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Estimating the boiling points of nitrogen bromofluorides by isoelectronic comparisons

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Abstract

The boiling points of fluorides (XYZ), formed by the insertion of moieties (X) into dihalogens or binary interhalogens (YZ), can be related when expressed as reduced quantities, viz. the ratio of the absolute boiling points of XYZ to XF_2 or XCl_2. Most notable is the identity of the ratios for CF_2 and PF insertions which suggests an isoelectronic effect. Support for isoelectronic effects is provided by the matched boiling points found between whole series and some individual compounds. The boiling points of NF_2Br, $NFBr_2$, NFBrCl and other unknown bromo compounds may be predicted using the reduced quantities obtained by isoelectronic comparisons.

Introduction

There has been considerable interest recently in the preparation of *N*-haloamines [1–3]. In particular, Thrasher and DesMarteau were unable to synthesize *N*-bromofluorides using catalyzed bromination of $NFCl_2$ [3]. The inertness of NF_3 and R_fNF_2 is a barrier to the usual redistribution methods for obtaining mixed halo compounds and it is possible that perhaps NF_2 and NF radicals are better precursors for bromination. Whatever the method to be adopted, a knowledge of the boiling points and vapour pressures of the unknown nitrogen bromofluorides should be helpful in planning syntheses. These are estimated here by making use of previous observations on the 'anomalous' values of other bromofluorides [4].

Results and discussion

Various halides are considered to be derived by the insertion of small moieties X, where X is CO, POF, PSF or SO_2, into dihalogens or binary interhalogens YZ. The boiling points of the XYZ compounds were close to the mean of the XY_2 and XZ_2 values when YZ was BrCl, but less so for ClF or BrF. Further examples are provided when $X = CF_2$, SO and PF, respectively producing difluoromethanes, thionyl halides and phosphorus trihalides. The *absolute boiling points* are ratioed to those of XF_2 compounds in Table 1. These reduced quantities are more appropriate for comparative purposes

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TABLE 1

Absolute boiling point ratios of XYZ to XF_2 compounds

X	YZ					
	F_2	ClF	Cl_2	BrF	BrCl	Br_2
CO	1.000	1.216	1.477	1.329	–	1.777
CF_2	1.000	1.321	1.677	1.482	–	2.051
PF	1.000	1.318	1.675	1.500	–	2.051
NF	1.000	1.433	1.878	–	–	–
SO	1.000	1.244	1.525	–	–	1.797
POF	1.000	1.184	1.397	1.301	1.513	1.642
PSF	1.000	1.266	1.531	1.399	1.680	1.806
SO_2	1.000	1.290	1.573	1.437	–	–

Mean $XClF/(XCl_2+XF_2)=0.495\pm0.004$; $XBrF/(XBr_2+XF_2)=0.490\pm0.006$.

than *normal boiling points*. Although the virtual identity of the two rows corresponding to CF_2 and PF insertions is remarkable and may be coincidental, nevertheless it draws attention to isoelectronic influences. (Strict isoelectronic identity should be based on a constant electron to atom ratio, but a constant valency electron count suffices when 'lone pairs' or 'electride ions' behave as pseudo atoms, cf. VSEPR theory.) Certainly, examples of 'isoelectronic boiling points' are found with the perfluorocarbon series. Thus CF_2, NF and CO act as 6e inserts in the perfluoroalkane series, giving a close fit between the corresponding boiling points in the $R_fCF_2R_f'$, R_fNFR_f' and R_fCOR_f' series or between the R_fNF_2 and R_fCF_3 pairs. Similarly, the correspondence between the R_fSO_2F and R_fSF_5 series can be regarded as due to terminal insertions of 10e SO_2 and SF_4 moieties. Close isoelectronic boiling points are also encountered between individual fluorides [e.g. 12e SOF_4 (−49 °C) and SO_2F_2 (−55.4 °C), 11e $(FSO_2)CF_3$ (−21.7 °C), $(SF_5)CF_3$ (−20.4 °C), $(SF_5)NF_2$ (−18 °C) and $(FSO_2)NF_2$ (−18.2 °C), 10e POF_3 (−39.7 °C) and SOF_2 (−43.8 °C), 8e PF_3 (−101.8 °C) and ClF (−100.1 °C]. However, there are many irregularities when the intermolecular forces governing boiling points are not well matched. 'Ionizing' fluoro solvents, with a high degree of association, deviate considerably from neighbouring isoelectronic fluorides [e.g. 8e GeF_4 (−36.8 °C subl.) and AsF_3 (62.8 °C), 10e AsF_5 (−53.2 °C), SeF_4 (106 °C) and BrF_3 (127 °C)] and care must thus be exercised to ensure valid comparison and prediction.

