

the same stability and are in reasonable agreement with the results of previous investigators (Table IV). The present investigation, however, does not give supporting evidence for the existence of the CdF_2 species previously suggested with a formation constant $\beta_2 = 3.4$.¹ The irreversibility of the reduction waves of Ni(II), Co(II), Cr(III), and Ti(III) prevented application of the method to these ions.

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Compound Formation by γ -Irradiation of Xenon–Fluorine Mixtures

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Mixtures of Xe and F_2 in slightly greater than 2:1 mole ratio of F_2 to Xe were exposed, in prefluorinated nickel containers, to high-intensity γ -radiation from Co^{60} sources. The pressure was observed to fall, as it would if the two elements combined, and a solid product was later obtained from the container, by sublimation. This resembled the product of the thermal reaction carried out according to the procedure of Claassen, *et al.*,¹ both in appearance and chemical behavior. Analysis of the solid obtained from one of the irradiations was carried out by hydrolyzing a weighed sample in NaOH solution and determining fluoride in the solution. Results of the analysis indicated a composition $\text{XeF}_{3.0}$, suggesting a mixture of difluoride and tetrafluoride. For a given composition it is possible to calculate a radiation yield from the pressure drop and other parameters of the experiment. Conditions of the experiment were as follows: initial F_2/Xe ratio, 2.6; initial pressure, 18.6 p.s.i.g.; volume of container, 330 cc.; temperature, 64°; length of irradiation, 130 hr.; ΔP , -6.0 p.s.i.; dose rate (to Fricke dosimeter), 4.0×10^6 rads/hr. Calculation gives a *G*-value for consumption of Xe of 3.4 atoms per 100 e.v. absorbed in the gas mixture.

The fact that radiation brings about fluorination of xenon suggests its use in the synthesis of other rare gas compounds. Several such experiments have been tried. Mixtures of krypton and fluorine, xenon and chlorine, and xenon and oxygen were irradiated in the Gamma Facility, and a mixture of xenon and oxygen was irradiated in the Brookhaven graphite reactor. No compounds were observed in any case. Apparently

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

any compounds which might be capable of formation with the help of radiation are unstable to either the radiation or the slightly elevated temperatures prevailing during the experiments.

The use of ionizing radiation provides a new approach to the study of the mechanics of the xenon–fluorine reaction. Due to the large number of primary processes involved in the radiation-induced reaction, one would not expect it to follow the same course as the photochemical reaction. Indeed the latter yields only XeF_2 , regardless of the initial xenon–fluorine ratio.² Further work is being done to determine the effect on product composition of varying the xenon–fluorine ratio in the radiation-induced reaction.

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(2) J. L. Weeks, C. L. Chernick, and M. S. Matheson, *ibid.*, **84**, 4612 (1962).

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Octahedral Silicon–Oxygen, Germanium–Oxygen, and Tin–Oxygen Bond Lengths from Interplanar Spacings in the Phthalocyanino Polymers $(\text{PcSiO})_x$, $(\text{PcGeO})_x$, and $(\text{PcSnO})_x$ ¹

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In the search for inorganic oligomers and polymers in this Laboratory, attention has been given to phthalocyanino rings linked together by metal–oxygen chains, *i.e.*, PcAlOAlPc , PcAlOSi(Pc)OAlPc , $\text{PcAlOSi(Pc)OSi(Pc)OAlPc}$, HOSi(Pc)OSi(Pc)OH , $(\text{PcSiO})_x$, and $(\text{PcGeO})_x$.² Both the phthalocyanino rings and the groups III and IV metal–oxygen chains used in these have the advantage of being inherently stable. In addition the use of the bonding positions of the metal rather than those of the benzene rings of the chelate for polymerization gives stable links between the monomer units. In the complexes formed in this way the symmetrical ring system is unsubstituted and thus unweakened by pendant groups on the benzene rings and the chain is stabilized because the metal in it is in a high coordination number and because the whole chain is encased by the ring.

Further work has now established that another member of this series, $(\text{PcSnO})_x$, can be prepared by the

(1) Support for this work came both from National Science Foundation Grant NSF-G15833 and from Air Force Office of Scientific Research Contract AF 49(638)-773. It is based on portions of the Ph.D. thesis of William J. Kroenke. Pc = the phthalocyanino ligand.

(2) R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960); J. E. Owen and M. E. Kenney, *Inorg. Chem.*, **1**, 334 (1962); R. D. Joyner and M. E. Kenney, *ibid.*, **1**, 717 (1962).