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THE ANOMALOUS BOILING POINTS OF SOME BROMO-FLUORIDES

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SUMMARY

All XBrF compounds (X = CO, POF, PSF and SO_2) boil below the corresponding XCl_2 compounds in spite of the higher masses of the former. By means of suitable plots it is shown that the anomaly is due to two factors. Firstly, the much lower association of XBrF species compared with bromine monofluoride, and secondly the exceptionally low boiling points of difluorine and XF_2 compounds. XBrF compounds boil close to the mean of XBr_2 and XF_2 compounds.

INTRODUCTION

Since boiling points almost invariably increase with relative molecular mass (RMM) it is interesting to encounter exceptions to this generalisation and provide explanations. The high boiling points of some first short period hydrides compared with those of latter periods are due to enhanced hydrogen bonding and provide the most familiar examples of anomalous behaviour. However, the opposite anomalous behaviour is found with a set of bromofluorides XBrF, where X = CO, POF, PSF and SO_2, which can be regarded as insertions of a moiety X into an interhalogen. All their boiling points are below these of corresponding XCl_2 compounds of lower RMM.

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RESULTS

The data, although incomplete, is condensed in Fig.1 by ratioing the absolute boiling points to those of XF_2 compounds and plotting this ratio against the mass of compound less that of X. The resulting curves show abrupt changes in slope with the bromo-fluoride points well below the upper linear portions. This contrasts with the analogous graph (Fig.2) when X is removed and where bromine monofluoride is above the line. As usual difluorine is exceptional being out of line with other dihalogens and boiling within a degree of the adjacent noble gas, argon. The binary interhalogens, formed from non-adjacent halogens, boil above the mean of the corresponding dihalogens in the increasing order CIF, ICl, BrF of increasing electronegativity difference, or partial charge on the halogens. This indicates a reduction in volatility of these interhalogens caused by dipole association. The interhalogens formed between adjacent halogens boil somewhat lower than the mean values.

Reverting to Fig.1 the boiling points of the three XBrF compounds for which figures are available are close to the mean of XBr_2 and XF_2 values.

TABLE 1

Boiling points of XBrF compounds relative to XBr_2 and XF_2

Compound	B.pts/°C		Mean
SPF_3	-52.5	\	36.4
$SPBr_2F$	125.3	/	
$SPBrF_2$	35.5		
OPF_3	-39.8	\	35.1
$OPBr_2F$	110.1	/	
$OPBrF_2$	30.5		
OCF_2	-83.1	\	-9.3
$OCBr_2$	64.5	/	
OCBrF	-20.6		

