

A SYNTHESIS OF XENON DIFLUORIDE NOT INVOLVING USE OF ELEMENTAL FLUORINE

Sir:

Although the existence of noble gas fluorides has excited intense interest in recent months, each of the preparative methods¹⁻⁴ heretofore described has involved manipulation of elemental fluorine. This Laboratory is engaged currently in the exploration of new approaches to the synthesis of noble gas compounds by techniques involving neither fluorine handling nor high pressure or high temperature instrumentation.

Among the pathways to xenon fluoride synthesis currently being explored here are the use of high voltage electric and microwave powered discharges in mixtures of xenon and a variety of perfluorinated species, and the vacuum ultraviolet photolysis of these mixtures using xenon and krypton resonance lamps. Among the fluorination reagents being evaluated are CF₄ and SiF₄.

These approaches were suggested by a considerable volume of literature pertaining to noble gas photosensitized reactions,⁵ and by the frequent observation of ionic species containing xenon in mass spectrometric studies.⁶

Abstraction reactions involving various ionic and electronically excited species of xenon, and simple perfluorinated species, seemed a promising route to the formation of xenon difluoride. The well known 1470 Å line of xenon, for example, corresponds to an available energy of 194.5 kcal. An estimate of the C-F bond dissociation energy in CF₄, for example, is 121 kcal.⁷ and the stripping of a second fluorine atom, to produce CF₂, would be expected to require substantially less energy. Further, CF₂ appears to be a relatively stable species capable, however, of elimination by polymerization.^{5,8}

We wish to report, at this stage, the demonstrated possibility of routinely successful syntheses of XeF₂ using a high voltage discharge in approximately equimolar mixtures of xenon and CF₄.

The apparatus consisted of a simple U-tube immersed in a refrigerant bath, and equipped with neon-sign electrodes, appropriate flow regulating valves and a high vacuum sampling train. The discharge was powered by a commercial neon-sign transformer operated near, or somewhat above, its rated capacity of 6000 v. at 120 ma.

The Pyrex discharge tube, having an approximate diameter of 25 mm. and a distance between electrodes of 360 mm., was refrigerated with Dry Ice and acetone, thus maintaining the walls of the reaction zone at temperatures above the boiling points of the reactants.

In a typical experiment, two l.-atm. of reaction mixture are permitted to flow through the discharge zone over periods of 1-2 hr. Upon terminating the discharge, a white microcrystalline or amorphous material is found, collected largely in the bottom of the U-tube.

After distillation, a white, nonvolatile organic residue remains in the discharge region. The volatile component, condensed in the sampling train, appears to contain at least two fractions condensable at -78°. The more volatile of these can be removed by flash evacuation at room temperature. The amounts of this material have been insufficient for physical characterization.

(1) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(2) J. H. Holloway and R. D. Peacock, *Proc. Chem. Soc. (London)*, **389** (1962).

(3) J. L. Weeks, C. L. Chernick and M. S. Matheson, *J. Am. Chem. Soc.*, **84**, 4612 (1962).

(4) A. V. Grosse, A. D. Kirshenbaum, A. G. Streng and L. V. Streng, *ibid.*, **85**, 360 (1963).

(5) See, for example: J. R. Dacey and J. W. Hodgins, *Can. J. Res.*, **28**, 173 (1950).

(6) See, for example: M. S. B. Munson, F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **37**, 1790 (1962).

(7) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958, p. 275.

(8) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).

The remaining fraction on standing undergoes spontaneous distillation with recrystallization at room temperature, forming clear, colorless, well formed crystals adhering to the walls of the storage vessel. Typical yields have been 50-150 mg. It must be emphasized that no serious effort has been made to optimize discharge conditions or to prefluorinate the sampling train.

Mass spectrographic analysis of these crystals was performed with a Consolidated Electrodynamics Model 21-103C instrument. The mass spectrum demonstrated conclusively that the crystals were the expected XeF₂. Peaks corresponding to XeF₂⁺, XeF⁺, Xe⁺ and Xe⁺⁺ were observed, having the correct isotopic distribution. Trace quantities corresponding to still higher masses were observed also.

It is noteworthy that the first injection of vapor into the mass spectrograph sampling manifold resulted merely in deactivation of interior surfaces and contaminants, producing as a consequence the mass spectrum of xenon in correct isotopic distribution. Analogous phenomena had been observed earlier, typically in distillation of the XeF₂ in the un-prefluorinated glass vacuum system.

The infrared spectrum of the vapor phase in equilibrium with these crystals was recorded at approximately 24°, using a 10-cm. gas cell equipped with KBr windows. A Beckman IR-4 spectrometer employing CsBr optics was used for these measurements. The vapor spectrum was found to exhibit a band with P and R components centered at 549 cm.⁻¹ and 564 cm.⁻¹, respectively. The previous observation by D. F. Smith⁹ that greater intensity is associated with the R branch is confirmed. In addition, an extremely weak absorption was observed at 520 cm.⁻¹. It may be significant to note that Smith has estimated a frequency of 515 cm.⁻¹ for the infrared inactive fundamental, ν_1 , on the basis of an apparent combination band at 1070 cm.⁻¹.

Acknowledgment.—We wish to thank Professor G. J. Mains for the mass spectrographic analysis.

(9) D. F. Smith, *J. Chem. Phys.*, **38**, 270 (1963).

MELLON INSTITUTE
PITTSBURGH 13, PENNSYLVANIA

DOLPHUS E. MILLIGAN
D. RICHARD SEARS

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NON-CHLOROPHYLLOUS PIGMENTS OF *CHLOROBIVUM THIOSULFATOPHILUM* *CHLOROBIVUMQUINONE*

Sir:

The anaerobic, photosynthetic bacterium, *Chlorobium thiosulfatophilum*, differs from all other known photosynthetic systems in having several unique chlorophylls.¹ This induced us to examine other pigments of this bacterium which may be related to its photosynthetic and oxidative phosphorylating systems, *viz.*, the carotenes and the quinones.

This organism had been reported² to contain γ -carotene, pro- γ -carotene, and rubixanthin. Also, Fuller, *et al.*,³ reported that *C. thiosulfatophilum* (strain L) is devoid of coenzyme Q and plastoquinone, but detected a substance, λ_{\max} 254 m μ , which they suggested was related to plastoquinone.

We have extracted¹ dried cells of *C. thiosulfatophilum* (strain PM) and chromatographed the non-chlorophyllous pigments on Decalco. A carotene fraction was eluted with isoöctane and established as γ -carotene, identical with an authentic sample⁴ by its visible

(1) J. H. Mathewson, W. R. Richards and H. Rapoport, *J. Am. Chem. Soc.*, **85**, 364 (1963), and references therein.

(2) T. W. Goodwin and D. G. Land, *Biochem. J.*, **62**, 553 (1956).

(3) R. C. Fuller, R. M. Smillie, N. Rigopoulos and V. Yount, *Arch. Biochem. Biophys.*, **95**, 197 (1961).

(4) We are indebted to Dr. G. McKinney for this sample.