Exchange Reactions of Adducts of Nitrogen Donors with Boron Halides

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The exchange reactions of the adducts of *NN*-dimethyl-*o*-toluidine with boron trichloride and with phenylboron dichloride (2) and of *NN*-dimethylaniline with phenylboron dichloride (3) have been examined by an n.m.r. technique. The results are similar to those obtained previously for the adducts of *NN*-dimethyl-*p*-chloroaniline (4) and *NN*-dimethylaniline (5) with boron trichloride. The rate-determining step in amine exchange is usually a unimolecular ionisation of the adduct but adducts (1), (2), and (3) show equilibrium ionisation an order of magnitude greater than do (4) and (5).

It is clear from previous experiments [1] that the dissociation and ionisation of the titled adducts is complex. Here we discuss the nature of the species present in solutious of the adducts (1)—(5) on the basis of spectroscopic and conductivity data and attempt to explain the kinetic data obtained for amine scrambling reactions of the adducts in the presence or absence of their respective free bases.

$o\text{-}MeC_6H_4NMe_2,BCl_3$ (1)
$o\text{-}MeC_6H_4NMe_2,PhBCl_2$ (2)
$C_6H_5NMe_2,PhBCl_2$ (3)
$p\text{-}ClC_6H_4NMe_2,BCl_3$ (4)
$C_6H_5NMe_2,BCl_3$ (5)
$2,4\text{-}Me_2C_6H_3NMe_2$ (6)

We consider all molecular adducts to dissociate in a concentration-dependent equilibrium between molecular adduct, ion pair, and boronium ions. Unfortunately no solid boronium salts for these adducts could be isolated although derivatives of boronium ions have been prepared.[2]

RESULTS

Exchange Reactions of Adducts in s-*Tetrachloroethane*.—*NN-Dimethyl-*o*-toluidine–boron trichloride*.—The exchange characteristics of this adduct are complex; up to four *N*-methyl ^1H n.m.r. signals are observed under varying conditions.

At 290 K the n.m.r. spectrum shows two ^1H signals attributable to *N*-methyl signals and two to *O*-methyl signals. The ^{11}B spectrum also contains two peaks. The ^1H and ^{11}B signals sharpen significantly with decrease in temperature (Figure 1).

The ratios of the intensities of the ^1H *N*-methyl and of the ^{11}B signals of the spectrum are almost identical and markedly concentration dependent [^1H *N* Me HFS*/LFS*: ^{11}B boron HFS/LFS = 1·0 : 0·8]. Thus almost the same amount of NMe_2- and boron-containing substituent is associated with each of the two signals, *or* the two signals do not correspond and the reaction given for example by equation (1) produces ^1H *N*-methyl signals (a) and (b) and ^{11}B signals (a), (b), and (c) with (b) and (c) coalesced, thus giving a B : D ratio of 1 : 1 for each site.

$$\underset{(a)}{2DBX_3} \rightleftharpoons \underset{(b)}{D_2\overset{+}{B}X_2} + \underset{(c)}{BX_4^-} \qquad (1)$$

D = amine

We assumed that the latter explanation was the more reasonable (see Discussion).

The temperature-dependent coalescence of the two ^1H *N*-methyl signals occurs with a population transfer from the LFS to the HFS. The transfer which is reversed on cooling represents 10—50% of the population of the LFS, the proportion being dependent on the adduct concentration

