★ BARTLETT, Neil

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WHILE INVESTIGATING the fluorides of the platinum metals, Bartlett in 1962 prepared the first chemical compound of a noble gas. The noble gases were discovered by Lord Rayleigh and by Sir William Ramsey and his co-workers in the 1890s. The first gas to be discovered and the most abundant, argon, was quickly subjected to intensive chemical and physical examination and found to be chemically inert. Henri Moissan, the first to prepare fluorine, attempted to prepare an argon fluoride in 1895, and his failure impressed him and his friend Ramsey with the inertness of the gas. Several perceptive chemists pointed to the greater likelihood of the heavier (and much rarer) gases, krypton and xenon, entering into chemical combination. L. C. Pauling, in particular, suggested in 1933 that xenon and krypton fluorides should be preparable, and in the same year an abortive attempt was made to prepare a xenon fluoride. The failure to sustain claims to noble gas compounds, together with the inability of experienced investigators to carry out the most favorable syntheses, contributed to an acceptance of the complete inertness of the gases, but it was probably not the most important contributing factor. Undoubtedly, the popularity of the simple electronic theories of valence, which emphasize the special stability of the noble gas configurations, had a major influence. The scarcity of the most favorable gas, xenon, and the instability of radon, which should be the most chemically active gas, were also contributing factors.

Bartlett started his independent research with the intention of better defining the factors which limit the oxidation states of the elements. The noble metals, in particular, attracted his interest because of the promise of a greater range of oxidation states. Investigation of these elements also promised to be of value in his concern to define more clearly the relationship of the ligand geometry of molecules and crystals to the valence electron configurations of the central atom. The synthetic work, which involved fluorides and oxyfluorides, was therefore accompanied by structural studies. This combination was to prove vital to the discoveries which followed.

The compound of prime importance in the discovery of xenon chemistry was investigated initially in the belief that it would prove to be an oxyfluoride of 6-valent platinum. The compound was first observed as a sublimable red solid produced when platinum or platinum compounds were treated with fluorine in glass apparatus at moderate temperatures. The red solid was marked by great chemical reactivity, and it proved necessary to develop special techniques to analyze it. In 1961 Bartlett, with D. H. Lohmann, established the empirical formula as PtO_2F_6. Extensive chemical and physical characterization clearly indicated the compound to be a salt, dioxygenyl hexafluoroplatinate, $O_2^+[PtF_6]^-$. This was the first example known to represent either of the ions. It was particularly remarkable for its oxidized oxygen cation. This formulation implied that the molecular fluoride, platinum hexafluoride, which had been reported by Bernard Weinstock and J. G. Malm in 1958, should be capable of oxidizing molecular oxygen. This proved to be so, the two gases combining spontaneously at ordinary temperatures and pressures:

$$O_2(g) + PtF_6(g) \rightarrow O_2^+[PtF_6]^-(s)$$

Although the salt formulation had seemed appropriate early in the research, it posed the difficulty that the electron affinity of platinum hexafluoride,

$$\Delta E(PtF_6(g) + e \rightarrow PtF_6^-(g))$$

needed to be greater than −160 kcal/mole (that is, approximately twice the value for atomic fluorine or atomic chlorine), so that oxidation of molecular oxygen should proceed spontaneously. The proof of the salt formulation, therefore, pointed to platinum hexafluoride as the most powerfully oxidizing molecular species recognized so far. Bartlett noted that the ionization potentials of the heavier noble gases (xenon, 12.2 ev; radon, 10.5 ev) were as low as, or lower than, molecular oxygen (12.2 ev), and hence he concluded that these gases should also be oxidizable. In his investigations in 1962

xenon gas proved to be as easy to oxidize as molecular oxygen. The orange-yellow solid formed in the spontaneous gas-gas reaction was designated xenon hexafluoroplatinate, $Xe^+[PtF_6]^-$. The work on xenon hexafluoroplatinate stimulated investigation of the other noble gases in a number of laboratories, and compounds of krypton, xenon, and radon are now well characterized chemically and physically. Major consequences of the discovery of the chemical activity of the heavier noble gases have been the development of a greater awareness of the limitations of simple valence theory and the focusing of attention on the nature of bonding in these and related compounds.

Bartlett was an undergraduate and graduate student at King's College, Newcastle-upon-Tyne, from 1951 to 1957; his Ph.D. work was done with P. L. Robinson. He was senior chemistry master at the Duke's School, Alnwick, for 1 year, and in 1958 moved to the University of British Columbia, where he served on the faculty for 8 years. In 1966 he was appointed a professor of chemistry at Princeton University. Among the honors awarded Bartlett were the 1962 Corday-Morgan Medal and Prize of the Chemical Society of Great Britain, the 1965 Research Corporation Award, and the 1965 E. W. R. Steacie Prize.

For background information *see* INERT GASES; VALENCE in the McGraw-Hill Encyclopedia of Science and Technology. □