Resonance Line Broadening Due to Chemical Exchange and Quadrupole-induced Relaxation in the Nuclear Magnetic Resonance Spectra of Some Boron–Nitrogen Adducts

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Quadrupolar induced relaxation and intermolecular exchange of AX molecules (where X is a quadrupolar nucleus and A contains six magnetically equivalent protons coupled to X) and of an AX molecule with an A molecule are illustrated. The rates and mechanism of exchange of some tertiary amine adducts of boron trichloride have been deduced from their temperature-dependent ^{1}H and ^{11}B n.m.r. spectra.

THIS paper describes the mechanism of amine scrambling in boron trichloride–tertiary amine adducts. Adducts of the type $ArNMe_2,BY_3$ (Y = halogen) exhibit a $^3J(^1HCN^{11}B)$ coupling of *ca.* 3 Hz.[1,2] The asymmetry at the boron nucleus causes quadrupole-induced relaxation of the ^{11}B spin states, consequently the $^3J(^1HCN^{11}B)$ coupling is often collapsed in many adducts. We discuss here the n.m.r. spectra of adducts for which the quadrupole-induced relaxation is fairly slow and the $^3J(HCNB)$ coupling is therefore partially resolved in the absence of chemical exchange. Temperature-dependent ^{1}H *N*-methyl n.m.r. spectra thus yield information about the activation processes controlling quadrupole-induced relaxation.

In the presence of chemical exchange the $^3J(HCNB)$ coupling collapses at a rate proportional to the exchange rate but the collapse rate is also modulated by the effective change in asymmetry of the ^{11}B nucleus during the exchange process.[3] Information about exchange rates and relaxation times of exchanging nuclei can thus be obtained.

Line-shape Analysis.—An analytical expression for the n.m.r. line shapes of spin $\frac{1}{2}$ nuclei coupled to a quadrupolar nucleus involved in chemical exchange and quadrupole-induced relaxation has been discussed.[4-7] The matrix used to calculate the line shape of the ^{1}H n.m.r. spectra of the magnetically equivalent methyl protons of the adducts of *NN*-dimethylarylamines with boron trichloride in the presence or absence of free *NN*-dimethylarylamines is illustrated in the Experimental section.

We have ignored the scalar spin coupling of ^{1}H or ^{11}B spins to nitrogen or chlorine; this seems acceptable because the couplings are relaxed very quickly by nitrogen or chlorine quadrupole-induced relaxations. ^{10}B occurs in 18·83% natural abundance and can be allowed for in calculations.

This rather crude model for temperature-dependent ^{1}H and ^{11}B spectra is adequate for present purposes. A more exact description will be discussed elsewhere.

In the presence of chemical exchange the collapse of the $^3J(HCNB)$ coupling is obviously complete for a B–N bond fission. If the effective quadrupole-induced relaxation time of the exchange site derived from a B–Cl bond fission is *much* shorter than its exchange life time the $^3J(HCNB)$ coupling is *also* completely collapsed before B–Cl bond recombination occurs (Appendix). The distinction between B–Cl and B–N bond fission is therefore unobservable for small exchange rates and the same exchange elements in the line-shape matrix can be used for either case.

RESULTS

Exchange Reactions of $PhNMe_2,BCl_3$ (1) *in* sym-*Tetrachloroethane*.—The temperature-dependent ^{11}B quadrupole-induced relaxation and chemical exchange of the *N*-methyl protons of the compound $PhNMe_2,BCl_3$ is shown in Figure 1,B. The expected quartet due to ^{11}B–^{1}H coupling $^3J(^1HCN^{11}B)$ 2·9 Hz can be observed. As the temperature

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is increased from 240 K the quadrupole relaxation rate decreases and the ^{1}H spectrum sharpens; further increase in temperature results in the recollapse of the ^{1}H spectrum owing to chemical exchange.