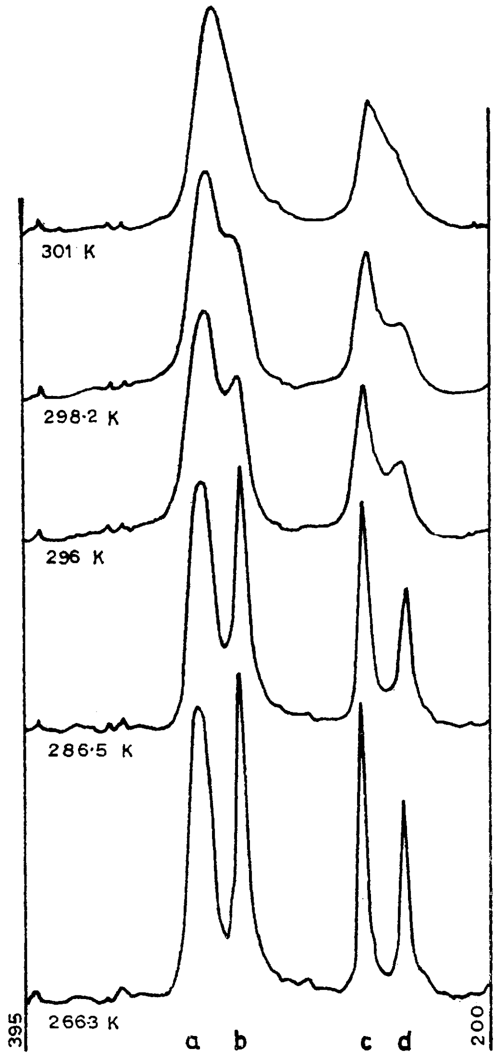

FIGURE 1 ^1H-Methyl spectrum of $o\text{-}MeC_6H_4NMe_2,BCl_3$ in *s*-tetrachloroethane. Markers indicate Hz from Me_4Si. a and b (LFS and HFS see text) are *N*-methyl signals and c and d are the corresponding *O*-methyl signals

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* HFS = high-field signal, LFS = low-field signal (Figure 1).

[1] J. R. Blackborow, *J.C.S. Dalton*, 1973, 2139.

[2] H. Noth, *Progr. Boron Chem.*, 1970, **2**, 244.

(Table 1). No other signals appear with decreasing temperature until viscosity broadening occurs (210 K).

The concentration-dependent ratio of the *N*-methyl sites is illustrated in Table 1. The *N*-methyl signal of added free base always associates with the HFS (Figure 1).

Addition of aliquots of chloride ion (tetraphenylarsonium chloride) to a solution of the adduct gradually removes the LFS and shifts the HFS upfield with an increase in intensity.

TABLE 1

Exchange data for o-$MeC_6H_4NMe_2,BCl_3$

Run	Total Adduct concn. (mol m^{-3} × 10^{-3})	Total Base concn. (mol m^{-3} × 10^{-3})	Composition of adduct † [Mol. adduct] (LFS)	[Ion pair] § LFS ⟶ HFS	[Ions] (HFS)	k_1 * (at 300 K) s^{-1}	$10^{-3}E^{\ddagger}$ J mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
(2)	0·0725	0·0	0·018	0·0125	0·042	24·3	94	88
(3)	0·1269	0·0	0·052	0·0145	0·0612	18·9	114	152
(4)	0·333	0·0	0·202	0·016	0·115	24·8	89	73
(1)	0·22	0·1	0·083	0·019	0·116	8·5	111	136
(5)	0·341	0·157	0·20	0·021	0·12	9·3	111	136

* Rate of dissociation of molecular adduct. † Determined from relative population of ^1H *N*-methyl sites before and after site transfer (Figure 1). § Ion-pair concentration is represented by the difference in LFS intensity before and after site transfer (see text).

Another site separates from the LFS; when both LFS have almost disappeared ($<3\%$ of total ^1H spectra) a decrease in temperature causes the HFS to split into two peaks one of which is the free-amine signal. The free-amine peak completely dominates the spectrum when further quantities of chloride ion are added (Figure 3). In relation to the chloride ion, free *o*-toluidine is a very weak nucleophile with respect to the boron centres, and it seems unlikely that free chloride ions exist in solution until an excess of tetraphenylarsonium chloride is present.

At concentrations at which the conductivity measurements were made (Figure 2) the adduct may be assumed to be almost completely ionised (see Discussion) and thus a comparison between the conductivities of the adduct and tetraphenylarsonium chloride reveals that the adduct has a far higher electrolytic mobility than a mono-charged 1 : 1 electrolyte.