In considering bromine substitution, comparison is possible between series when absolute boiling points are ratioed to those of dichlorides rather than difluorides, since the incremental increases on replacing chlorine by bromine are nearly constant in these series unlike the variations found on replacing fluorine by chlorine. The latter variations are inversely related to the mass of the insert X with the exception of three oxy inserts (Fig. 1). The ratios listed in Table 2 divide clearly into two sets separated by more than the mean deviations, one associated with 6e and with 8e inserts, and

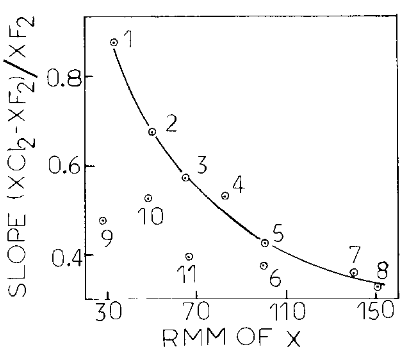

Fig. 1. Boiling point variations on replacing F in XF_2 by Cl as a function of the X mass. Key: XCl_2 and XF_2 values are absolute boiling points. 1, NF; 2, PF and CF_2; 3, SO_2; 4, PSF; 5, CF_3CF; 6, CF_3P; 7, SF_5N; 8, C_2F_5CF; 9, CO; 10, SO, and 11, POF.

TABLE 2

Absolute boiling point ratios of XYZ to XCl_2 compounds

Ratio	X=	CO	PF_2	PF		Mean
$XBrF/XCl_2$		0.897	0.884	0.896		0.892 ± 0.006
XBr_2/XCl_2		1.203	1.223	1.224		1.217 ± 0.009

Ratio	X=	SO	SO_2	POF	PSF	Mean
$XBrF/XCl_2$		–	0.914	0.931	0.914	0.920 ± 0.008
XBr_2/XCl_2		1.179	–	1.175	1.180	1.178 ± 0.002

the other one associated with 10e inserts. For calculating the boiling points of NF insertions, comparison is made with CF_2 and PF insertions but not with CO ones, since planar carbonyl halides would be expected to be more associated with a closer dipole approach possible than with the other tetrahedral molecules.

The estimated boiling points of the missing entries in Table 1 are collected in Table 3, the errors arising from the deviations in Table 2 being within ± 1 °C. Approximate vapour pressures may be obtained for the NFYZ compounds assuming the NF_2Cl values of 88 J K^{-1} mol^{-1} [5] hold for all the Trouton constants. The vapour pressure p (mm Hg) at T(K) is related to the normal boiling point T_b by $\ln(p/760) = 10.59\ (1 - T_b/T)$, whence $p = e^{[10.59(1-T_b/T)+6.633]}$.

More generally, boiling points in other *related* series may be similarly estimated, e.g. those in the unknown SF_2YZ series by comparison with the corresponding thionyl thalides, or in the incomplete series formed with PCF_3 or SF_5N inserts [7].

TABLE 3

Estimated boiling points of unknown bromo compounds XYZ expressed in °C

X	YZ		
	BrF[b]	BrCl[a]	Br_2[b]
CO	+	36.1	+
CF_2	+	−2.2	+
PF	+	46.2	+
NF	−32.3	27.7	57.9
SO	51.3	107.8	+
SO_2	+	99.8	130.3

+Known values.

[a] Taken as mean of XBr_2 and XCl_2 values.

[b] Calculated from XBr_2/XCl_2 ratios listed in Table 2 using boiling point for $NFCl_2$ of −2.5 ± 0.5 °C [6].

References

1 J. Foropoulos and J. M. Shreeve, *Inorg. Chem.*, *30* (1991) 2699.
2 J. V. Gilbert, R. Conklin, R. D. Wilson and K. O. Christe, *J. Fluorine Chem.*, *48* (1990) 361.
3 J. S. Thrasher and D. D. DesMarteau, *J. Fluorine Chem.*, *52* (1991) 51.
4 A. A. Woolf, *J. Fluorine Chem.*, *46* (1990) 255.
5 R. C. Petry, *J. Am. Chem. Soc.*, *82* (1960) 2400.
6 B. Sukornik, R. J. Stahl and J. Gordon, *Inorg. Chem.*, *2* (1963) 875.
7 D. D. DesMarteau, H. H. Eysel, H. Oberhammer and H. Günther, *Inorg. Chem.*, *21* (1982) 1607.