Meetings

Noble Gas Compounds

The first publication dealing with an authentic chemical reaction of xenon appeared in June 1962 (*1*). The synthesis of xenon tetrafluoride was announced in September 1962 (*2*), and a paper summarizing the research at Argonne on fluorine compounds of xenon and radon appeared in October (*3*). In order to discuss recent research, a conference on noble gas compounds was held at Argonne National Laboratory, 22–23 April. Approximately 40 speakers reviewed and discussed new investigations.

The chemistry of xenon compounds and indeed of the xenon fluorides alone is by no means exhausted. For the most studied compound, xenon tetrafluoride, neutron diffraction and x-ray studies have defined the square-planar assemblage of fluorines around the xenon and the precise shape of the assemblage of squares in the crystal to a precision second to none among molecular crystals (J. H. Burns, P. A. Agron, and H. A. Levy, Oak Ridge National Laboratory; D. H. Templeton, A. Zalkin, J. P. Forrester, and S. M. Williamson, University of California, Berkeley; W. C. Hamilton and J. A. Ibers, Brookhaven National Laboratory).

Infrared and Raman observations in the gas phase seem to eliminate conclusively any significant deviation from the square-planar array in the vapor as well (H. H. Claassen, C. L. Chernick, and J. G. Malm, Argonne; D. F. Smith, Oak Ridge). Confusingly, however, electron diffraction observations seemed at first to suggest a square pyramid arrangement with a 15° angle between the xenon-fluorine bonds and the plane containing the fluorines (R. K. Bohn, K. Katada, J. V. Martinez, and S. H. Bauer, Cornell). A reexamination since the conference has removed this discrepancy and confirmed the square planar arrangement.

The linear shape of XeF_2 molecules and the crystal structure of the solid had been well established prior to the meeting (*4*). However a solid phase hitherto interpreted as a low-temperature, high-density modification of xenon tetrafluoride was reinterpreted as a regular stoichiometric compound made up of equal proportions of linear XeF_2 and square-planar XeF_4 molecules (Burns, R. D. Ellison, and Levy, Oak Ridge). The existence of this compound explains the absence of evidence for a phase transition in pure xenon tetrafluoride in heat capacity and magnetic measurements from room temperature down to liquid nitrogen (or even liquid hydrogen) temperatures (W. V. Johnston, W. R. Bisbee, D. Pilipovich, and D. F. Sheehan, North American Aviation; R. Blinc, P. Podnar, J. Slivnik, and B. Volavšek, Jožef Stefan Institute; S. Maričic and Z. Veksli, Ruder Bošković Institute.)

The structure of XeF_6 in either solid or vapor phase has not yet been established. Experimental difficulties in working with the solid at room temperature suggest that low-temperature work will be required. The molecular geometry of the gaseous XeF_6 molecule seems to be of crucial importance for testing various descriptions of the chemical binding between xenon and fluorine.

The most complete analysis of the scanty infrared and Raman data available appears to lead to a rejection of octahedral symmetry (Smith, Oak Ridge). In some part, however, this analysis may depend on attributing to xenon hexafluoride absorption bands which other observers attribute to as yet unidentified impurities. For example, an absorption band at 520 cm^{-1} has been observed by a number of experimenters, but only Smith attributes this to XeF_6 molecules. At present no well-established alternative species is known to have an absorption band at 520 cm^{-1}, although several possibilities were suggested.

No sample of xenon hexafluoride in an infrared cell appears to be completely free of impurities. Although some of these are present in the sample as prepared, it is likely that others result from the reaction of xenon hexafluoride with the cell.

The existence of XeF_8 has been postulated as a significant constituent of XeF_6 samples prepared at high temperatures and very high pressures and mole ratios of fluorine to xenon (Slivnik, Volavšek, J. Marscl, V. Vrščaj, A. Šmalc, B. Frlec, and A. Zemlič, Jožef Stefan Institute). The data are persuasive rather than conclusive in that while high ratios of fluorine to xenon in the products are well established, the absence of additional atoms, especially hydrogen, has not yet been rigorously demonstrated. Experiments in the same region of excess fluorine pressure, though at somewhat lower temperatures, have not shown the presence of the octafluoride (G. L. Gard, F. B. Dudley, and G. H. Cady, University of Washington). Studies on the exchange of radioactive fluorine with xenon hexafluoride are best interpreted in terms of an associative rather than a dissociative mechanism (I. Sheft and H. H. Hyman, Argonne). While this suggests possible expansion of the coordination sphere around xenon, again it is far from proof of the existence of a stable octafluoride.