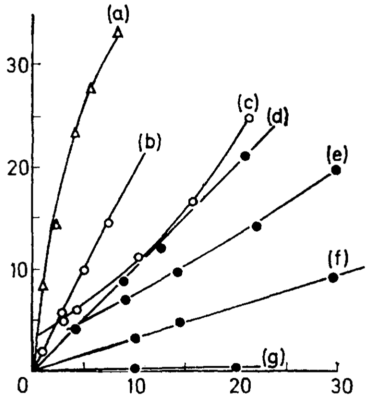

FIGURE 2 Conductivity (μΩ^{-1} m^{-1} mol^{-1} × 10^{-2}) * *vs.* conc. (mol m^{-3} × 10^{-1}): (a) o-$MeC_6H_4NMe_2,BCl_3$; (b) $(C_6H_5)_4AsCl$; (c) $C_6H_5NMe_2,BCl_2C_6H_5$; (d) p-$ClC_6H_4NMe_2,BCl_3$; (e) o-$MeC_6H_4NMe_2,BCl_2C_6H_5$; (f) $2,4$-$Me_2C_6H_3NMe_2,BCl(C_6H_5)_2$; (g) $C_6H_5NMe_2,BCl_3$

* The conductivity measured is the inverse of the resistance across opposite faces of a metre cube of solution.

A kinetic study indicates that in the presence of free base the two-signal coalescence is first order in concentration of LFS *after* the population transfer has occurred. This is identical to the behaviour of adducts (4) and (5). In the absence of free *o*-toluidine the same coalescence process is not truly first order and the activation energy varies slightly with concentration.

NN-*Dimethyl*-o-*toluidine–phenylboron dichloride* (2). The *N*-methyl ^1H proton signal for the adduct appears as two peaks below 260 K and a concentration-dependent variation in the peak intensities similar to that for adduct (1) is observed. The ^1H resonances of the *N*-methyl groups of free *NN*-dimethyl-*o*-toluidine associate with the HFS, but in contrast to the adduct (1) no signal transfer occurs either in the presence or absence of free base before coalescence.

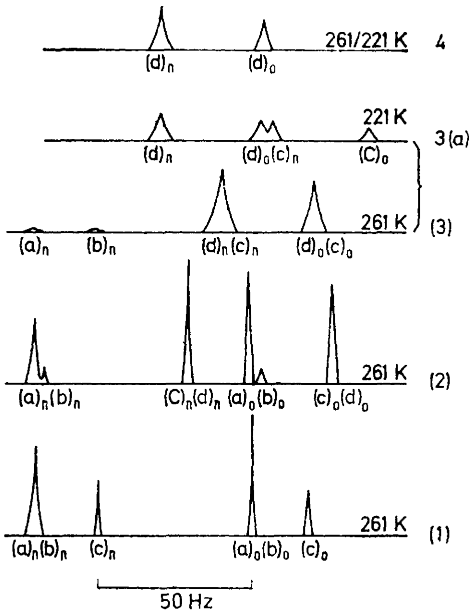

FIGURE 3 Changes in the ^1H methyl signals † of o-MeC_6H_4-NMe_2,BCl_3 with increasing addition of Ph_4AsCl (1) ⟶ (4). (1) No Ph_4AsCl: DBX_3 (a) $\overset{s}{\rightleftharpoons}$ $DB\overset{+}{X}_2X^-$ (b) $\overset{s}{\rightleftharpoons}$ Scrambling boronium ions (c); (2) and (3) Ph_4AsCl + (a) $\overset{s}{\rightleftharpoons}$ (b) $\overset{s}{\rightleftharpoons}$ (c) $\overset{f}{\rightleftharpoons}$ free base (d); (3a) Ph_4AsCl + (c) $\overset{s}{\rightleftharpoons}$ (d) (4) Ph_4AsCl + (d)

† Subscript (n,o) refers to *N*-methyl or *O*-methyl signal. s = slow exchange on n.m.r. time-scale, f = fast exchange on n.m.r. time-scale. Solution (3a) corresponds to solution (3) cooled to 221 K.

The addition of tetraphenylarsonium chloride is accompanied by a decrease in the LFS intensity and a corresponding increase and high-field shift of the HFS. No new signals are observed at any temperature above the viscosity broadening limit.

The rate of *N*-methyl signal scrambling is first order in the concentration of LFS, but unlike that for adduct (1) the rate of exchange is larger in the presence of base (Table 2); the reaction is still approximately first order in LFS intensity however.

