

Xenon Difluoride as an Oxidative Fluorinator

By NEIL BARTLETT* and F. O. SLADKY

(Frick Chemical Laboratories, Princeton University, Princeton, New Jersey 08540)

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 energy³ (~ 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 solution⁴ 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 $\text{Xe}_2\text{F}_3^{+\dagger}$

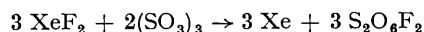
Xenon difluoride dissolves in the following solvents without oxidation or reduction, the solubility being: BrF_5 , very good; BrF_3 , very good; IF_5 , good⁶; CH_3CN , good; HF , fair⁶; SO_2 , fair⁷; WF_6 , poor. Of these only IF_5 gives a stable adduct. Xenon difluoride does not interact with NH_3 (liq.) 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

† 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.

with γ -sulphur trioxide. This reaction proceeds spontaneously, well below room temperature, according to the equation:

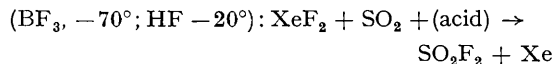


Acid catalysis of I₂ oxidation by XeF₂, in CH₃CN solution

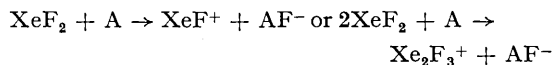
Acid	Temp. at reaction onset	Induction period	Comments
None (CsF present)	23°	—	No reaction even after several days.
Neat soln. . . .	23	Several hours	Trace of H ₂ O? + XeF ₂ → HF (footnote).
SO ₂ (trace) . . .	23	Several minutes	These reactions were complete within a few seconds of their onset. IF ₃ and Xe were the only identified products (but see footnote).
HF (trace)	-20	Immediate	
BF ₃ (trace) . . .	-70	Immediate	

The reaction in "neat" CH₃CN proceeded more slowly than in the "acid-catalysed" cases. The initial, transient, product was dark brown, which suggests, from Schmeisser's description,⁹ IF₃. This colour quickly disappeared; IF₃ was the sole iodine fluoride detected in the products.

Sulphur dioxide solutions of XeF₂ behaved similarly: SO₂ 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



These findings may be simply rationalized by supposing that the acids facilitate XeF₂ ionization:



Presumably the electron affinity of XeF⁺ and Xe₂F₃⁺ is greater than that of XeF₂ 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 Xe₂F₃⁺ could contribute to their reactivity.

The utility and strength of xenon difluoride as an oxidizer is well illustrated by the interaction

The peroxydisulphuryl difluoride, S₂O₆F₂, 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 S₂O₅F₂ in the product, suggests that the rather stable SO₃F radical¹¹ is the product of attack on the oxygen bridged trimer (γ -SO₃). An ionic mechanism involving ring opening by F⁻ addition followed by XeF⁺ electrophilic attack on the terminal [SO₃] group, *e.g.*, F(O)₂S-O-S(O)₂-O-SO₃⁻ + XeF⁺ → F(O)₂S-O-SO₃⁻ + FSO₃ + Xe, *etc.*, can provide an adequate explanation for the reaction, although there are at present no kinetic data to support such a hypothesis.

We acknowledge support of this work by The National Science Foundation.

(Received, May 6th, 1968; Com. 569.)

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.