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RADON: CHEMICAL AND PHYSICAL STATES OF RADON PROGENY

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Professor A. W. Castleman, Jr.

**Department of Chemistry
Pennsylvania State University
152 Davey Laboratory
University Park, PA 16802
(814)865-7242**

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INTRODUCTION

The evolving chemical and physical form of radon progeny influence their transport to the bioreceptor and the extent to which that receptor can take up these species into various tissues. When first born following radioactive decay processes, the potentially deleterious radon progeny undergo various physical and chemical transformations as they transcend from a highly charged to a neutral state, and interact with various constituents of the environment. These transformations impact on the extent to which the radon progeny become associated with aerosol particles on the one hand, and their ultimate chemical form that is available for uptake in the biosystem, on the other.

Our program, which originally commenced in 1987, dealt with the basic chemistry and physics of radon progeny and hence impacted on several themes of importance to the DOE/OHER radon program. One of these is dose response, which is governed by the physical forms of the radon progeny, their transport to the bioreceptor and the chemical forms that govern their uptake. The second theme had to do with cellular responses, one of the major issues motivating our work. It is well known that various sizes of ions and molecules are selectively transported across cell membrane to differing degrees. This ultimately has to do with their chemical and physical forms, charge and size. For example, if the progeny are bound to molecules with extended polar groups, or alternatively with non-polar heads extending outward, this can impact their attachment to lung tissues and ultimately influence their incorporation within cells. On the other hand, the size of the progeny and the molecules to which they become bound and/or subsequently interact with in cells, influences their degree of transport and retention in the bioreceptor. We were able to study this by investigating relative interactions of various functional groups with these ions as they are influenced by hydration which occurs when these are introduced into the human body. Indeed, hydration has considerable impact on the ultimate structure and function of these constituents after they are introduced into cells. In another phase of the program we also used laser techniques to determine responses of various molecules to the impact of ionizing radiation, which the progeny cause, work which also falls within the theme of cellular responses to radiation.

The overall objective of our work was threefold: 1) quantifying the mechanisms and rates of the chemical and physical transformations, 2) ascertaining the ultimate chemical forms, and 3) determining the potential interactions of these chemical species with biological functional groups to ascertain their ultimate transport and incorporation within cells.

BRIEF SUMMARY OF FINDINGS

Upon birth, radon progeny initially undergo substantial clustering with various molecules present in the environment, especially those with large dipole moments. The evolving chemistry was investigated using several different techniques developed in our laboratory that enable study of the rates of the initial chemical transformations. Using these various specialized apparatuses we were able to study the growth and changes in physical form of the small particles with which radon progeny can become incorporated. Other techniques in our laboratory enabled us to study their changing chemical form which occurs on a longer timescale consistent with that available as the radon progeny are transported in the environment to the potential bioreceptor. Other techniques were then used to investigate how these physical and chemical forms interact with biological functional groups that influences their ultimate incorporation and retention within molecular cells and tissues. The techniques we employed involved sophisticated chemical flow reactors, fast laser techniques and associated newly developed mass spectrometers to measure the necessary parameters to assess and quantify the above-mentioned phenomena.

Early phases of the program identified the chemical evolution of the charged radon progeny species following their birth in various charged states. Our thermochemical experiments provided the basis for assessing the expected degree of hydration of the species in the environment, followed by investigations that led to knowledge of the extent to which other polar molecules present in the indoor environment would become incorporated. These investigations yielded information from which to assess the mobility of the radon species and their transport in the environment.

A major aspect of the more recent program was related to providing information for assessing cellular responses to radiation and involves studies of the interactions of radon progeny with biological molecules, particularly with various function groups which are important in determining their uptake in and binding to the bioreceptor. Ascertaining the effects of ionizing radiation on biological functional groups is a related problem which was also investigated. Another

major phase of the research involved studies designed to provide knowledge of the interaction of neutral progeny in both the ground and excited states, and ions in their excited state, with small aggregates. The small neutral aggregates being studied represented model systems that served to quantify the uptake of radon progeny by aerosol particles. Elucidating cation cluster-anion cluster interactions which are thought to be responsible for the formation of the small size neutral progeny species detected in certain indoor air environments was also an objective of the work, and was directly related to this aspect of the program. Finally, in terms of instrumentation needs, we pursued the development of techniques enabling study of aggregates of ever increasing size. We expected that these new instrumentation developments would lead to an important tool for calibrating conventional aerosol counting devices used to investigate the radon progeny-containing small-size aerosol spectrum.

Since its inception, our program has led to 35 publications in the open scientific literature. A listing is provided at the end of this final report.

Chemical Interactions with and Transport in the Bioreceptor

Radon gas, once in an indoor environment undergoes decay to progeny which chemically or physically transform and eventually can be inhaled or ingested. Certain isotopes of lead are products of the decay scheme and are radioactive, and these are the species which form the main thrust of our work. Determination of the fate of these radioactive species, particularly their incorporation into the body, is key to understanding, and possibly diminishing, their harmful effects. The mechanism responsible for a cell's ability to effectively select one ion type over another has been the center of much debate. Most of this has centered around the issue of how a cell discriminates potassium cations over sodium cations. Living system potassium channel studies by biochemists Miller, Toney, MacKinnon and others (1-3) was the basis for computer calculations by Kumpf and Dougherty (4) and their proposal that cation- π interaction establishes ion selectivity in potassium channels. Recent evidence, in the form of theoretical calculations, offers the cation- π mechanism for potassium channel selectivity. Our objective of learning how radon progeny becomes incorporated in cell has led us to investigate the possibility of a similar cation- π mechanism for the transport of radon progeny lead cations into the body. The prior computational work has provided a foundation for our own investigation of partially hydrated lead cations coordinating to aromatic molecules. It is

expected that the results from our work can be applied to studies of radon progeny incorporation into living systems. Mass spectrometric studies involving partially solvated cations and their affinity to coordinate to aromatic molecules provide an experimental foundation for assessing the viability of this mechanism.