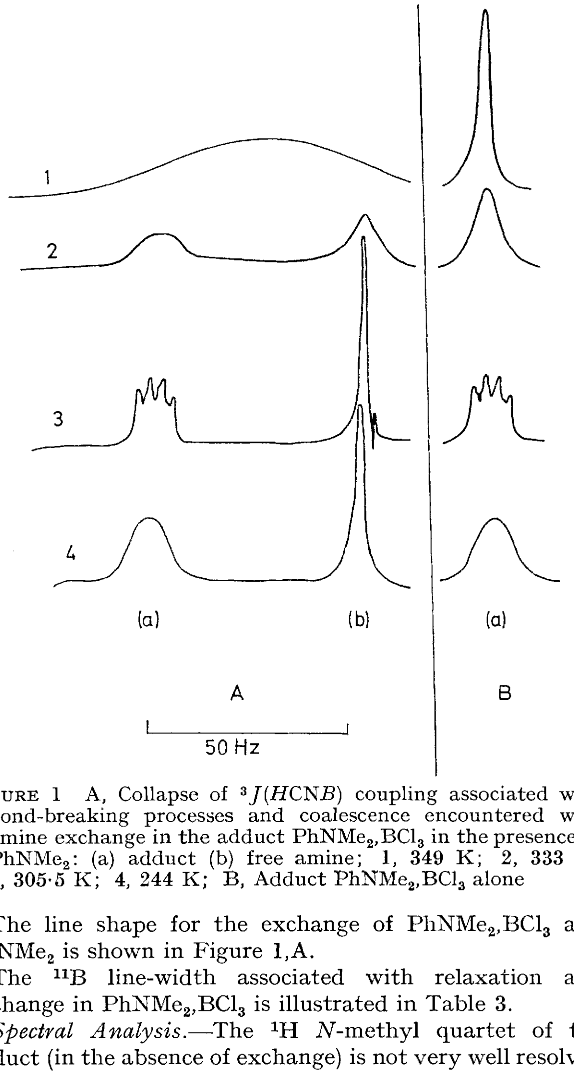

FIGURE 1 A, Collapse of $^3J(HCNB)$ coupling associated with bond-breaking processes and coalescence encountered with amine exchange in the adduct $PhNMe_2,BCl_3$ in the presence of $PhNMe_2$: (a) adduct (b) free amine; 1, 349 K; 2, 333 K; 3, 305·5 K; 4, 244 K; B, Adduct $PhNMe_2,BCl_3$ alone

The line shape for the exchange of $PhNMe_2,BCl_3$ and $PhNMe_2$ is shown in Figure 1,A.

The ^{11}B line-width associated with relaxation and exchange in $PhNMe_2,BCl_3$ is illustrated in Table 3.

Spectral Analysis.—The ^{1}H *N*-methyl quartet of the adduct (in the absence of exchange) is not very well resolved (Figure 1). There could be two reasons: (*a*) an insufficiently slow quadrupole-induced relaxation in the absence of exchange or (*b*) the presence of another species with a signal underneath the adduct methyl peak.

In the presence of amine the population of the adduct site decreases by 10% (before peak broadening due to chemical exchange is appreciable) with a corresponding increase in amine site population. After this site-transfer equilibrium has been established two-site exchange subsequently occurs in the normal way.

The adduct spectrum returns to its original contour when the reaction mixture is cooled. The effect of change in population is not therefore an approach to equilibrium, neither is it due to the presence of free ions, because the adduct is a non-electrolyte. The rate of collapse of $^3J(HCNB)$ is of the first order (Table 1) in adduct in the presence or absence of amine. The site transference is here ascribed to the effects of an ion pair which reacts (*via* amine exchange) with free base at a higher activation energy than with the adduct (Scheme).