Both signals are broad and show no evidence of $^3J(^1HCN^{11}B)$ coupling and it is by no means certain how many species contribute to each signal. The significantly lower conductivity of this adduct compared to that for adduct (1), in a region where both adducts may be considered to be totally ionised, can be seen from Figure 2.

TABLE 2

Exchange data for *o*-$MeC_6H_4NMe_2,BCl_2C_6H_5$

Run	Adduct concn.† mol m^{-3} × 10^{-3}	Base concn. mol m^{-3} × 10^{-3}	Percentage HFS in absence of base	k^1 * (at 230 K) s^{-1}	$E^‡$ J mol^{-1} × 10^{-3}	$S^‡$ J mol^{-1} K^{-1}
(1)	0·61	0·0	20	8·7	36·5	−73
(2)	0·305	0·0	26	9·4	39·5	−59
(3)	0·1525	0·0	33	10·0	40	−57
(4)	0·34	0·14	28	20·5	82·5	134
(5)	0·443	0·22	23	19·0	82	132

* Rate of dissociation of molecular adduct. † Adduct concn. refers to LFS (sec text) free base associates with HFS.

TABLE 3

Exchange data for $C_6H_5NMe_2,BCl_2C_6H_5$

Run	Adduct concn.† mol m^{-3} × 10^{-3}	Base concn. mol m^{-3} × 10^{-3}	Ion concn. §	k_1 * (at 265 K) s^{-1}	$E^‡$ J mol^{-1} × 10^{-3}	$\Delta S^‡$ J mol^{-1} K^{-1}
(1)	0·465	0·16	0·10	20·8	88	107
(2)	0·360	0·203	0·10	23·1	94	130
(3)	0·660	0·475	0·12	20·8	88	107

* Rate of dissociation of molecular adduct. † Concentration of LFS in the presence of base (see text). § Addition of base causes a site transfer from the 'adduct' site (see text), therefore ion concn. represented by difference in 'adduct' concn. before and after addition of base.

The ^{11}B spectrum consists of a single broad line ($w_{\frac{1}{2}}$ 200 Hz) which broadens with a decrease in temperature. Variation in scrambling rates at boron sites may be deduced from the variation in the position of the peak maximum with temperature. This is caused by a preferential collapse of some particular ^{11}B site with a short, transverse relaxation time.

The exchange reaction of the adduct alone has a negative entropy and low activation energy. The presence of base leads to a high activation energy and positive entropy (Table 2). The identity of the species composing the two signals can only be guessed at but the similarity in behaviour of adducts (2) and (1) in the presence of tetraphenylarsonium chloride suggests that the LFS is the relatively unsolvated non-ionic species, *i.e.* the molecular adduct.

NN-*Dimethylaniline–phenylboron dichloride* (3). Although the ^1H n.m.r. signals of the *N*-methyl groups show only one peak down to the viscosity-broadening limit (190 K), the peak-width increases substantially with decreasing temperature (300—220 °K); this increase is so great that it can not be explained in terms of spin-lattice or quadrupole-induced relaxation changes. The ^{11}B signal broadens and disappears at 230 K. The ^1H *N*-methyl signals of *NN*-dimethylaniline scramble with the corresponding adduct signals at 300 K; two peaks separate at 260 K. A comparison of the relative intensities of these two peaks leads us to believe that the adduct signal is a scrambled signal of at least two components, one of which scrambles rapidly with base below 260 K. The temperature-dependent rate of coalescence of the two signals observed below 260 K is first order in the LFS (Table 3).

Conductivity of Adducts.—The conductivities of the adducts (1)—(5) and that of the adduct *NN*-2,4-tetramethylaniline–diphenylboron chloride (6) are shown in Figure 2. The significant conductivity of (1) (Figure 2a) compared to the 1 : 1 electrolyte tetraphenylarsonium chloride (Figure 2b) suggests that the moieties present in (1) when fully dissociated into ions may be multiply charged. Decrease in conductivity of adducts of the chlorides is in the order $BCl_3 > BPhCl_2 > PPh_2Cl$. Although this decrease may be attributable to a progressive decrease in the number of ionisable chloride ions other factors such as adduct strength and ionic mobility may well be important.

