

0.1828 g.; F/Xe = 5.79. (2) XeF₆ taken, 0.2256 g.; Xe found 0.1195 g., calculated 0.1208 g.; F found, 0.0996 g., calculated 0.1048 g.; F/Xe = 5.76.

The radiochemical work was done in a similar manner but using smaller amounts, about 0.07 millimole of xenon and 4 millimoles of fluorine, and heating for only one hour. The final pressure in the reaction vessel was about 50 atmospheres. Xe¹³³ and F¹⁸ were used as tracers to measure the combining ratios of xenon and fluorine. The reaction vessel could be placed in the well of a sodium iodide scintillation crystal which fed a single channel analyzer. The counting technique is more fully described elsewhere.⁵ The specific activities of the xenon and fluorine were measured initially and in the product after heating. In two experiments at 300° and two at 400° the fluorine to xenon ratios obtained were 5.8, 5.9, 5.8 and 5.8.

Mass spectrographic analyses of purified samples showed the presence of XeF₆⁺ and its fragmentation products.

Xenon hexafluoride is a colorless solid, with a vapor pressure of about 7.5 mm. at 0° and 30 mm. at 25°. In a polychlorotrifluoroethylene tube it was observed to turn yellow at about 42° and melt to a yellow liquid at 46°. On solidifying it was again colorless. The vapor has a pale yellow color.

The compound is stable at room temperature and has been stored for weeks in a nickel can without decomposition. Samples sealed in quartz cells appear to react slowly to produce a clear, colorless liquid.

Xenon hexafluoride reacts violently with hydrogen or water at room temperature. It dissolves without reaction in anhydrous hydrogen fluoride.

A preliminary scan of the infrared spectrum of the vapor has been made from 4000 to 400 cm.⁻¹. Only one strong infrared band at 612 cm.⁻¹ was found. This frequency is in the region where ν_3 has been observed for hexafluorides with bond lengths of about 2 Å., e.g., UF₆.⁶

The spectral region from 26,000 to 1900 Å. has been investigated for XeF₆ vapor, revealing an intense absorption maximum at 3300 Å. some 500 Å. wide at half-height and a still more intense absorption at wave lengths shorter than 2750 Å.

(5) I. Sheft, H. H. Hyman, R. M. Adams and J. J. Katz, *J. Am. Chem. Soc.*, **83**, 291 (1961).

(6) H. H. Claassen, *J. Chem. Phys.*, **30**, 968 (1959).

ARGONNE NATIONAL LABORATORY
CHEMISTRY DIVISION
ARGONNE, ILLINOIS

J. G. MALM
I. SHEFT
C. L. CHERNICK

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XENON HEXAFLUORIDE

Sir:

Recently, Claassen, Selig, and Malm reported the direct fluorination of Xe vapor at 400° to form XeF₄ and an unidentified lower xenon fluoride,¹ which subsequently was identified as XeF₂.^{2,3} No indication of the existence of a higher fluoride than XeF₄ has been reported. This communication reports the preparation of XeF₆ and some of the properties of this compound.

The reactor used in the preparations was a cylindrical high pressure stainless steel vessel of 250 ml. volume provided with an internal electric heater made with nickel gauze. All of the reactions were carried out at an initial total pressure of 1000 p.s.i. The ratio of

(1) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

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

(3) D. F. Smith, *J. Chem. Phys.*, in press.

fluorine to xenon was varied from 6 to 40. Filament temperatures in the range 350–450° were used. The walls of the reactor were either maintained at about -115° or at 80°. In all cases a mixture of volatile products was obtained. These were partially separated by a series of bulb-to-bulb distillations using a variety of reservoirs and collecting temperatures below 0°. The more volatile fractions always concentrated XeF₆. The less volatile fractions concentrated XeF₂, XeF₄, and an unidentified xenon fluoride of comparable volatility.

