

were fixed in space. The constraint was that the center of the fifth atom should lie in a fixed potential well. Figure 1 shows how the variable step size eliminates many computations. The minimum step size was set so that forty discrete points might be considered on each circle of rotation. If any atom assumed a position such that the end of the chain could not possibly reach to the potential well no matter what the angular dependence, this entire branch of possibilities was eliminated. Of the 64,000 potential computations of coordinates, only 3000 were actually made, and of these, only 100 combinations satisfied the constraint. The computation took about 1 min. of IBM 7090 time, a saving of tenfold over the complete search of 64,000 combinations.

The second program considered the problem of the protein α -helix structure solved by Pauling and Corey.⁶ The helix is composed of equivalent planar groups stabilized by the resonating double bond between the carbonyl oxygen and the nitrogen of the protein backbone. The bond lengths and angles are the same as those occurring in similar small molecules. The only rotational freedom is then about the α -carbon atom. Three degrees of freedom characterize the structure, the tilt of the equivalent planar groups with respect to the helix axis, the minimum radius of the line between α -carbons, and the displacement along the axis from one α -carbon to the next. The condition for the stability of the helix, that the hydrogen and nitrogen of one plane be nearly in position to form a hydrogen bond with the oxygen of a plane on the next turn, was readily programmed in terms of the three variables. The computer search for possible combinations of the parameters took less than $1/3$ min. Bond lengths and angles of interest were calculated for all configurations satisfying the constraint. The values proposed by Pauling and Corey were confirmed.

A detailed description of the programming system and a listing of the Fortran instructions are available from the author.⁷

Acknowledgments.—The author wishes to thank Mrs. Marie Chang for her technical assistance in this work. The computations were made at the University of Maryland Computer Center.

(6) L. Pauling and R. B. Corey, *Proc. Natl. Acad. Sci. U. S.*, **37**, 235 (1951); *Proc. Roy. Soc. (London)*, **141**, 21, (1953).

(7) The programming system, written in Fortran, is available from the National Biomedical Research Foundation, Silver Spring, Md. We would be glad to collaborate with groups having use for the programs.

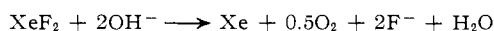
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Characterization of Divalent Xenon in Aqueous Solution¹

Sir:

The hydrolysis of XeF₂ in alkaline solution is reported to proceed according to the equation²



We find no reference in the literature, however, to hydrolysis of XeF₂ in water or acidic solution.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. G. Malm, B. D. Bolt, and R. W. Bane, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago Ill., 1963, p. 167.

We took *ca.* 0.5-g. samples of XeF₂ which Weeks had prepared by the photochemical method,³ froze them in liquid nitrogen, pipetted about 20 ml. of ice-cold water onto them, and allowed them to warm to 0°. The resulting solutions were stored in Kel-F containers. We determined oxidizing power by adding acid iodide and titrating with thiosulfate. Hydrofluoric acid was determined by potentiometric titration with sodium hydroxide, and xenon and oxygen were determined by mass spectrometry. We measured absorption spectra with a Cary Model 14 recording spectrophotometer.

In a typical experiment 488 mg. of XeF₂ was hydrolyzed in 20 ml. of water to yield a colorless solution with a pungent odor. It was analyzed 50 min. after mixing and was found to contain 4.6 mequiv. of oxidizing power, which at 0° was lost with a half-life of about 7 hr. Extrapolation to the time of mixing gives an initial yield of 5.0 mequiv. or 87% of the oxidizing power present in the XeF₂. At room temperature the decomposition was much faster. After 30 hr. at *ca.* 24° less than 0.03% of the original oxidizing power remained. The decomposed solution was found to contain 5.62 mmoles of HF, compared to the 5.76 mmoles calculated from the weight of XeF₂ taken. The gases evolved on decomposition of this solution were found to consist of Xe and O₂ in the ratio 2.08:1.

When we attempted to dissolve more than 25 mg. of XeF₂ per ml. of water at 0° we obtained what appeared to be a saturated solution, with solid remaining in the vessel.