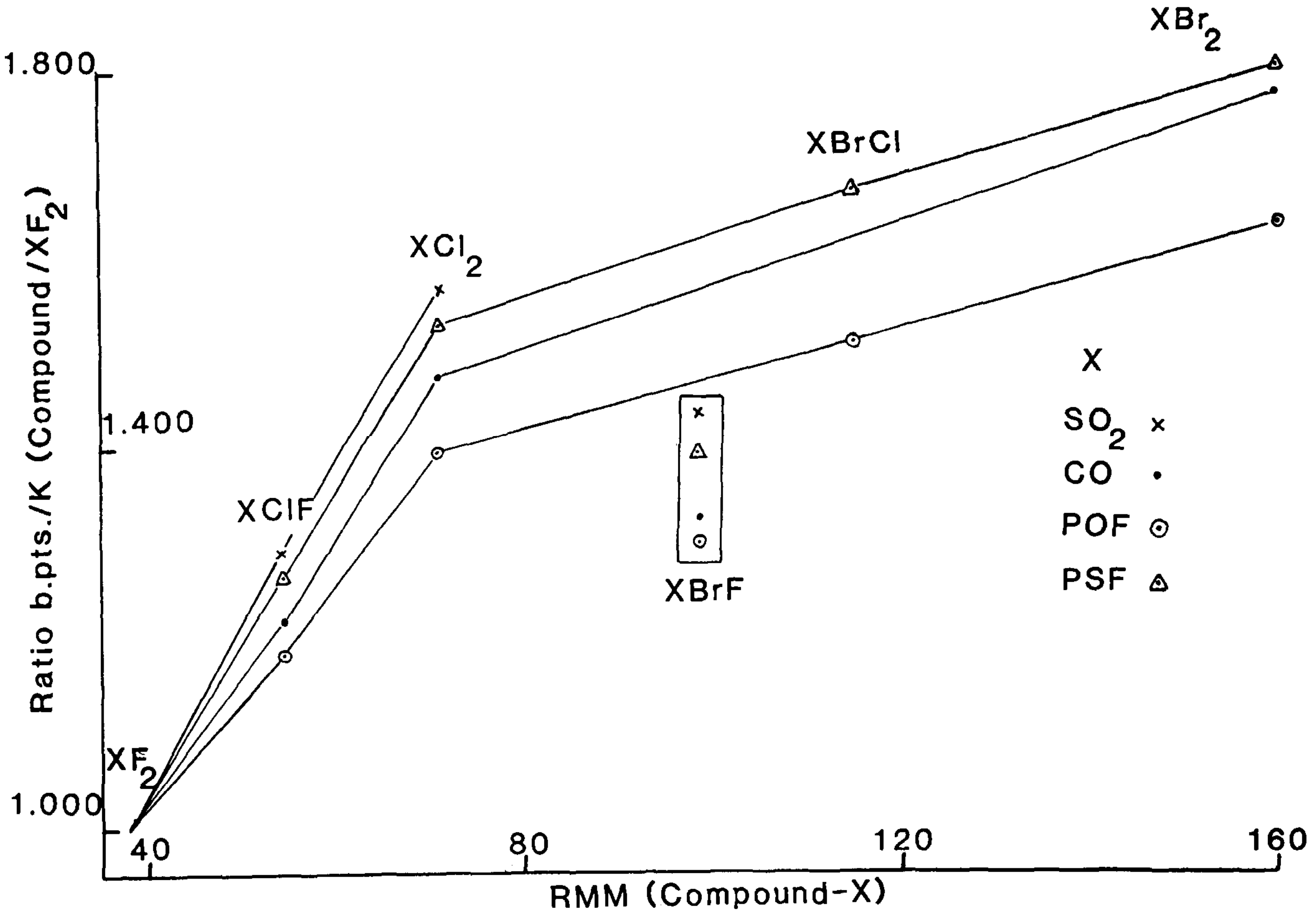

Fig.1. Boiling point ratios of compounds to difluorides as a function of relative molecular mass.