The purity of the samples was monitored by infrared spectroscopy. The identifying feature of XeF₆ is a strong fundamental at 610 cm.⁻¹, presumably ν_3 . Three other strong absorptions were observed in the KBr range, with the impure samples: ν_3 of XeF₂ at 550 and 566 cm.⁻¹,³ the stretching frequency of XeF₄ at 582 and 592 cm.⁻¹,^{1,2} and a broad band at 520 cm.⁻¹ not associated with any of the xenon fluorides mentioned above. In the highest purity sample of XeF₆ obtained thus far, all of the three above bands were absent. In the purest XeF₆ sample, the twin bands, $\nu_2 + \nu_3$ and $\nu_1 + \nu_3$, characteristic of all the other hexafluorides, were observed at 1154 and 1189 cm.⁻¹. The details of the infrared spectra of XeF₆ obtained to date are consistent with a symmetrical structure for the molecule. If the band at 1189 cm.⁻¹ is $\nu_1 + \nu_3$, then ν_1 is 579 cm.⁻¹. This is the lowest value for the totally symmetrical vibrational frequency, ν_1 , observed for the sixteen known hexafluoride molecules and suggests that XeF₆ is the least stable hexafluoride. This latter statement is also consistent with our qualitative chemical observations.

The formula for XeF₆ was established by chemical analysis. Samples of XeF₆ were distilled into a nickel weighing vessel containing mercury and the weight of sample determined from the weight increase. The reaction between XeF₆ and Hg was carried out at 100° and the Xe produced subsequently distilled out of the cooled weighing vessel. The procedure was continued until no further loss in weight of the container was observed. The increase in weight of the container over its initial weight gave the fluorine content of the sample; the xenon content was calculated by subtracting the weight of fluorine from the total weight of sample. The xenon released was weighed separately to provide a mass balance. The purity of the xenon released was established to be better than 99% by mass spectroscopy. Two samples weighing 0.0911 and 0.1920 g. were analyzed in this way and atom ratios of F to Xe of 6.0 and 5.9 were obtained, in agreement with the formula XeF₆.

An attempt to confirm the formula, XeF₆, by mass spectroscopy was only partially successful. At first, the peaks of highest mass obtained were the XeF₄⁺ group. Seasoning of the mass spectrometer manifold with PtF₆ did not change the XeF₆ spectra, but allowed the PtF₆ mass spectrum to be obtained. Spectra initially showing the XeF₆⁺ group in greatest intensity (except for Xe⁺) were obtained by condensing the

sample into a glass manifold of small volume adjacent to the molecular leak and repeatedly scanning the mass spectrum as the sample was allowed to warm slowly. Subsequently, the intensity of the XeF_6^+ decreased rapidly relative to that of the lower mass ions, indicative of chemical decomposition. No evidence was obtained for the XeF_6^+ ion. The mass spectrum of WF_6 reported by Inghram⁴ similarly shows the WF_6^+ peak to be less than 1% the intensity of the WF_6^+ peak. These mass spectroscopic observations are taken to be a partial corroboration of the formula XeF_6 .

XeF_6 can be handled in glass but appears to decompose similarly to PtF_6 .⁵ It can be reduced with H_2 to form HF and Xe. Preliminary vapor pressure measurements give: 0°, 6 mm., and 20°, 27 mm. It is thus the least volatile of the known hexafluorides.

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(5) B. Weinstock, J. G. Malm, and E. E. Weaver, *J. Am. Chem. Soc.*, **83**, 4310 (1961).

SCIENTIFIC LABORATORY
FORD MOTOR COMPANY
DEARBORN, MICHIGAN

E. EUGENE WEAVER
BERNARD WEINSTOCK
CHARLES P. KNOP

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ON THE PROBABLE STRUCTURE OF XeF_4 AND XeF_2 Sir:

No reliable data exist as yet from which the structures of XeF_4 ¹ and XeF_2 ² can be deduced. There exist, however, reasons to believe that the molecular structures of these molecules may be predicted.

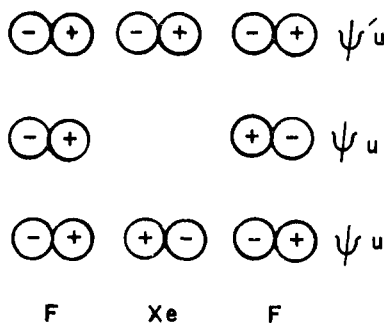


Fig. 1.—MOs for 3c-4e bond.

