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Correlating boiling points of fluorinated amines

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Abstract

The elevations of boiling point (Δ) when NH or NR groups are inserted into alkanes, and NR_f into perfluoroalkanes, are linearly related to the mass ratios (R) before and after insertion by $\Delta = A + BR$ where A and B are nearly equal constants for each series, resulting in a convergence of boiling points of amine and alkane on extrapolation to long chain length ($R = 1$). This does not hold for NCF_3 insertion into the C−C bonds of alkanes. Instead members of the CF_3NRR' series are predicted to boil below those of the corresponding alkanes containing more than 14 carbon atoms. It is suggested that the difference in behaviour of NCF_3 and NCH_3 insertions is due to the presence of dipoles of opposite polarity in the mixed alkyl–perfluoroalkyl amines. NF insertions into R_f-R_f' and R_f-F give non-linear relations. However NF, as well as CO, behave as pseudo CF_2 groups when considering their effect on the boiling points of perfluoroalkanes.

Introduction

Fluorinated amines can be divided into the inert perfluorinated amines $N(R_f)_3$ resembling perfluoroalkanes in stability; $(R_f)_2NF$ and R_fNF_2 regarded as NF_3 derivatives; and the mixed alkyl–perfluoro or polyfluoroalkyl amines typified by the *N*-trifluoromethyl-dialkyl amines used as fluorinating agents, in which, surprisingly, the CF_3 groups are easily hydrolysed [1–3]. In a recent survey of boiling points (b.p.s) in homologous series, formed hypothetically by inserting small entities into C−H or C−C bonds in alkanes, a simple relation emerged between the elevation of the alkanes' b.p. (Δ) after insertion and the relative masses (R) before and after insertion, viz. $\Delta = A + BR$. In most instances this approximates to $\Delta = A(1 - R)$ where A and B are constants for a particular series [4]. The elevation is ascribed to the intermolecular association of the dipoles formed on insertion, the effect of which diminishes as the chain lengthens. The predominant dipolar attractions are isolated from the van der Waal's ones by taking the alkanes as the reference series. In the normal series the increase in b.p. is proportional to the amount of dipole present. In the limit, the dipole effect should vanish at $R = 1$ if $A = -B$. (The precision in b.p. data, and the required extrapolation, limits this equality. Generally correlation coefficients r are -0.998 or better, and $(A + B)$ values are zero within 10° limits). Deviations from this behaviour reveal the presence of other forces. Thus with alcohols and diols, and less so for dithiols, deviations from linearity show the additional effect of hydrogen

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bonding. Another deviation from linearity encountered with bromofluorides has also been described [5]. It was hoped that an examination of b.p. relations in amine series might throw some light on the above mentioned differences between the fluorinated amines.

Results and discussion

The genesis of some amines is indicated in Table 1.

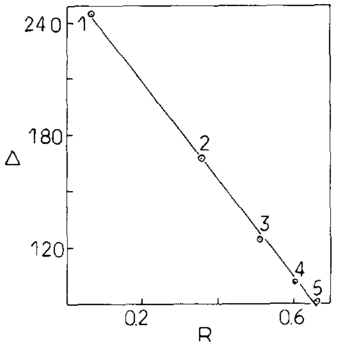
Good linear relations are found for NH insertions into alkanes, e.g. $\Delta = 326.1 - 333.3R$ for NH into R—R holds with the available data up to C_{16} with $r = -0.998$. The relation $\Delta = 262.1 - 262.3R$ ($r = -0.999$) for NMe into R—H is shown in Fig. 1 with the extrapolation back to insertion into H—H to form methylamine. Similarly NR_f insertions into perfluoroalkanes give linear relations. The NC_2F_5 insertion, which yields $\Delta = 200.5 - 199.5R$ ($r = -0.9995$) in Fig. 2 and Table 2 can also be extrapolated back to an insertion into F—F. The extrapolated b.p. of $C_2F_5NF_2$ is 156 °C compared with the experimental value of 150 °C.

Insertion of NCF_3 into C—C alkane bonds is compared with the corresponding insertion of NCH_3 in Fig. 3. The latter is fitted by $\Delta = 181.8 - 171.2R$

TABLE 1

Formation of amines by NX insertion into hydro- or fluoro-carbons

Insertion	Bond to be inserted		
	R—H, R_f—H	R—R′, R_f—R_f′	R_f—F
NH	primary	secondary	
NR, NR_f	secondary	tertiary	tertiary
NF	—	tertiary	tertiary



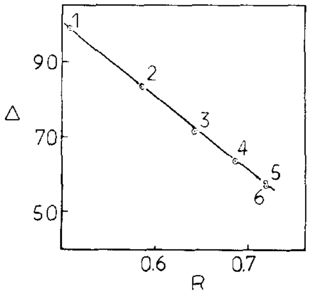


Fig. 1. Elevations of b.p. (Δ) on insertion of NMe into R—H bonds plotted versus mass ratio (R). 1, $MeNH_2$; 2, Me_2NH; 3, Et_2NH; 4, Pr_2NH; 5, Bu_2NH.

Fig. 2. Elevations of b.p. (Δ) on insertion of NC_2F_5 into R_f—R_f′ bonds plotted versus mass ratio (R). See Table 2 for numbering of perfluoroamines.