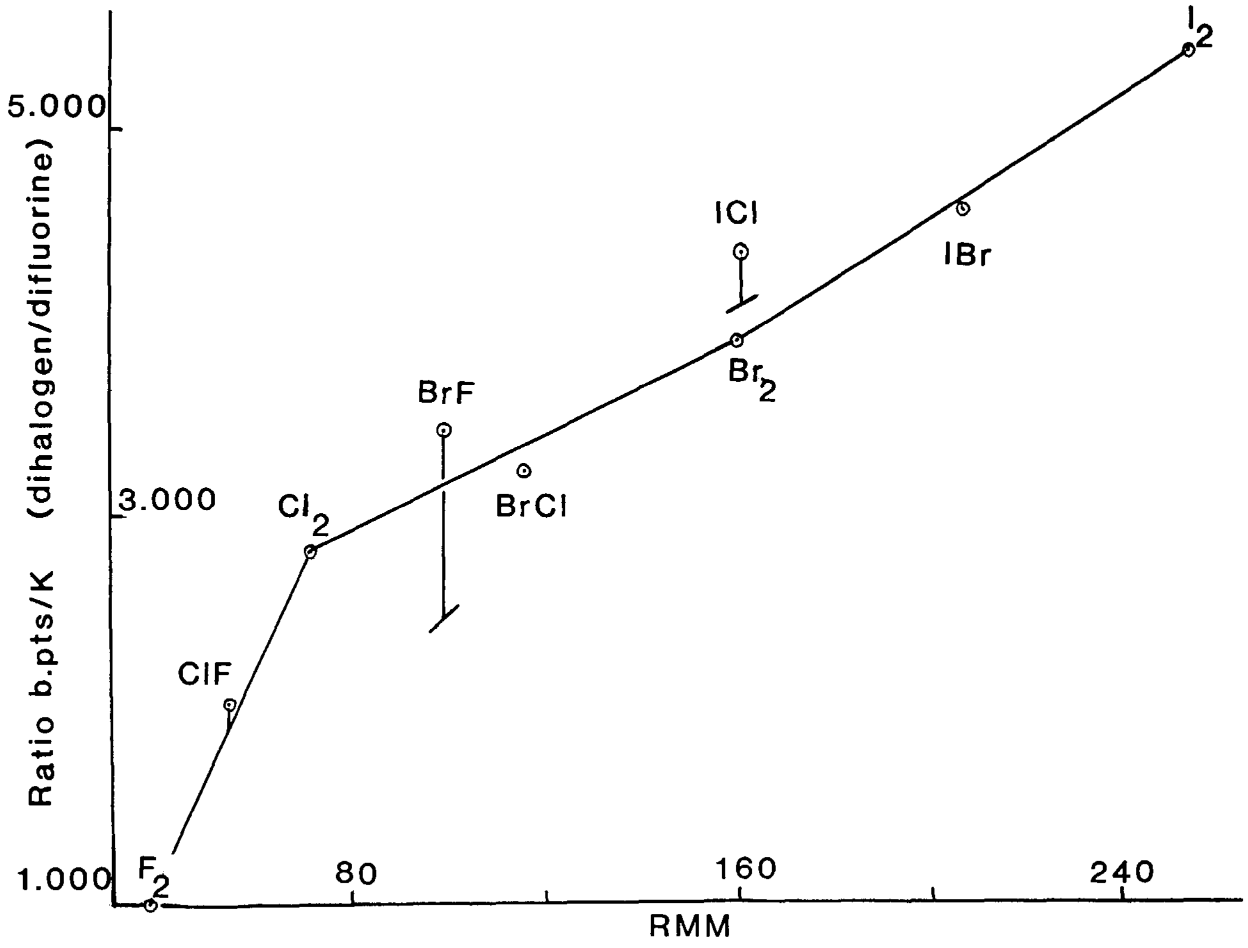

Fig.2. Boiling point ratios of dihalogens to difluorine as a function of relative molecular mass.

The implication is that BrF when modified by insertions becomes much less associated as expected from the almost complete self-cancellation of dipoles in the tetrahedral phosphorus compounds and the lesser effect in the triangular carbonyl compound.

The same treatment cannot be used with sulphuryl bromofluoride since the dibromide is unknown although one could estimate a boiling point from the pattern of Fig. 1. An alternative approach, relating the boiling points of SO_2BrF and BrF, is needed. This approach uses the linear relation between the elevation of boiling point , caused by inserting a moiety X in a fluorine bond, with the ratio R of RMM's before and after insertion i.e. $\Delta = A + BR$ where A and B are constants [1] Examples of SO_2 insertions into C-F bonds, collected in Table 2 and plotted in Fig.3, illustrate this relation. The corresponding insertions of SO_2 into three dihalogens Cl_2, F_2 and ClF gives a best line fit parallel to the fluorocarbon line (Table 3). However, the fourth point corresponding with insertion into BrF is far from the extrapolated elevation. The latter would give a predicted boiling point of 105°C for SO_2BrF about 65°C above the measured value.

From an examination of numerous homologous series [2] we know that deviations from linear relations occur when there is an appreciable difference in the states of association before and after insertion along the series. Thus a positive deviation is often encountered for the first member of a series which presents the minimum steric hindrance to dipole association. In this instance there is a negative deviation from the extrapolated boiling point of SO_2BrF because a less associated SO_2BrF is being formed from a more associated BrF. Hence a reduction by 84° to the boiling point of BrF, the difference between the boiling point of associated BrF and the mean of those for Br_2 and F_2, would be a first order correction to give a 'non-associated' boiling point for Br_2SO_2F bringing the $BrSO_2F$ point in Fig.3., much nearer the estimated value. A similar correction of 11° to the boiling point of ClF brings it in line with the other values.