First, XeF_4 and XeF_2 are electronic analogs of ICl_4^- and ICl_2^- , and hence may be expected to be square planar and symmetrically linear, respectively, by analogy with these ions.^{3,4} (This is consistent with such information as is currently available.²)

(1) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(2) C. Chernick, H. Claassen, P. Fields, H. Hyman, J. Malm and W. Manning, *Science*, **138**, 136 (1962).

(3) R. C. L. Mooney, *Z. Krist.*, **98**, 324 (1938).

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(5) L. Pauling, "Nature of the Chemical Bond," 1st and 2nd Editions, Cornell Univ. Press, Ithaca, N. Y. (1939) and (1940); R. B. Heslop and P. L. Robinson, "Inorganic Chemistry," Elsevier, Amsterdam, 1960.

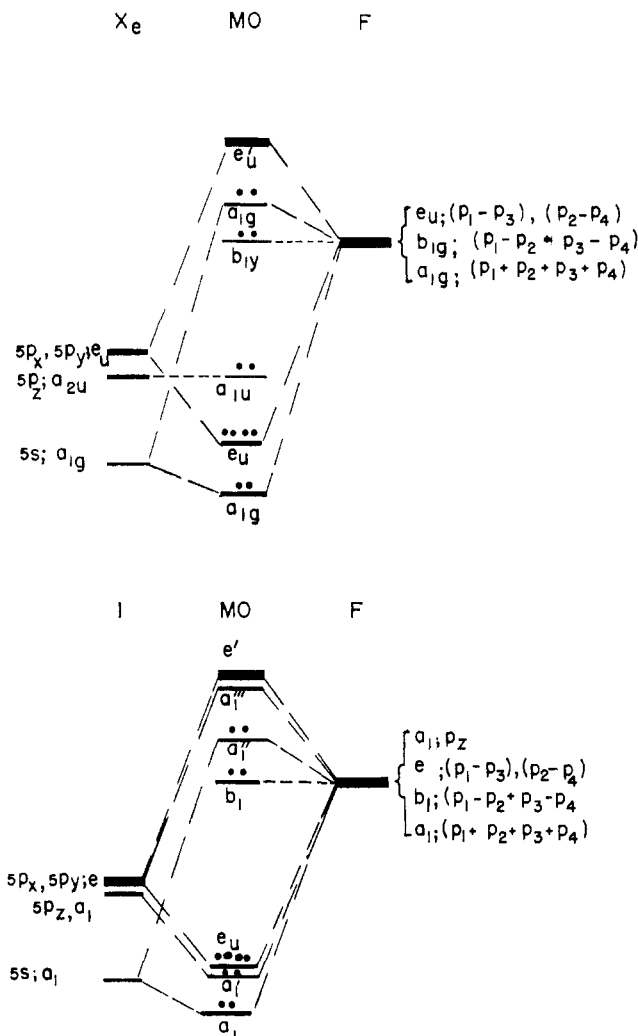


Fig. 2.—MOs for XeF_4 and IF_5 . The signs for the linear combinations of the p-orbitals of the fluorines are for the inner lobes, pointing toward Xe or I.

Second, of the two proposals for such bonding, that using outer s and d orbitals⁵ is less likely than one based on delocalized bonds using only p-orbitals of the valence shell,⁶ because of the especially high promotional energies of the rare gases.⁷ Indeed the existence of XeF_2 and XeF_4 is not insignificant evidence in favor of the latter suggestion.

Details of the proposal are shown for XeF_2 in Fig. 1. Filling all valence shell orbitals of F and Xe except the p-orbitals (taking z as the molecular axis) the problem becomes one of three orbitals, four valence electrons. As shown in Fig. 1, the four electrons will then occupy the bonding three-center MO, ψ_u , and the non-bonding MO, ψ_g , which places electrons on the fluorine atoms only. The bonding orbital will necessarily withdraw some electron density from Xe, placing it on F, giving the bond ionic as well as covalent character.

This three-center, four electron bonding, hereafter 3c-4e, requires that the terminal atoms be more electronegative than the central atom, and that the 3c-4e bonds be longer than electron pair bonds between the same elements, since there is only one bonding pair for the two bonds. Recently this proposal has been generalized, and it has been shown that polyhalide and polyhalogen structures are in good agreement with it.⁸

(6) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951); G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(7) C. E. Moore, "Atomic Energy Levels," Circular No. 467 of the National Bureau of Standards (1949).