Interaction between Tertiary Amines and Perfluoro-organo-halides

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WE report the detection of solid adducts of simple stoicheiometry between the compounds R_fX and tertiary amines where X is Br or I, and R_f is a fully fluorinated alkyl or aromatic group. The group R_f is strongly electron-attracting and it might be expected that electron donor–acceptor complexes $[R_fX,NR_3;\ (R = \text{alkyl})]$ similar to (I_2,NR_3),[1] would exist. Such complexes dissociate reversibly into unchanged acceptor and donor.

Phase studies similar to those of Holmes[2] were undertaken on the systems indicated in the Table, enabling the stoicheiometries of the solid adducts to be established.

The figure shows a typical phase diagram. A detailed explanation of this type of diagram has been given by Hill.[3] Starting from pure halide, region A consists of two phases, vapour and liquid solution, and is univariant at constant temperature. Region B is invariant at constant temperature, the phases present being vapour, liquid solution, and

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[1] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1600.
[2] R. R. Holmes, *J. Phys. Chem.*, 1960, **64**, 1295.
[3] A. E. Hill, *J. Amer. Chem. Soc.*, 1935, **53**, 2598.

solid adduct. Similar considerations apply to regions E and D. The abrupt pressure change in region C corresponds to solid adduct in equilibrium with vapour and gives the stoicheiometry of the adduct. These phase changes can be seen in the reaction vessel.

This interpretation is supported by preliminary infrared-spectroscopic study of the solid complexes of CF_3Br and CF_3I with trimethylamine. In the complexes the frequencies of the halogen stretching vibrations are decreased and the intensities markedly relative to solid CF_3Br and CF_3I. This behaviour is similar to that reported for the complexes of ICl, ICN, Br_2, and Cl_2 with electron donors.[5]

TABLE

Amine	*Halide*	*Amine : Halide*[a]	*Temperature*[b] (°c)	
Trimethylamine	CF_3I	1 : 1	−96	−84
Trimethylamine	CF_3Br	1 : 1	−96	−84
Trimethylamine	n-C_3F_7I	1 : 1	−65	−23
Trimethylamine	C_6F_5I	1 : 1	−37	−23
Trimethylamine	$Br[CF_2]_2Br$	2 : 1	−65	−50
$Me_2N[CH_2]_2NMe$	CF_3Br	1 : 2	−96	−65

[a] Stoicheiometries of solid adducts.

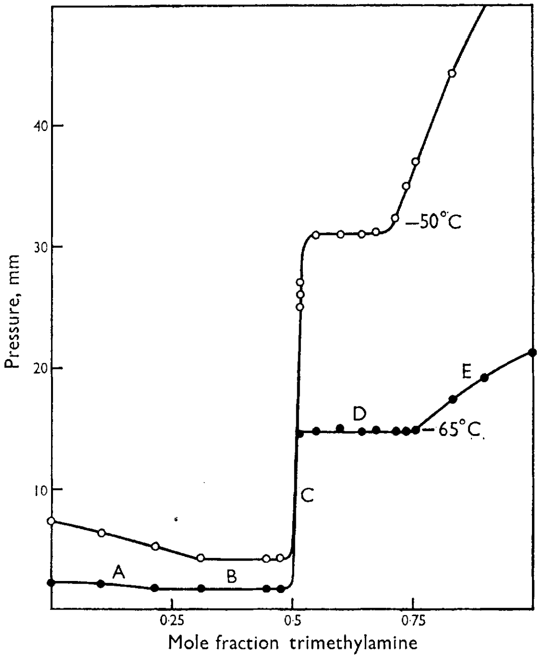
[b] Temperature ranges within which a solid was studied.

Since irreversible adduct formation between trifluoroiodomethane and trimethylamine has been found,[4] it was important to be sure that this was not taking place under our experimental conditions. In preliminary experiments, a small quantity of a white solid, involatile at room temperature, was deposited in the vacuum line. This was not characterised as it was not formed following changed experimental conditions. All subsequent work was carried out in subdued light between −96° and 0°c, the duration of a separate experiment being less than twelve hours.

In all systems the interaction appeared to be reversible. The trifluoroiodomethane–trimethylamine adduct was formed at −83°c (dissociation pressure 3·5 mm.), and distilled into a trap containing n-heptanoic acid. 83% of the initial trifluoroiodomethane was easily recovered unchanged, together with some of the remainder contaminated with trimethylamine.

All systems in the table exhibited large negative deviations from Raoult's Law at temperatures such that the solid phase was absent. Similar behaviour was observed with the systems n-heptafluorobromopropane–trimethylamine and pentafluorobromobenzene–trimethylamine, the deviations observed being significantly less than those involving the corresponding iodo-halides.

The reversible nature of these interactions and the stoicheiometries of the solid adducts suggest an explanation of our results in terms of electron donor–acceptor interaction involving the nitrogen atoms of the amines and the X-atoms of the halides.



The system n-heptafluoroiodopropane–trimethylamine

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[4] R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, **1956**, 3631.

[5] W. B. Person, R. E. Erickson, and R. E. Buckles, *J. Amer. Chem. Soc.*, **1962**, **82**, 29.