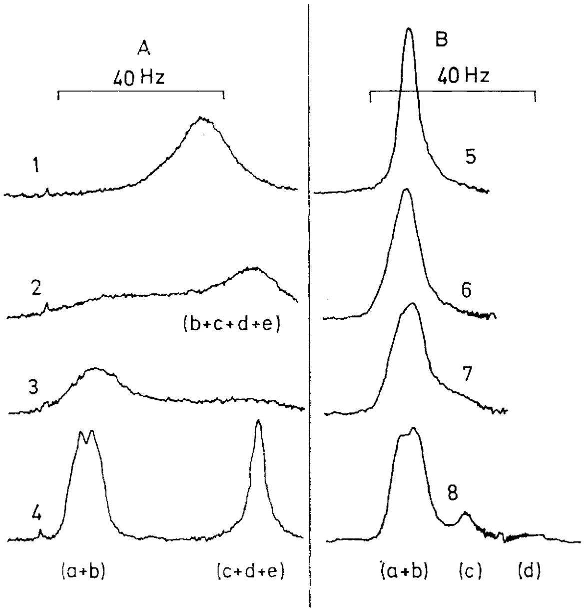

FIGURE 2 A, Exchange of p-$ClC_6H_4{\cdot}NMe_2,BCl_3$ in the presence of p-$ClC_6H_4{\cdot}NMe_2$. Site transfer of the ion pair (b) and partial quadrupolar relaxation of (a) is illustrated; 1, 326 K; 2, 320 K; 3, 316·5 K; 4, 300 K B, Adduct alone. Illustration of the coalescence of ion sites (c) and (d) followed by coalescence of (c + d) with (a + b); 5, 330 K; 6, 323 K; 7, 312 K; 8, 306·5 K

Allowance was made for the contribution of the ion pair ^{1}H signal to the adduct peak and an activation energy for the stationary random Markovian process describing quadrupole-induced relaxation of the adduct molecule was determined at temperatures where no chemical exchange took place.

TABLE 1

Exchange data for $PhNMe_2,BCl_3$

Run	10^{-3}[Adduct] [a] / mol m^{-3}	10^{-3}[Base] / mol m^{-3}	k_1/s^{-1} [b] at 325 K	$10^{-3}E^‡$ / J mol^{-1}	$10^{-3}\Delta S^‡$ / J K^{-1} mol^{-1}	$1(/2\tau)$/s^{-1} [c] at 273 K	$10^{-3}E^‡_{quad}$ / J mol^{-1}
3	0·140	0·0	7·39	109	96	5·9	12·6
4	0·168	0·0	7·54	104·5	104·5	5·5	12
5	0·105	0·163	7·25	105	96		
6	0·320	0·340	6·96	104·5	96	5·8	12
7	0·435	0·273	7·39	104	96	5·5	12

[a] Concentration of molecular adduct (a) (Scheme). [b] See Scheme. [c] T_{1q} ^{11}B = 0·36 s at 273 K and 0·90 s at 325 K.

$$\frac{T_{1q}\text{ (adduct)}}{T_{1q}\text{ (ion pair)}} = \frac{9{\cdot}0 \times 10^{-1}}{7{\cdot}5 \times 10^{-2}} = ca.\ 12{\cdot}0\,(325\text{ K})$$

A variable-temperature study of the ^{11}B spectra of the adduct showed a line shape possessing broader wings than a

TABLE 2

Exchange data for p-$ClC_6H_4{\cdot}NMe_2{\cdot}BCl_3$

	10^{-3}[Adduct]/mol m^{-3}	10^{-3}[Base]/mol m^{-3}	10^{-3}[Ion]/mol m^{-3}		k/s^{-1}* at 325 K		$10^{-3}E^{\ddagger}$/J mol^{-1}		$10^{-3}S^{\ddagger}$/JK^{-1} mol^{-1}	
Run	(a)	(e)	(b)	(c + d)	k_1	k_2	k_1	k_2	k_1	k_2
1	0·162	0·509	0·105	0·080	196		188		370	
2	0·134	0·161	0·080	0·064	257		189		372	
3	0·053	0·155	0·063	0·047	221		187		370	
4	0·186	0·00	0·115	0·085		118		112(k_2)		164
5	0·087	0·00	0·068	0·052		122		112		164

* See Scheme and Figure 2.

Lorenzian curve but with a half-height line-width which varied in a way characteristic of the expected relaxation changes (Table 3; Appendix).

