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LETTER

Halogen exchange in boron trihalides: the BCl_3–BI_3 reaction

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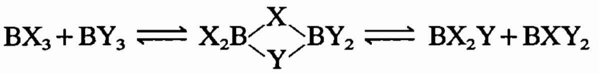
Halogen redistribution reactions [1] between boron halides have been studied by a variety of vibrational [2–5], mass spectroscopic [6] and nuclear magnetic resonance methods [7–10]. The reactions occur between most mixtures of halides with equilibria being quickly established. For example, the distribution of species formed from mixtures of BCl_3 and BI_3 using ^{11}B NMR has been reported by Lappert *et al.* [9, 10]. The labile compounds BCl_2I and $BClI_2$ are present but no other intermediates are detected. Figure 1 shows the ^{11}B NMR spectrum (at 28.75 MHz using a JEOL FX90Q spectrometer) of a CH_2Cl_2 solution containing BCl_3 21.7%, BCl_2I 22.0%, $BClI_2$ 25.3% and BI_3 32.0%. For this mixture the equilibrium constant of reaction (1) is 0.8, in agreement with the value of 0.75 previously measured in 1,1-dichloroethane [9].

It has been proposed [11] that these redistributions occur via reaction (1) involving the formation of a



$$BX_3 + BY_3 \rightleftharpoons X_2B\langle{}^{X}_{Y}\rangle BY_2 \rightleftharpoons BX_2Y + BXY_2 \qquad (1)$$

short-lived di-μ-halogeno bridged four-centre transition state species between two boron halide molecules such as is found in the structure of dimeric aluminium trihalides. This complex may then dissociate to give either the mixed boron halides or the initial reactants. Other possible reaction paths involving ionic mechanisms have also been suggested such as eqn. (2) although these are considered to be less likely as the exchange reactions take place in both solution, with little sensitivity to solvent polarity, and in the gas phase.

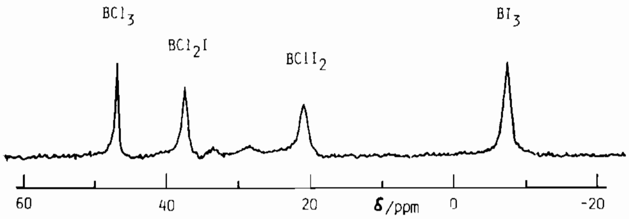


Fig. 1. ^{11}B NMR spectrum of a mixture of BCl_3 and BI_3 in dichloromethane solution at 295 K. Chemical shifts are relative to $Et_2O \cdot BF_3$.

$$BX_3 + BY_3 \rightleftharpoons [BX_2]^+ + [BY_3X]^- \rightleftharpoons BX_2Y + BXY_2 \qquad (2)$$

In this work we report a study of the mechanism of such a reaction using the MNDO and AM1 SCF molecular orbital method [12]. The MNDO and AM1 method as implemented in the program MOPAC [13] is well suited to studies of this type and has been parametrised for boron [14] and all halogen [15–18] atoms. Table 1 shows the results of MNDO and AM1 calculations of the thermodynamic, structural and vibrational properties of the boron(III) halides. It can be seen that satisfactory geometries and heats of formation may be calculated by this method.

A search was made, using the MNDO and AM1 methods, for the possible existence of dimeric boron trihalides with topologically similar structures to those in dimeric aluminium trihalides. In all cases except the fluoride such structures were found, Table 2, Fig. 2. Both the MNDO and AM1 methods predict an increasing stability for the dimer with respect to the monomer trihalides although the quantitative results differ significantly between the models. In the case of BI_3 the dimer is calculated to be stable with respect to the monomer in both cases, Table 2.

A detailed investigation of the reaction of BCl_3 and BI_3 was then undertaken. The reaction coordinate was chosen as the B–B distance and points on the reaction potential energy surface calculated with optimisation of all other coordinates. It was found that on close approach of the two halides the initial interaction that led to a halogen exchange reaction occurred through binding of a halogen atom (in this case a chlorine atom) from BCl_3 to the boron of BI_3, Fig. 3. This is followed on closer approach by the formation of a weakly stable complex between the halides with a di-μ-halogen bridge between the boron atoms, Fig. 3. The activated complex corresponds to the initial formation of this di-μ-bridged species. This complex is unstable with respect to dissociation into the monomeric halides, however there are now two pathways open for this dissociation either to the parent or the mixed boron halides thus leading to possible halogen exchange. The activation energy to this process from the weakly stable dimer, Fig. 3, is small, the dimer lying in a shallow energy minimum.

