only 11.5 ± 1.5 kcal. mole⁻¹, whereas step k_7 for the complex should require an activation energy of about 33.8 kcal mole⁻¹, if its heat of dissociation is assumed to be about the same as for the boron trichloride analogue.¹⁶ Reaction in acetonitrile presumably occurs by displacement of both solvent and halogen from the solvent complex.

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¹⁶ A. W. Laubengayer and D. S. Sears, J. Amer. Chem. Soc., 1945, **76**, 164.