TABLE 2

Boiling point elevations (Δ) after insertion of SO_2 into C-F bonds (in °C)

Fluoride Number	Fluoride (XF)	(1)	Sulphonyl Fluoride (XSO_2F)	(2)	(2-1)	RMM ratio (XF/XSO_2F)
1	C_8F_{18}	104	$C_8F_{17}SO_2F$	155	51	0.872
2	C_7F_{16}	82	$C_7F_{15}SO_2F$	135	53	0.858
3	C_6F_{14}	57	$C_6F_{13}SO_2F$	114	57	0.841
4	C_5F_{12}	29	$C_5F_{11}SO_2F$	90	61	0.818
5	C_4F_{10}	-1	$C_4F_9SO_2F$	64	65	0.788
6	C_3F_8	-38	$C_3F_7SO_2F$	36	74	0.746
7	C_6F_6	81	$C_6F_5SO_2F$	154.6	73.6	0.744
8	C_2F_6	-78	$C_2F_5SO_2F$	8	86	0.683
9	CF_4	-128	CF_3SO_2F	-21.7	106.3	0.579
10	C_6H_5F	85	$C_6H_5SO_2F$	207	122	0.600
11	C_2H_5F	-37.7	$C_2H_5SO_2F$	135	172.7	0.429
12	CH_3F	-78	CH_3SO_2F	124	202	0.347