An alternative explanation of the absorption at 520 cm^{-1} was offered by B. Weinstock (Ford Motor Company Scientific Laboratory). In studying the equilibrium pressures in mixtures of xenon and fluorine, he came to the conclusion that the data in the region having a high ratio of fluorine to xenon could be fit best by postulating the existence of another species, XeF_5. A yellow color was also attributed by Weinstock to the hypothetical XeF_5 which should be an odd-electron free radical. A search for an odd-electron spin resonance signal at low temperature was unsuccessful in a sample presumably containing the pentavalent xenon species. If such a species exists it may be present as a dimer, at least at room temperature. Note that a solid-phase XeF_4-XeF_6 compound which dissociates in the vapor cannot account for the data that the XeF_5 hypothesis was proposed to explain, but a stable Xe_2F_{10} molecule in the vapor phase might fit.

The odd-electron species XeF has been positively identified by electron spin resonance techniques in XeF_4 crystals irradiated by Co^{60} gamma source

(J. R. Morton and W. E. Falconer, National Research Council, Canada). This result appears to be consistent with observations of flash photolysis experiments in gaseous mixtures of xenon and fluorine (M. Matheson and J. Weeks, Argonne). This species, however, is stable only at low temperatures.

A number of fluorinating agents react with xenon on heating or in the electric discharge. In most cases (for example, in CF_3OF, FSO_3F), XeF_2 is formed (Gard, Dudley, and Cady, University of Washington). With OF_2, analyses suggesting that the products contain oxygen are reported: $XeOF_2$ when the discharge is used and $XeOF_3$ (not necessarily a pure phase) after heating (A. G. Streng, A. O. Kirshenbaum, L. V. Streng, and A. V. Grosse, Temple University).

For krypton, in addition to the previously announced tetrafluoride (5), evidence was presented for formation of KrF_2 by ultraviolet irradiation of a mixture of Kr and F_2 in an argon matrix frozen on the surface of an infrared absorption cell (G. C. Pimentel and J. J. Turner, University of California, Berkeley). Radon compounds undoubtedly exist in profusion, but isolation and reliable characterization of such compounds await experiments in more heavily shielded equipment and on a larger scale than has been employed to date.

In anhydrous hydrogen fluoride, xenon tetrafluoride is sparingly soluble with no reaction or ionization, xenon difluoride is very soluble with little ionization or interaction though there is some fluorine exchange at room temperature, and xenon hexafluoride is very soluble with extensive ionization. Interpretations of both electrical conductivity (Hyman and L. A. Quarterman, Argonne) and nuclear magnetic resonance data have led to the same conclusions (J. C. Hindman and A. Svirmickas, Argonne; T. H. Brown, E. B. Whipple, and P. H. Verdier, Union Carbide Research Institute).

At least preliminary data on the heats of formation of some noble gas compounds have been reported. The fluorides studied are all thermodynamically stable at room temperature. For XeF_2 the suggested value for the heat of formation of −19.4 kcal/mole leads to a bond energy of 28 kilocalories per XeF bond (Weinstock, E. E. Weaver, and C. P. Knop, Ford Motor Company Scientific Laboratory). For XeF_4 the heat of reaction has been measured for a number of reactions. These observations lead to values of 30 kilocalories per XeF bond (S. R. Gunn and S. M. Williamson, Lawrence Radiation Laboratory) and 32 kilocalories per XeF bond (L. Stein and P. Plurien, Argonne). For XeF_6 a value of 31.5 kilocalories per bond is quoted (Stein and Plurien, Argonne). The explosively unstable XeO_3 as expected was found to have a positive heat of formation of about 96 kilocalories per mole (S. R. Gunn, Livermore). Interestingly enough, however, this positive heat of formation requires a bond energy for an Xe=O bond of about 20 kcal, significantly smaller but comparable to the strength of the XeF bond and in good agreement with the ready formation and reasonable stability of the oxyfluorides.

The hydrolysis reactions of XeF_4 and XeF_6 yield aqueous solutions containing combined xenon (Malm, R. W. Bane, and B. D. Holt, Argonne; Koch and Williamson, University of California, Berkeley). All of the chemistry of such species containing xenon and oxygen is far from elucidated.