Exchange Reactions of p-$ClC_6H_4{\cdot}NMe_2,BCl_3$ (2) *in* sym-*Tetrachloroethane.*—An explanation of the behaviour of the exchange reaction of this adduct in terms of the mechanism suggested for adduct (1) (Scheme) is possible. The adduct (2) is an electrolyte and the ^{1}H N-methyl n.m.r. spectra are illustrated (Figure 2). Site (a) is attributed to the signal of the molecular adduct because of a marked change in line shape associated with temperature-dependent quadrupole-induced relaxation of the partially resolved $^3J(HCNB)$ coupling in the absence of chemical exchange; such behaviour is not observed in the spectrum of boronium ions. Site (b), an ion-pair signal, has been assigned by analogy with a similar site in the solution spectrum of the non-electrolyte, adduct (1); the behaviour of the ion-pair signals of (1) and (2) under varying temperature conditions is very similar. The sites (c) and (d) which appear more intensely in similar but more highly ionised adducts (either coalesced or separately) have been attributed to boronium ions.* Their concentrations relative to that of the molecular adduct increase with dilution which is found to be characteristic of such ionisation equilibria. The rate of coalescence of (c + d) † with (a + b) was measured. Free base (e) exchanges rapidly with (c + d) and a site transfer of (b) to the free base site occurs before a two-site coalescence of (a) with (b + c + d + e) is observed. The behaviour of adduct (2) has been interpreted as a fast exchange reaction of free base with ions (c) and (d) followed by fast exchange of the ion pair (b) with (c + d + e) as the temperature is increased. The exchange of (a) with (b + c + d + e) is of the first order in (a) (Table 2) and has been assumed to involve a rate-determining decomposition of the adduct (a) followed by fast exchange of amine in the other components.

TABLE 3

Half-height line-widths of ^{11}B signals

$PhNMe_2,BCl_3$									
Hz	38	33	31	26	50	36	18	11	6
T/K	240	260	280	300	320	340	349	360	370
p-$ClC_6H_4{\cdot}NMe,BCl_3$									
Hz	24	28	10						
T/K	330	360	376						

Complex matrix for the 'A' spectrum of the $AX + A^* \rightleftharpoons A^*X + A$ exchange. The inner matrix describes exchange in the absence of the A*/A site

$$I(\omega)_{^{11}B} = -\mathrm{R_e}\left[\begin{array}{c|cccc} i[(\omega_A-\omega)] - R' - K_{AB} & K_{BA} & K_{BA} & K_{BA} & K_{BA} \\ \hline K_{AB}/4 & -i[(\omega_B-\omega)] - R - K_{BA} - \frac{1}{\tau} - \frac{3}{4}K_s & \frac{1}{2\tau}+\frac{1}{4}K_s & \frac{1}{2\tau}+\frac{1}{4}K_s & +\frac{1}{4}K_s \\ K_{AB}/4 & \frac{1}{2\tau}+\frac{1}{4}K_s & -i[(\omega_B-\omega)+J] - R - K_{BA} - \frac{1}{\tau} - \frac{3}{4}K_s & +\frac{1}{4}K_s & \frac{1}{2\tau}+\frac{1}{4}K_s \\ K_{AB}/4 & \frac{1}{2\tau}+\frac{1}{4}K_s & +\frac{1}{4}K_s & -i[(\omega_B-\omega)+2J] - R - \mathrm{K_{BA}} - \frac{1}{\tau} - \frac{3}{4}K_s & \frac{1}{2\tau}+\frac{1}{4}K_s \\ K_{AB}/4 & \frac{1}{4}K_s & \frac{1}{2\tau}+\frac{1}{4}K_s & \frac{1}{2\tau}+\frac{1}{4}K_s & -i[(\omega_B-\omega)+3J] - R - K_{BA} - \frac{1}{\tau} - \frac{3}{4}K_s \end{array}\right]^{-1}\begin{bmatrix} P_A \\ P_B/4 \\ P_B/4 \\ P_B/4 \\ P_B/4 \end{bmatrix}$$

K_s = Adduct exchange rate. K_{AB} = Adduct-amine exchange rate. $(1/2\tau)$ = ^{11}B spin site exchange rate; $\Delta M = \pm 1$. P_A,P_B = Populations of ^{1}H sites.

The ^{11}B spectrum (one peak) of adduct (2) shows a parallel behaviour to that of adduct (1) (Table 3). The Scheme illustrates the most probable mechanism for exchange.