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TABLE 1. Calculated heats of formation, bond lengths and vibrational spectra[a] of boron halides (AM1 values in square brackets)

		ΔH_f (kcal mol^{-1})	R (B–X) (Å)	$\nu_1(A_1')$ (cm^{-1})	$\nu_2(A_2'')$ (cm^{-1})	$\nu_3(E')$ (cm^{-1})	$\nu_4(E')$ (cm^{-1})
BF_3	Calc.	−261.0	1.32	669	1113	1701	500
		[−272.1]	[1.31]	[618]	[1218]	[2108]	[429]
	Exp.	−269.7	1.30	888	718	1446	558[b]
BCl_3	Calc.	−87.4	1.76	455	516	1069	236
		[−97.0]	[1.71]	[469]	[479]	[810]	[272]
	Exp.	−97.1	1.75	473	448	951	254[c,d]
BBr_3	Calc.	−33.6	1.86	313	398	966	140
		[−50.1]	[1.86]	[319]	[403]	[952]	[152]
	Exp.	−49.7	1.87	279	378	815	151[c,e]
BI_3	Calc.	9.4	2.02	226	350	904	94
		[19.4]	[1.99]	[240]	[345]	[981]	[91]
	Exp.	6.3		192	329	692	101[c,e]

[a] ^{11}B isotope. [b] Ref. 19. [c] Ref. 20. [d] Ref. 21. [e] Ref. 22.

TABLE 2. Calculated heat of formation (kcal mol^{-1}) for di-μ-halogeno dimers

	ΔH_f		ΔE (dimer–monomer)	
	MNDO	AM1	MNDO	AM1
B_2Cl_6	−149.7	−191.6	25.1	2.4
B_2Br_6	−53.8	−101.2	13.4	−1.0
B_2I_6	13.5	31.0	−5.3	−12.2
$B_2Cl_3I_3$	−59.6	−69.2	18.4	8.4

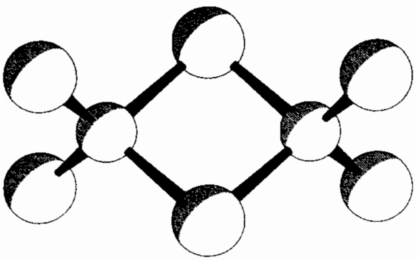

Fig. 2. Calculated (AM1) structure of B_2Cl_6 (B–B = 2.79 Å).

There is experimental support for the formation of a mono-μ-halogen bridge between boron atoms in the anions $B_2F_8^-$ [23], $B_2F_6Cl^-$ and $B_2Cl_7^-$ [24] which are analogous to the series of aluminium complexes $Al_2X_7^-$ for which calculations have been recently reported [25]. Molecular orbital calculations for the bridge bonding in diborane have recently been extended to $B_2H_7^-$ and the 'half-opened' form of diborane, H_2B–H–BH_3 [26]. B–Cl–B bridge bonds have also been found by X-ray crystallography in a novel bis-boron chelate [27]. Raman spectroscopic studies of liquid BCl_3 have also suggested the presence of a Lewis acid–Lewis base type of interaction between the boron of one molecule and the chlorine of another [28, 29].

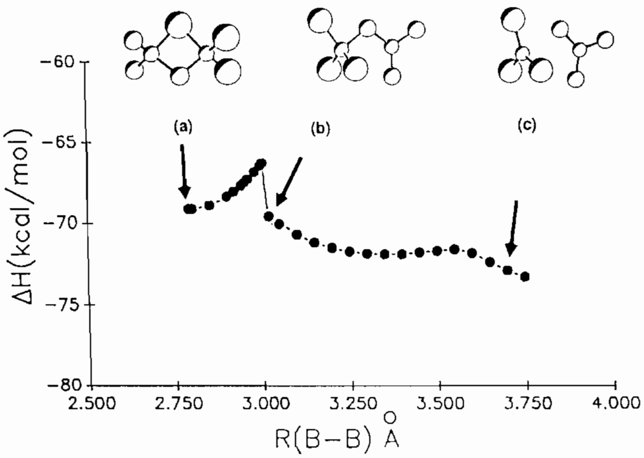

Fig. 3. Reaction path (AM1) for BCl_3/BI_3 interaction to form di-μ-halogen bridged intermediate (a).

The four-coordinate adducts of boron halides also undergo halogen redistribution with BX_3 molecules and an associated bridging mechanism has been proposed [30]. However, this awaits further experimental proof, or testing by methods such as those presented here.

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