In acid solutions the most stable species obtained either from XeF_6 or XeF_4, and involving in the latter case a disproportionation reaction, appears to be a xenon with an oxidation number of 6. The oxidation number is determined by reaction with reducing reagents, for example, by titration with iodide ion. The kinetics of the reaction of this species with bromide and iodide have been studied (Williamson and Koch, University of California).

In alkaline solution, on the other hand, the predominant species, obtained usually by hydrolysis of the hexafluoride, appears to be a species with an oxidation number of 8 (Malm, Bane, and Holt, Argonne). Attempts to identify this species with a peroxide or any oxidizing species except Xe(VIII) have not been successful (E. H. Appelman and M. Kilpatrick, Argonne). In alkaline solution this octavalent state appears to be reasonably stable and this stability is enhanced as solids such as $Na_4XeO_6 \cdot xH_2O$ are precipitated from strongly alkaline media. In acid solutions this species readily decomposes to give the hexavalent xenon whose properties were described previously. The opposite conversion, Xe(VI) to Xe(VIII), takes place in strongly alkaline solutions in the presence of ozone. Absorption spectrophotometry in the ultraviolet region for solutions of this octavalent species, and infrared absorption of KBr discs containing solids with the same anion are consistent with the formulation of an XeO_6^{4-} species, not unlike IO_6^{5-} (D. M. Gruen, Argonne). The silver salt is much less stable than the sodium salt. A number of phases associated with the sodium salts have been identified by x-ray analysis, including, up to the present, two orthorhombic phases and a face-centered cubic (S. Siegel and E. Gebert, Argonne).

The Mössbauer effect for Xe^{129} in crystals containing xenon has shown significant differences between the chemical binding in xenon tetrafluoride and in the sodium salts precipitated from aqueous solution. While there is a large and not very well explained quadrupole splitting in the velocity spectrum in xenon tetrafluoride, in the oxygen-containing species the velocity spectrum of the xenon shows little evidence of chemical combination (G. V. Perlow, C. E. Johnson, and M. R. Perlow, Argonne).

As might be expected, mass spectrometric studies have been very useful in identifying even small samples of xenon compounds. While the time-of-flight mass spectrometer first revealed the presence of XeF_2 and $XeOF_4$, these are now available in substantial amounts. A careful study of the evidence for the origin of $XeOF_3^+$ fragments has led to the conclusion that in the samples available these fragments have derived from $XeOF_4$ molecules and there is as yet no evidence for origin in an unidentified compound. On the other hand evidence for an XeO_2F_2 species arising in incompletely hydrolyzed samples of XeF_6 seems conclusive evidence for the existence of this compound although it has not yet been isolated in substantial amounts (M. H. Studier and E. N. Sloth, Argonne).

Now that the first shock of the synthesis of normal chemical compounds containing noble gases has worn off, there seems to be widespread agreement among theoretical chemists that the understanding of the electronic structure and chemical binding in these compounds will not require the introduction of new concepts in quantum chemistry. Rather, the study of these compounds will forcefully bring home the necessity of pushing our reasoning based on the usual features in the molecular orbital or the valence bond method to its logical conclusions. Indeed, the existence of normal compounds of xenon had been suggested by the use of each of these methods long ago (6). At the Argonne meeting several treatments were based on each of these approaches.

The need for reconciliation of the classification of "inert" gases in the periodic table with their demonstrated ability to form simple molecules was stressed by L. C. Allen (Princeton). He emphasized the role of instantaneous electron-electron correlations.

R. J. Gillespie (McMaster University, Hamilton, Ontario) presented predictions, based on the localized electron-pair theory, for molecular geometries and bond lengths of xenon oxides, fluorides, and oxyfluorides. In particular, his arguments suggest that XeF_6 is unlikely to be octahedrally symmetric in the vapor phase.

Evidence was presented (J. Hinze and K. S. Pitzer, Rice) that unoccupied *d*-orbitals for the noble gas atoms are of little importance to their formation of stable compounds. The unimportance of *d*-orbitals and the similarity of the halogen fluorides and inert gas fluorides was emphasized by R. E. Rundle and A. J. Serewicz (Iowa State) and the reverse argued by Smith (Oak Ridge Gaseous Diffusion Plant).

A comparison of six possible geometries for XeF_6 (L. L. Lohr, Jr., and W. N. Lipscomb, Harvard) indicates that the octahedrally symmetric structure is the most stable form considered, as judged by semiempirical molecular orbital calculations.