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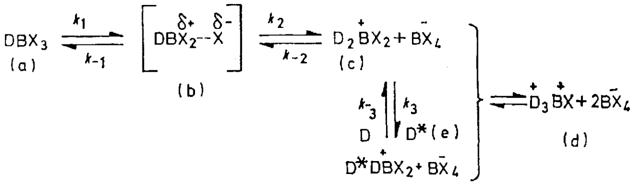
* It has been shown by further studies on many adducts that in some circumstances the equilibrium $D_2\overset{+}{B}X_2 + DBX_3 \rightleftharpoons \overset{+}{D}_3\overset{+}{B}X + \overset{-}{B}X_4$ may be established. Thus more than one cationic species may exist in solution.

† (c) and (d) coalesce with each other before coalescence with (a + b).

For adducts (1) and (2) the concentration of (a) and (b) can be determined from the extent of (b) site transfer in the presence of base: k_1 can then be determined (Tables 1 and 2).



SCHEME

For adduct (1) in the absence of base k_1 can be redetermined from the rate of $^3J(HCNB)$ coupling collapse with the appropriate allowance for (b) at the same chemical shift as (a) (see Appendix for ^1H line-width).

For adduct (2) in the absence of base a knowledge of the intensities of (b) and (c + d) enables k_2 to be determined. The value of k_3 seems to be an order of magnitude greater than k_2 (Scheme) and no experimental work was carried out to determine this rate constant.

It is noticeable from Figure 2 (curve 2) and Table 2 that the exchange of (b) with (c + d + e) clearly does not occur at a rate k_2. It is assumed that (b) therefore exchanges with amine (e) more rapidly than with the ions (c + d). Unlike adduct (1) the spectra of adduct (2) show an irreversible shift of site (b) to site (c + d + e) [Figure 2 (curve 2)]. This can be interpreted as the establishment of a slow preferential solvation of the ion pair with amine molecules followed by a fast exchange process between (b) and (e).

DISCUSSION

The significance of the kinetic date of Tables 1 and 2 seems to be that the amine exchange occurs *via* a unimolecular ionisation [2] and not dissociation of the B–N bond even in the relatively weak adduct (2). This inference is substantiated by the observation of an increase in the activation energy and entropy of the k_1 step on going from adduct (1) to (2), a fact not in accord with the expected difference in the B–N bond energy of the adducts (1) and (2).

The entropies of dissociation of both adducts are fairly high as would be expected from the formation of a solvated ion pair, or free ions.

If unimolecular ionisation *via* ion-pair formation is a general scheme of exchange for amine adducts of boron halides, the rate of exchange in poor hydrogen-bonding donor solvents should be lower. Thus the exchange of $PhNMe_2,BCl_3$ in $PhNMe_2$ is slow below 100 °C.[2]

The kinetic analysis of adducts which exhibit a $^3J(HCNB)$ coupling in the absence of exchange is in general complicated by multiple boronium ion formation in chlorohydrocarbon solvents and lack of reactivity in donor solvents. This paper has dealt with two relatively uncomplicated exchange processes and we shall report on more complicated systems elsewhere.

EXPERIMENTAL

Solvents were dried (Na or CaH_2) and distilled before use. *sym*-Tetrachloroethane was shaken with barium oxide, filtered off, and stored over CaH_2 before distillation. *p*-Chloro-*NN*-dimethylaniline was prepared from the pyrolysis products of *p*-chloro-*NNN*-trimethylanilinium hydroxide as described elsewhere.[8]

Boron trichloride (B.D.H.) was used without further purification. *NN*-Dimethylaniline–boron trichloride (1) (Found: B, 4·5; Cl, 44·3. Calc. for $C_8H_{11}BCl_3N$: B, 4·5; Cl, 44·6%) and *p*-chloro-*NN*-dimethylaniline–boron trichloride (2) (Found: B, 4·00; hydrolysable Cl, 38·9. Calc. for $C_8H_{10}BCl_4N$: B, 3·96; hydrolysable Cl, 39·0%) were prepared by standard procedures,[9] recrystallised from *sym*-tetrachloroethane, and stored under nitrogen.