DISCUSSION

Assignment of ^1H N-*Methyl and* ^{11}B *Signals of* NN-*Dimethyl-*o*-toluidine–Boron Trichloride.*—^1H N-*Methyl spectra.* The LFS (molecular adduct and ion pair) and the HFS (boronium ions) of adduct (1) (Figure 1, Table 1) have been assigned on the basis of previous work on adducts (4) and (5).[1] The large linewidth of the LFS has been interpreted as a partial resolution of the $^3J_{HCNB}$ coupling in the molecular adduct.

We suggest the LFS is removed preferentially by chloride ion [with the formation of tetrachloroborate ion (7) and free *NN*-dimethyl-*o*-toluidine (8)], because the adduct and ion pair are less solvated than the boronium ions and therefore more easily attached by the Cl^- nucleophile; this explanation can apply equally well to adduct (2). The free base produced in this reaction scrambles rapidly with the boronium ions and the HFS moves to higher field [Figure 3; (2)]. Eventually the scrambled signal is at a higher field than the free-base signal [Figure 3; (3)]. This behaviour can be explained only in terms of a displacement of a labile equilibrium involving at least *two* boronium ions, one of which must have a ^{1}H *N*-methyl n.m.r. signal at a higher field than the free base.

^{11}B *Spectra*. The HFS of the ^{11}B spectrum of a solution of adduct (1) at 290 K shows a gradual shift in position as chloride ion is added to the solution; its final position (—4·5 p.p.m. from Et_2O,BF_3) corresponds to the position for the tetrachloroborate ion. The LFS of the ^{11}B spectrum disappears at the same rate as the LFS of the ^{1}H spectrum. The ^{11}B HFS therefore correspond to the signals of scrambling boronium and tetrachloroborate ions. Each of the boronium ions will have a fairly short T_2 for ^{11}B because of the asymmetry of the boron environments (confirmed by the *narrow* linewidth of the ^{1}H HFS). Therefore for a fairly narrow signal to be observed the exchange life time for boron scrambling between boronium ions and tetrachloroborate must be much shorter than the shortest T_2 of the boronium ions (a full explanation of this effect is given in ref. 1).

Since the half-height linewidths of the ^{11}B HFS and LFS decrease slightly with temperature (70—63 Hz at 290 K, 50—45 Hz at 260 K), the rate of boron scrambling *between signals* must not only be slow, but also slowly decrease with decrease in temperature (as confirmed from the ^{1}H n.m.r. data); yet boron scrambling within the HFS must still be very rapid at all temperatures.

Kinetics.—In the presence of their respective free bases, the rate-determining step in amine scrambling of molecular adducts with the other species in solution can be interpreted in terms of a unimolecular boron–chlorine bond fission (k_1 Tables 1—3). High entropies and enthalpies of activation are consistent with this idea. The ease of a boron–chlorine bond-breaking process can be related to the ease of polarisability of the bond which necessarily involves the other bonds to boron. In this respect we would expect the order of reactivity of adducts (1)—(4) to be (1) > (4) and (2) > (3) when stronger donor boron–nitrogen bonds produce more electron polarisability for the same Lewis acid, and (3) > (4), (2) > (1) when for the same nitrogen donor a phenyl–boron system may be regarded as more polarisable than a chlorine–boron system. The reactivities of adducts (1)—(4) are consistent with this hypothesis.

The similar ionisation processes in the absence of free bases proceeds at a different rate for adducts (1) and (2) and is not truly first order; why this should be so is not clear. We fear that the tremendous lability of these adducts towards hydrolysis might be responsible for producing trace amounts of HCl which would undoubtedly catalyse any exchange process. In the presence of base the trace is effectively removed to form the ammonium chloride salt which is probably inactive as a catalyst (rate-determining steps of amine scrambling in the presence of base are little affected by tetraphenylarsonium chloride). Despite all precautions we could never get consistent rate data in the absence of amine.

