Xenon Difluoride as an Oxidative Fluorinator

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XENON DIFLUORIDE is easy to make, and[1,2] relative to other xenon fluorides, safe to handle. It is therefore attractive as a reagent. Because of its low average bond energy[3] (~30 kcal. mole^{-1}) and the "inertness" of its reduction product (Xe) it has considerable potential in oxidative fluorinations. However, others have shown that the compound has considerable kinetic stability, *e.g.* it may be retrieved from aqueous solution[4] in which it is thermodynamically unstable towards hydrolysis.

In the course of a systematic study of the difluoride we have found that fluoride-ion acceptors promote its oxidative fluorinator ability. Structural evidence suggests that the important reactive species may well be XeF^+ and $Xe_2F_3^+$.†

Xenon difluoride dissolves in the following solvents without oxidation or reduction, the solubility being: BrF_5, very good; BrF_3, very good; IF_5, good[6]; CH_3CN, good; HF, fair[6]; SO_2, fair[7]; WF_6, poor. Of these only IF_5 gives a stable adduct. Xenon difluoride does not interact with NH_3 (liq.) but the solubility can only be slight. A similar observation has been made by Meinert *et al.*[7] All of the solutions are stable if dry or acid-free. Stability can be assured by the addition of caesium fluoride which presumably owes its effectiveness to its ability to combine with acid.

Dry acetonitrile solutions showed no evidence of interaction between dissolved I_2 and XeF_2; indeed the solutions could be preserved for several days

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† See following Communication.

without diminution of the purple iodine colour, particularly if alkali fluoride was present. On the other hand, the introduction of a trace of acid led to rapid oxidation of the iodine as indicated in the Table.

Acid catalysis of I_2 *oxidation by* XeF_2, *in* CH_3CN *solution*

Acid	Temp. at reaction onset	Induction period	Comments
None (CsF present)	23°	—	No reaction even after several days.
Neat soln.	23	Several hours	Trace of H_2O? + $XeF_2 \rightarrow HF$ (footnote).
SO_2 (trace)	23	Several minutes	These reactions were complete within a few seconds of their onset. IF_5 and Xe were the only identified products (but see footnote).
HF (trace	−20	Immediate	
BF_3 (trace)	−70	Immediate	

The reaction in "neat" CH_3CN proceeded more slowly than in the "acid-catalysed" cases. The initial, transient, product was dark brown, which suggests, from Schmeisser's description,[8] IF. This colour quickly disappeared; IF_5 was the sole iodine fluoride detected in the products.

Sulphur dioxide solutions of XeF_2 behaved similarly: SO_2 is itself an effective reducer and the addition of a trace of acid led to very rapid production of xenon and sulphuryl fluoride at low temperatures

$$(BF_3,\ -70°;\ HF\ -20°):\ XeF_2 + SO_2 + (\text{acid}) \rightarrow SO_2F_2 + Xe$$

These findings may be simply rationalized by supposing that the acids facilitate XeF_2 ionization:

$$XeF_2 + A \rightarrow XeF^+ + AF^- \text{ or } 2XeF_2 + A \rightarrow Xe_2F_3^+ + AF^-$$

Presumably the electron affinity of XeF^+ and $Xe_2F_3^+$ is greater than that of XeF_2 and the transfer of an electron to either of these cations would generate the XeF radical, as an effective fluorine-atom source. The dipolar nature of XeF^+ or $Xe_2F_3^+$ could contribute to their reactivity.

The utility and strength of xenon difluoride as an oxidizer is well illustrated by the interaction with γ-sulphur trioxide. This reaction proceeds spontaneously, well below room temperature, according to the equation:

$$3\ XeF_2 + 2(SO_3)_3 \rightarrow 3\ Xe + 3\ S_2O_6F_2$$

The peroxydisulphuryl difluoride, $S_2O_6F_2$, was characterized by its strong i.r. bands at **1490**, **1246**, **846** (PQR), and **752** cm.$^{-1}$.[9] The yield is quantitative. This compound has proved to be a valuable reagent and this synthesis provides an attractive alternative to those given by Cady and his co-workers.[10] The efficiency of the synthesis and, particularly, the lack of $S_2O_5F_2$ in the product, suggests that the rather stable SO_3F radical[11] is the product of attack on the oxygen bridged trimer (γ-SO_3). An ionic mechanism involving ring opening by F^- addition followed by XeF^+ electrophilic attack on the terminal $[SO_4]$ group, *e.g.*, $F(O)_2S\text{–}O\text{–}S(O)_2\text{–}O\text{–}SO_3^- + XeF^+ \rightarrow F(O)_2S\text{–}O\text{–}SO_3^- + FSO_3 + Xe$, *etc.*, can provide an adequate explanation for the reaction, although there are at present no kinetic data to support such a hypothesis.

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[1] L. V. Streng and A. G. Streng, *Inorg. Chem.*, 1965, **4**, 1370.
[2] J. H. Holloway, *Chem. Comm.*, 1966, 22.
[3] B. Weinstock, E. E. Weaver, and C. P. Knop, in "Noble-Gas Compounds", ed. H. H. Hyman, University of Chicago Press, Chicago, 1963, p. 50.
[4] E. H. Appelman and J. G. Malm, *J. Amer. Chem. Soc.*, 1964, **86**, 2297.
[5] H. Meinert and S. Rüdiger, *Z. Chem.*, 1967, **7**, 239.
[6] H. H. Hyman and L. A. Quarterman, in "Noble-Gas Compounds", ed. H. H. Hyman, University of Chicago Press, Chicago, 1963, p. 275.
[7] H. Meinert, G. Kauschka, and S. Rüdiger, *Z. Chem.*, 1967, **7**, 111.
[8] M. Schmeisser and E. Scharf, *Angew. Chem.*, 1960, **72**, 324.
[9] F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 513.
[10] J. M. Shreeve and G. H. Cady, *Inorg. Synth.*, 1963, **7**, 124.
[11] F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, 1963, **85**, 3375.