N.m.r. tubes were filled with a known weight of adduct and volume of tetrachloroethane, free amine, and tetramethylsilane. The tubes were sealed and spectra recorded within 2 h of solution preparation. The temperature of the spectrometer was stable to ±0·5 °C as recorded by a copper–Constantan thermocouple. Temperature calibration was with a methanol solution. ^1H Spectra were recorded at 90 MHz, with frequency locked to the proton signal of tetramethylsilane. ^{11}B Spectra were accumulated (c.a.t.) twice before print-out.

A programme for line shapes was prepared in Fortran IV and run on an IBM 360 computer interfaced with a graph-plotter.

It became clear, as had been found by previous workers,[10] that for exchange between sites of largely differing chemical shifts the rate of spin–lattice and quadrupole-induced relaxation has little effect on the line shape around the coalescence region (Figure 1,A). This is not true for the exchange of adduct alone and these results are therefore inherently less accurate than those for the two site process (Figure 1,B).

Effect of the ^{10}B *Nucleus*.—The value of the coupling constants $^3J(^1HCN^{10}B)$ is related to the $^3J(^1HCN^{11}B)$ values by the ratio of the gyromagnetic ratios in the usual way. Experimental results confirm this.[3,11] Similarly an effective value of $T_2(^{10}B)/T_2(^{11}B)$ can be obtained. No preferential collapse of ^{10}B coupled spectra seems likely so the values of $^3J(^1HCN^{10}B)$ and $T_2(^{10}B)$ can be used directly in computer simulations.

Line Shapes.—The ^1H *N*-methyl n.m.r. spectrum for the exchange process was calculated from formula (1).

$$I(\mathrm{w}) = 0{\cdot}8117I(\mathrm{w})^{11}\mathrm{B} + 0{\cdot}1883I(\mathrm{w})^{10}\mathrm{B}^* \qquad (1)$$

The values of R^1 ($R = 0$) were derived from the half-height line-widths of free base, at various temperatures The values of $(1/\tau)$ of ^{11}B and ^{10}B were set equal to zero in the presence of exchange; conversely in the absence of exchange with all K's equal to zero, the rate of quadrupole-induced transitions were calculated by varying the boron $(1/\tau)$.

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* An anisotropic isotope shift of 0·04 p.p.m. for ^{10}B spectra was allowed for.

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APPENDIX

^{11}B *Line-widths of Molecular Adducts*.—In the presence of chemical exchange the ^{11}B nucleus of the adduct molecule spends some time in a new environment for which the quadrupole-induced relaxation is quite different. Usually this environment is less symmetric than the adduct site and so relaxation is much faster. For a slow exchange rate the ^{11}B nucleus will have relaxed completely before returning to the adduct site, thus all the ^{11}B spin sites of the adduct are reoccupied at an equal rate; when the effective quadrupole-induced relaxation time of the new site is longer than the exchange life time of the site the ^{11}B spin states have not relaxed completely in an exchange cycle and so the ^{11}B line shape of the adduct site reflects the individual relaxation time of each ^{11}B spin state in the new site multiplied by the ratio 'exchange life time: average quadrupole-induced relaxation time of the new site'; in these circumstances the ^{11}B line-width progressively decreases with increase in exchange rate. Eventually the line-width approaches the value obtained from random Markovian motion of the electric-field gradients at the ^{11}B nucleus and further increase in rate of exchange has a negligible effect on the line-width.

The ^{11}B line-width of the adduct affected by a gradual increase in temperature will thus initially decrease (corresponding to the region of decreasing correlation time in the absence of exchange), pass through a minimum, increase proportionally to the exchange rate, pass through a maximum (effective T_2 of the new ^{11}B site comparable with the exchange life-time), and decrease toward the value due to random field movements (correlation time effect).

Table 3 illustrates this behaviour for the adducts (1) and (2). The effective T_2's of the new ^{11}B sites (the ion pairs $DBX_2^+ \cdots X^-$) obtained from the value of the exchange rate at maximum width are estimated to be $7{\cdot}5 \times 10^{-2}$ s for $PhNMe_2BCl_2^+ \cdots Cl^-$ and $0{\cdot}56 \times 10^{-3}$ s for p-$ClC_6H_4{\cdot}NMe_2BCl_2^+ \cdots Cl^-$.

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