The oxidizing species in these solutions is more volatile than water and distills preferentially under vacuum. The vapor formed in such a distillation was examined by Studier in a time-of-flight mass spectrometer,⁴ and XeF₂ was the only xenon compound observed.

The rate of decomposition of these solutions is unchanged in the presence of 1 M KHF₂, but the half-life at 0° decreases to about 5 hr. in 1 M HClO₄ and to about 3 hr. in 30% HF. The result in HF, however, may be due to impurities introduced with the acid. In alkaline solution decomposition is complete within minutes regardless of whether sodium or barium hydroxide is used. A bright yellow color appears momentarily during the alkaline decomposition. Nearly instantaneous decomposition is brought about in acid solution by excess thorium ion or by hydrous zirconium oxide.⁵ An excess of lanthanum ion, however, does not cause rapid decomposition.

Potentiometric titration of a fresh solution with base indicates very little HF to be present initially. However acid is evolved as the solution decomposes, causing the pH to drift downward.

The oxidizing species in these solutions can be extracted into CCl₄. The distribution ratio is about 2.3 in favor of the aqueous phase. The ratio is not appreciably different in 1 M HClO₄ or in 4 M KHF₂.

These solutions are extremely powerful oxidants. They fairly rapidly oxidize HCl to chlorine, iodate to periodate, Ce(III) to Ce(IV), Co(II) to Co(III), and Ag(I) to Ag(II). Alkaline solutions of Xe(VI) are oxidized to Xe(VIII).

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

(4) M. H. Studier, *Rev. Sci. Instr.*, **34**, 1367 (1963).

(5) Obtained from Bio-Rad Laboratories, Richmond, Calif.

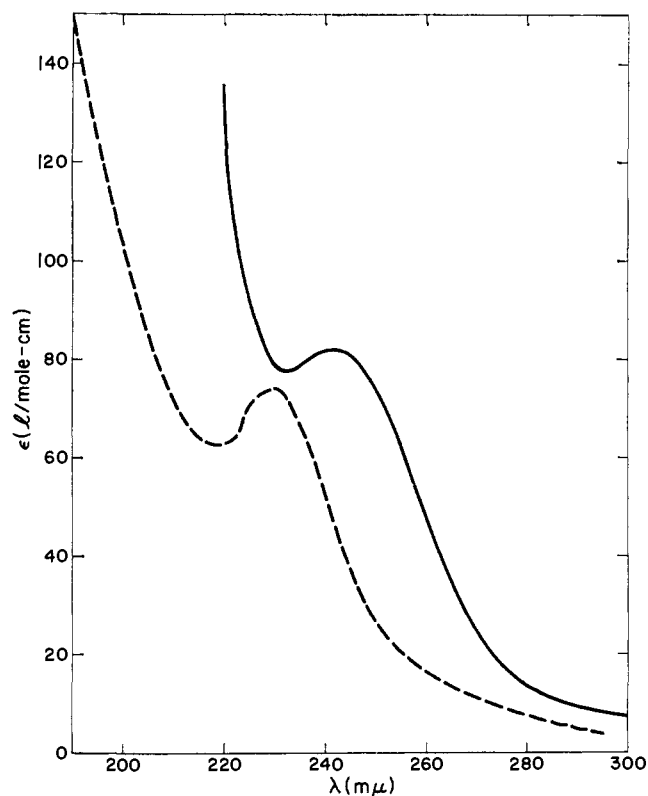


Fig. 1.—Ultraviolet absorption spectra of XeF_2 : —, aqueous solution at ca. 5° ; - - - - - , gas at 30° .⁶

From these results it seems clear that XeF_2 dissolves in water to the extent of about 0.15 M and is present in solution as undissociated molecules which do not form complex anions with F^- . From Fig. 1 we see that the ultraviolet absorption spectrum of these solutions is similar to that of gaseous XeF_2 .⁶ It appears that hydrolyzed Xe(II) cannot persist in aqueous solution, and reagents that remove the fluoride from XeF_2 bring about the rapid evolution of xenon and oxygen. We estimate the Xe-XeF_2 potential in acid to be about 2.2 v.