Finally, J. Jortner discussed absorption spectra in the near and the vacuum ultraviolet for XeF_2 and XeF_4 (Jortner, E. G. Wilson, and S. A. Rice, University of Chicago). He concluded that the semiempirical molecular orbital description of these compounds is in good agreement with their physical and chemical properties.

The alternative prediction of symmetrical versus non-symmetrical arrangements for xenon hexafluoride deepened the apparent conflict between the alternative approaches to the formulation of chemical bonds.

It is clear that additional refinement can bring either approach into agreement with the experimental observations as they are ultimately established. Nevertheless, many chemists prefer concepts that come closer to reality with fewer ad hoc adjustments.

The experimental observation and the remaining uncertainty has been discussed previously. The difficulties are formidable but do not appear insuperable. This particular discrepancy may well be resolved before this report appears in print.

All of the contending parties agreed that few discoveries in recent years have been more stimulating to the application of modern concepts of chemical binding to inorganic chemistry than the synthesis of simple xenon compounds. The weaknesses of available theoretical tools have been sharply emphasized; perhaps their strength will appear with more thorough investigation.

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Anticholinesterase Agents

An intersociety symposium on anticholinesterase (anti-ChE) agents was held at the meetings of the Federation of American Societies for Experimental Biology on 18 April. Since the mid-1940's approximately 250 publications have been issued annually on the subject of these agents. Because of this wide coverage and the broad scope of the topic, participants were requested to concentrate on two aspects of these agents: the possible physiological functions of acetylcholine (ACh) and acetylcholinesterase (AChE), and the dissociation between the effects of anti-ChE agents attributable to inhibition of AChE and those due to other actions.

G. B. Koelle discussed current theories of the physiological functions of acetylcholine and acetylcholinesterase. It has been proposed that acetylcholine, in association with the enzyme, serves (i) as a neurohumoral transmitter at synaptic and neuroeffector junctions; (ii) as the triggering agent for the propagation of conducted impulses in nerve axons and striated muscle fibers; (iii) as a local hormone, released by and acting upon various types of muscle fibers; and (iv) in regulating permeability and active transport in several non-excitable membranes.

The classical concept of acetylcholine as a neurohumoral transmitter, as proposed by Loewi, Dale, Feldberg, and others, assumes that this agent is released at the axonal terminal by a nerve impulse and combines with postjunctional receptors, thereby initiating a localized depolarization (the postsynaptic or endplate potential), which in turn triggers electrogenically the propagated action potential. Others (for example, Masland and Wigton, Abdon, W. R. Riker) have emphasized the prejunctional actions of cholinomimetic and cholinergic blocking drugs and have implied a function of acetylcholine at this site. Two general histochemical findings in the speaker's laboratory could not be explained satisfactorily in terms of the classical concept: nearly exclusive presynaptic localization of the enzyme occurred in sympathetic ganglia, in contrast to its predominantly postjunctional localization at the motor endplate, and varying concentrations were present in presumably noncholinergic neurons. On the basis of this and certain pharmacological evidence, it was proposed that acetylcholine has a dual neurohumoral role: an immediate action, at the axonal terminals from which it is released, which prolongs the depolarization of these terminals and hence promotes the release of (i) enough additional acetylcholine to act postjunctionally or (ii) another transmitter. The latter concept is consistent with Burn and Rand's hypothesis of the participation of acetylcholine in adrenergic transmission.

According to Nachmansohn's hypothesis, the propagation of the nerve action potential is dependent upon the electrogenic release of acetylcholine at successive sites along the axon, where it initiates the permeability changes which produce a reversal of the membrane's polarization. The same sequence is claimed to occur at junctional sites, where transmission would therefore also be electrogenic. Evidence along five general lines is difficult to reconcile with this proposal: (i) extreme variations in the concentrations of acetylcholine, acetylcholinesterase, and choline acetylase in various types of axons (for example, primary afferent versus motor); (ii) extremely high concentrations of anticholinesterase, cholinomimetic, and cholinergic blocking agents required to modify axonal conduction; (iii) irreducible latent period for junctional transmission; (iv) insufficient ionic content of axonal terminals to provide the current necessary for electrical transmission; and (v) electrical inexcitability of most postjunctional sites.

A local hormonal function of acetylcholine was inferred by Burn, Feldberg,