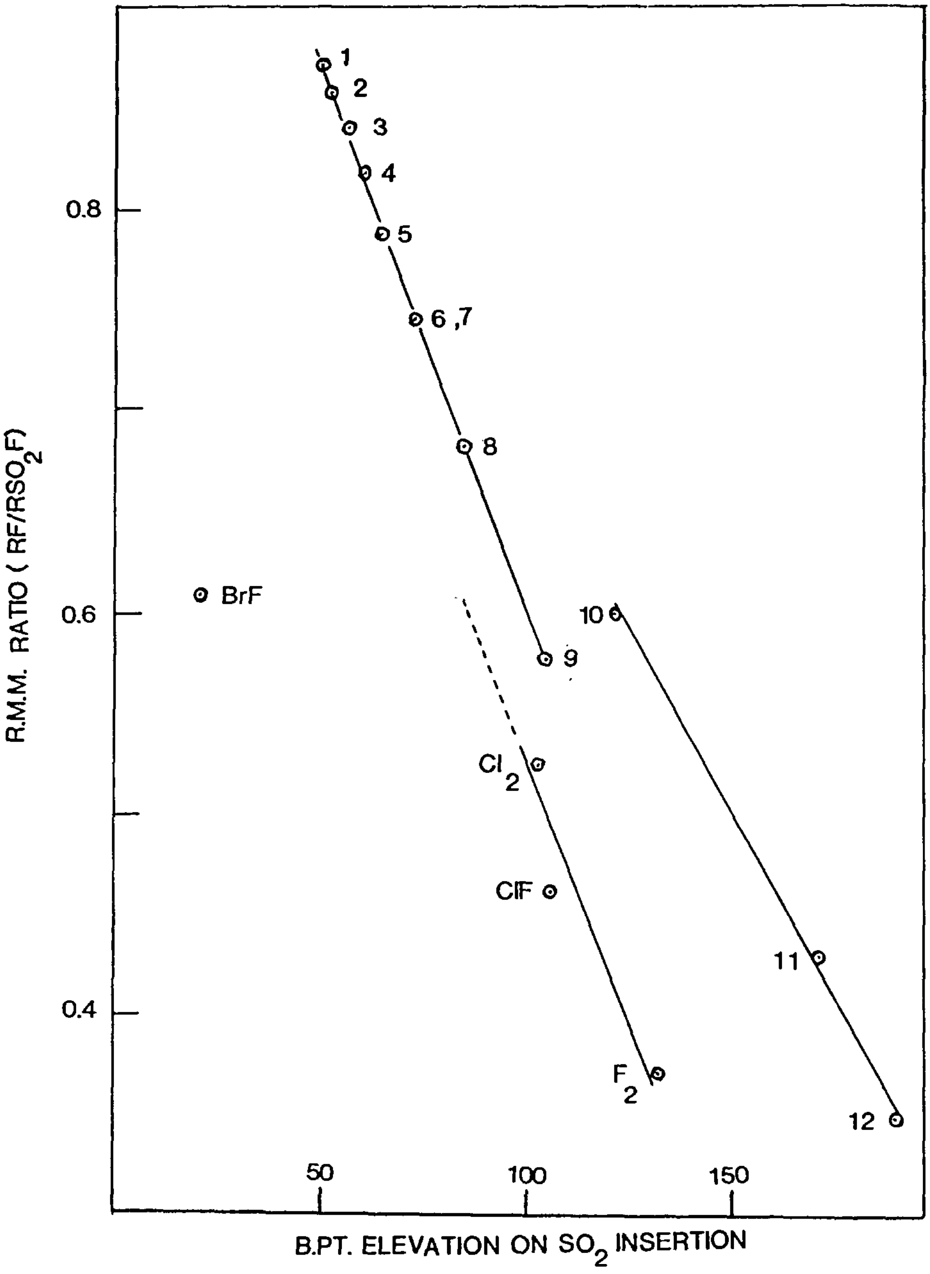

Fig.3. Boiling point elevations caused by SO_2 insertions into fluorides as a function of mass ratios before and after insertion.

TABLE 3

Boiling point elevations on insertion of SO_2 into dihalogens or interhalogens

	Boiling points in °C				
	(1)		(2)	(2-1)	X_2/X_2SO_2
F_2	-188.4	FSO_2F	-55.4	133	0.372
Cl_2	-34.7	$ClSO_2Cl$	69.3	104	0.525
ClF	-100.1	$ClSO_2F$	7.1	107	0.460
BrF	20	$BrSO_2F$	40	20	0.607

Linear regression equations $\Delta = A + BR$*

Process	A`	B	r
$R_fF + SO_2$	214.653	-188.336	0.9992
$RF + SO_2$	309.223	-313.204	0.9989
$X_2 + SO_2$	203.144	-195.601	0.9418

*B is the slope, R the RMM ratio, r the correlation coefficient
X_2 = dihalogen, or interhalogen fluoride.

However the BrF correction is probably overestimated because the quoted boiling point may be too high [3,4]. Bromine monofluoride cannot be isolated as a pure liquid or vapour; it is always contaminated with its main disproportionation products Br_2 and BrF_3 [5,6]. The boiling point of thermally stable* SO_2BrF

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* The first appearance of colour does not occur till it is heated to 320°C in a silica tube, and a value of $\Delta G^{\circ} = + 96.3$ kJ mol^{-1} can be estimated for the decomposition

$$SO_2BrF_{(l)} = SO_2(g) + BrF(g)$$

however, is likely to be reliable since it has been made on a large scale and the vapour pressure-temperature relation

$$\log p/\mathrm{mm} = 8.03 - \frac{1{,}610}{T/K}$$ established [7]

We conclude that the anomalously high volatility of XBrF compounds is due to two factors; firstly their non-associated nature which reduces their boiling points near to the mean of XF_2 and XBr_2 compounds, and secondly to the shape of the curves in Fig.1 and 2 resulting from the exceptionally low boiling points of F_2 or modified XF_2 compounds. A combination of the two factors causes deviations from the usual relation between boiling point and RMM, and this should apply to other low polarity bromofluorides as yet unknown eg XeO_2BrF and CrO_2BrF.

There are chemical implications. For example SO_2BrF in the liquid state would show little self dissociation and should be a mild reagent compared with BrF. In order to bring out its positive bromine character in reactions it would require the assistance of suitable donor species such as solvents. Apart from the hydrolysis no chemical reactions of SO_2BrF have been studied.

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