Kirschenbaum and Grosse reported that by hydrolyzing XeF_4 in water at 0° they obtained an unstable, volatile, and pungent-smelling xenon compound which they considered to be a compound of hexavalent xenon,⁷ although other workers have found Xe(VI) to be odorless, stable, and nonvolatile in aqueous solution.^{8,9} In a private communication Grosse has informed us that the XeF_4 he used was severely contaminated with XeF_2 and that he now feels his solutions contained a mixture of the stable, nonvolatile XeO_3 and another hitherto unknown compound. We believe that this new compound is aqueous XeF_2 .

The transient bright yellow color observed when a XeF_2 solution is made basic is interesting. Presumably it is the same as the yellow color formed on the surface of the solid when XeF_2 is hydrolyzed in base.² However, it also resembles the yellow color that appears on the surface of solid XeF_4 when it is hydrolyzed,⁷

(6) E. S. Pysh, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, **40**, 2018 (1964).

(7) A. D. Kirschenbaum and A. V. Grosse, *Science*, **143**, 3592 (1963), and information presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(8) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).

(9) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964), and information presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

and it is similar to the flash of yellow that is seen when a strongly alkaline Xe(VI) solution is reduced with H_2O_2 . The hydrolysis of XeF_4 has been postulated to proceed through Xe(II) ,² and divalent xenon may also be produced during the peroxide reduction of Xe(VI) . The yellow color may thus possibly belong to an oxygen compound of divalent xenon.

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Preparation and Properties of Methoxy Complexes of Divalent Metal Ions

Sir:

A recent paper¹ reported the preparation of polymeric bis(3-nitropentane-2,4-diono)di- μ -methoxydi-beryllium from the corresponding diol complex. The diol complex was prepared by treating beryllium acetylacetonate with beryllium nitrate in acetic anhydride.

We have employed a more general method for the preparation of methoxy complexes of divalent metal ions with various chelating anions. The metal chelates ML_2 react with base in methanol to produce the insoluble methoxy compounds $[\text{ML}(\text{CH}_3\text{O})(\text{CH}_3\text{OH})_x]$. Divalent metal ions which have been employed include cobalt, nickel, copper, and magnesium; chelating agents employed have included acetylacetonate (hereafter abbreviated A), 3-ethylacetylacetonate, salicylaldehyde, and 2'-hydroxyacetophenone.

$\text{CoA}(\text{CH}_3\text{O})(\text{CH}_3\text{OH})$.—In the initial preparations of this complex, weak nitrogen bases were employed and poor yields were obtained; later studies showed that potassium hydroxide gave almost quantitative yields. Further investigation of the reaction showed that continued reflux of CoA_2 in methanol without added base produced a small amount of the methoxy compound. The ease of preparation of this and similar complexes is evidently a result of the extremely low solubility of these complexes in methanol.

Heating the complex to 100° *in vacuo* resulted in the removal of 1 mole of methanol; the color changed from deep red to violet.

The complex reacted with *p*-nitrobenzoyl chloride to give substitution at the 3-position of the chelate ring. Similar reaction of the bis(acetylacetonato)-metal(II) compounds has been reported.²

The infrared spectrum was similar to that of CoA_2 , but had additional absorptions indicative of methanol and methoxy groups; the carbonyl stretching band was much sharper than that of CoA_2 . The spectrum of the violet compound, $\text{CoA}(\text{OCH}_3)$, was identical except in the region of O-H absorptions.

The ultraviolet spectrum of the complex was identical, with respect to absorption position, with that of CoA_2 ; the extinction coefficient at the band maximum was only half as great as that of CoA_2 .

Similarity of the visible spectrum of the complex and CoA_2 indicates that the ligand field is essentially "octahedral," which would require some type of molecular association. The molecular weight obtained with a Mechrolab vapor pressure osmometer for a 0.05 F solution in chloroform was above 4000. The associa-

(1) R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1189 (1963).

(2) D. C. Nonhebel, *J. Chem. Soc.*, 4628 (1962).