TABLE 2

Elevation of b.p.s (Δ) on insertion of NC_2F_5 into R_f-R_f' bonds

R_fF	B.p. (°C)	[a]	$R_fR_f'NC_2F_5$	B.p. (°C)	Δ	R[b]
C_2F_6	−78.7	1	$(CF_3)_2NC_2F_5$	20.5	99.2	0.509
C_3F_8	−37.5	2	$C_2F_5CF_3NC_2F_5$	46	83.5	0.586
C_4F_{10}	−1.3	3	$(C_2F_5)_2NC_2F_5$	70.3	71.6	0.642
C_5F_{12}	29.3	4	$C_3F_7C_2F_5NC_2F_5$	93	63.7	0.684
C_6F_{14}	57.2	6	$(C_3F_7)_2NC_2F_5$	114	57.0	0.718
		5	$C_4F_9C_2F_5NC_2F_5$	115	58.0	0.718

[a] Numbering in Fig. 2.
[b] RMM ratio for $R_fF/R_fR_f'NC_2F_5$; R for $F_2/C_2F_5NF_2 = 0.222$.

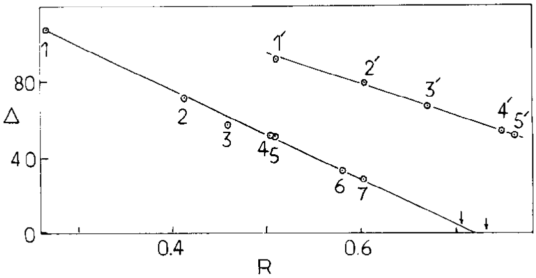


Fig. 3. Elevations of b.p. (Δ) on insertion of NMe and NCF_3 into R—R bonds plotted versus mass ratio (R). See Table 3 for numbering of N-trifluoromethyl amines (1–7). 1′, NMe_3; 2′, NMe_2Et; 3′, $NMeEt_2$; 4′, $NMe_2C_5H_{11}$; 5′, $NMe_2C_6H_{13}$. The arrows indicate the R values for tetra- and hexa-decanes.

TABLE 3

Elevation of b.p.s (Δ) on insertion of NCF_3 into R—R bonds

Alkane	B.p. (°C)	[a]	N-Trifluoromethyl amine	B.p. (°C)	Δ	R
C_2H_6	−88.6	1	$(CH_3)_2NCF_3$	20	108.6	0.266
C_4H_{10}	−0.5	2	$(C_2H_5)NCF_3$	71	71.5	0.412
cyclopentane	50	3	$(CH_2)_5NCF_3$	107	57	0.458
cyclohexane	81	4	$(CH_2)_6NCF_3$	133	52	0.503
Pr^i_2	58	5	Pr^i_2 NCF_3	109	51	0.509
Bu^i_2	109.4	6	Bu^i_2 NCF_3	143	33.6	0.579
1,1,2,2-tetramethyl cyclopentane	142[b]	7	$[Me_2C(CH_2)_3CMe_2]NCF_3$	171	29	0.603

[a] Numbering in Fig. 3.
[b] Estimated from other cyclopentane values.

($r = -0.999$). However, NCF_3 insertion, admittedly with a more varied set including cycloalkanes (Table 3), while still linear ($\Delta = 169.0 - 234.3R$) differs in having a very negative Δ value of -65.3 at $R = 1$ which implies that members of the CF_3NRR' series will have lower b.p.s than the corresponding alkanes with more than 14 carbons. This distinctive behaviour has not been previously encountered with any other linear series. A possible explanation is that only the mixed alkyl–perfluoroalkyl amines possess dipoles of opposite polarity ($\overleftarrow{N-R}$ and $\overrightarrow{N-CF_3}$). The overall dipolar effect decreases to zero before reversing leading to a zero elevation before $R=1$. The influence of the CF_3 group seems to predominate in the present series of compounds as evidenced by the loss of nitrogen basicity inhibiting adduct formation with BF_3. However, the effect of the $N-CF_3$ dipole should decrease as the alkane chains lengthen. It would be instructive to examine compounds containing 16 or more alkane carbons, corresponding with the crossover point in Fig. 3, to see whether there is any basicity change perhaps using a 'super' proton acid system at low temperature as a more sensitive indicator than the simple Lewis acid. The susceptibility to hydrolysis and the fluorinating ability may also change.

Finally NF insertions into R_f-F and R_f-R_f' bonds produce non-linear relations. However, the b.p.s of the R_fNF_2 or R_fNFR_f' series, as previously observed, correspond quite closely with those of the next higher perfluoro homologues, *i.e.* $R_fNF_2 \equiv R_fCF_3$ and $R_fNFR_f' \equiv R_fCF_2R_f'$. In this respect NF, CO or a combination of both as in $R_fR_f'NCOF$, behave as pseudo CF_2 groups possibly because they are isoelectronic, but not isostructural, if only valency electrons are counted ($>\overset{5}{N}-\overset{1}{F}$; $>\overset{4}{C}=\overset{2}{O}$; $>\overset{4}{C}\overset{2}{F_2}$) (e.g. $C_5F_{11}NF_2$, 57.5°; C_6F_{14}, 57.2°: $C_3F_7COCF_3$, 29.8°; $C_2F_5COC_2F_5$, 27°; C_5F_{12}, 29.3: and $(C_2F_5)_2NCOF$, 59°; $C_3F_7CF_3NCOF$, 58°; C_6F_{14}, 57.2°). This treatment can be extended to $N(R_f)_3$ amines where the b.p.s of n-perfluoroalkanes formed by replacing N by CF lie 10° higher, e.g. $N(C_3F_7)_2C_2F_5$, 115°; C_9F_{20}, 125.3°: $N(CF_3)_3$, -10.5°; C_4F_{10}, -1.3°:, etc. Similar isoelectronic equivalence is encountered between the R_fSO_2F and R_fSF_5 series, in this instance with 10e SO_2 and SF_4 groups as insertions.

References

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