Chemical Equilibria of Adduct (1).—If chloride ion selectively removes the least-solvated moieties from solutions of (1) to form (7) and (8) and the degree of solvation depends on the net charge on the moiety, it is clear the order of removal should be $DBX_3 > D\overset{+}{B}X_2\overset{-}{X} > D_2\overset{+}{B}X_2 > D_3\overset{++}{B}X$. A set of equilibria (2)—(4) define the species in solution (though these are obviously not the only possibilities). The observations of Figures 3—3a,

$$DBX_3 \rightleftharpoons D\overset{+}{B}X_2 \cdots \overset{-}{X} \qquad (2)$$

$$2D\overset{+}{B}X_2 \cdots \overset{-}{X} \rightleftharpoons D_2\overset{+}{B}X_2 + BX_4^- \qquad (3)$$

$$3D_2\overset{+}{B}X_2 \rightleftharpoons 2D_3\overset{++}{B}X + BX_4^- \qquad (4)$$

the kinetic data, and the selective removal of species connected *via* equilibria (2)—(4) lead us to propose the following. (a) Equilibrium (2) rate determining (above 300 K) with respect to boron exchange. (b) Equilibrium (3) non-labile (below 300 K) with respect to boron exchange and amine scrambling (D). (c) Equilibrium (4) labile (all temperatures) with respect to boron exchange. (d) Free amine exchange with $D_3\overset{++}{B}X$ labile at all temperatures. (e) Free amine exchange with $D_2\overset{+}{B}X_2$ non-labile (at 221 K). (f) Boron scrambling between $D_2\overset{+}{B}X_2$, $D_3\overset{++}{B}X$, and BX_4^- labile at all temperatures. Thus DBX_3, $D\overset{+}{B}X_2 \cdots \overset{-}{X}$, and $D_2\overset{+}{B}X_2$ are selectively removed *via* Cl$^-$ ion but the lability of reaction (4) allows the equilibrium to move to the LHS in the presence of increasing amounts of $B\overset{-}{X}_4$ ions at 290 K.

Halogen scrambling can occur in all equilibria without being detected spectroscopically except possibly in equilibrium (2); in this case halogen scrambling might effect the effective correlation time of molecular motion of DBX_3 which would certainly influence the quadrupole broadening of the ^{1}H *N*-methyl spectrum. The spectrum, in fact, shows only a slow broadening (with low $D\overset{+}{B}X_2 \cdots \overset{-}{X}$ concentration, Table 1) with decrease in temperature (290 ⟶ 220 K) which is consistent with a non-chemical exchange broadening of low activation energy. Therefore we suspect that halogen scrambling in equilibrium (2) is undetectably slow below 290 K.

The concentration-dependent ratio of the HFS and LFS of adducts (1) and (2) can be measured using the ^{1}H *N*-methyl spectral intensities. It was, however, impossible to relate this dependence to equilibrium constants of the various possible equilibria in solution. The activity coefficients of the solvated ions must, therefore, vary considerably owing to changes in concentration.

Conclusion.—We consider that the existence of multiply charged boronium ions has been established upon the basis of conductivity studies and spectral changes of systems in the presence of tetraphenylarsonium chloride, and that unimolecular bond fission of a boron–chlorine bond in the molecular adduct is the rate-determining step for amine scrambling.

EXPERIMENTAL

Solvents, bases, boron halides, and adducts were prepared and purified by standard procedures.[1,3,4] All operations were carried out in a dry box or Schlenk apparatus. Conductivities were measured in a dry box with a standard conductivity bridge.

Analyses

	Found (%)		Calc. (%)	
	B	Cl	B	Cl
o-$MeC_6H_4NMe_2,BCl_2Ph$	3·7	24·2	3·68	24·12
o-$MeC_6H_4NMe_2,BCl_3$	4·3	42·3	4·28	42·13
$C_6H_5NMe_2,BCl_2Ph$	3·8	25·5	3·86	25·32
$C_6H_3NMe_2,BClPh_2$	3·05	10·2	3·09	10·14

The n.m.r. spectra were obtained from a Brucker Spectrospin spectrometer and analysed utilising a line-shape programme discussed in ref. 1.

[2/2630 *Received, 20th November,* 1973]

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[3] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1971, 49.

[4] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1969, 816.