In order to gain insight as to the ultimate fate of radon progeny, in recent months we sought to explore the physical feasibility that lead cations, because of their size, might act like potassium cations in potassium channels. In order to acquire the requisite data to assess this possibility, we made some modifications to our flow tube apparatus which enabled an investigation of the relative bonding of waters of hydration and benzene, the latter being a model system for determining the interactions between the progeny ion and the cell membrane. The ion source, a heated filament coated with a 1:2:1 slurry of aluminum oxide, silicon dioxide and metal nitrate, was coupled to a helium/water bubbler device in the relatively high pressure source region. This facilitated production of partially solvated cations. These ions were then allowed to react with neutral aromatic molecules, introduced through a reactant gas inlet, downstream. The resultant ions were then sampled, mass filtered with a quadrupole, and detected by pulse counting with a channeltron electron multiplier.

Reactions, involving partially hydrated lead cations (up to four water molecules), with neutral benzene clearly show a dehydration of the lead-water cluster forming lead-benzene (one and two benzene molecules). Similar results were observed with pyridine, another neutral aromatic molecule which serves as a prototypical model membrane. The facile attachment of one and two water molecules is evident from the experimental findings. Hence this represents the nature of water interactions leading to partial hydration of the progeny ion. The extent of interaction with a model π system is found to be quite large. This is evidenced by a mass spectrum showing that waters of hydration are totally replaced through interactions with benzene introduced into the flow tube reactor. Even trace additions were sufficient to fully dehydrate the Pb^+ , leading to the formation of complexes with one and two benzene molecules attached to the radon progeny ions. This finding suggests that if only waters of hydration are attached to radon progeny as they are transported through the environment, they will be very readily dehydrated upon incorporation into the bioreceptor. Indeed, the interactions with a cell membrane should be sufficiently strong to result in dehydration and facile transport of the comparatively small bare radon progeny ion into the cell.

Computations were also conducted in our laboratory on the extent of interaction of the radon progeny with π systems representing models of the cell membrane. Examples of a stable lead-benzene sandwich are found from the results. A rather strong interaction accounts for the observation of dehydration followed by a complete surrounding of the progeny ion by the model cell molecule. The dehydration of the lead-water clusters indicates an exceptional stability offered by cation- π interaction, leading to lead-benzene "sandwiches" being produced. There is reason to believe that, if ion selectivity in potassium channels is governed by cation- π interactions, a lead cation could effectively "mimic" a solvated potassium cation and be incorporated into the cell.

Further evidence for the extent of interaction of the π system with the lead-radon progeny ion is found in further studies made under other conditions. At higher concentrations of benzene, typical of the encounter of a progeny with model π systems representative of cell membrane, additional interactions beyond the sandwich complex are expected. For instance, as seen in a typical mass spectrum, Pb^+ takes up not only two benzene molecules, but in fact is readily coordinated by four as observed in the experiments. There is no hint of a fifth or sixth coordination from these experimental measurements. An especially suggestive finding was obtained through the use of some laser vaporization-SIDT techniques. No hydration of Pb^+ is found until after benzene is coordinated to the progeny ion. Indeed, there is seen to be a strong preference for benzene coordination before hydration. Collision induced dissociation experiments reveal that water is preferentially lost compared to benzene, offering further evidence for the strong interaction with π systems which model the cell membrane.

The Environmental Chemistry of Radon Progeny Ions

The issue concerning the reaction of both ionized, as well as neutral forms of radon progeny with various molecules of atmospheric importance, continues to be raised in assessing the chemistry of radon as it is transported through the indoor environment to the bioreceptor. Earlier work in our laboratory suggested that Pb^+ does not undergo extensive chemistry through interactions with oxygen. Further evidence of this fact is seen from data shown in Figure 1. Here Pb^+ (seen as the left-most peak in the mass spectrum) is not observed to interact with oxygen atoms even for those

Figure 1

weakly bound in the N_2O molecule chosen as the reactant in these studies. Our work continues to suggest that the radon progeny ion will be a bare species upon birth, and will not interact with common constituents of the atmosphere except through weak association reactions. Interestingly, from the results of our experiments shown in this figure, it is obvious that there is quite a difference in the case where two lead atoms are bound together as a dimer cation. Indeed, these are readily oxidized as seen in the mass spectrum; refer to the second and third peaks from the left which display that Pb_2^+ does oxidize forming Pb_2O^+ and $Pb_2O_2^+$. The former species also readily coordinates the molecule N_2O , forming larger complexes as seen in the mass spectrum shown in Figure 1.

Other studies were conducted during the last part of the grant period to investigate the interaction of radon progeny ions with model aerosol particles. In the indoor environment these are likely to be characterized by two types of species, namely ones for which there is an appreciable hydration layer surrounding the particles (under high humidity conditions) and others typical of particles generated in heating and cooking which are likely to have a substantial organic component tied to their outer periphery. The studies shown in Figure 2, which reveal the extent of interaction of Pb^+ with benzene, provide a prototypical example of the latter case. Work on larger cluster systems of this and related types are now needed.

With regard to interactions with the aqueous-type aerosol particles, experiments were conducted on the interaction of excited states of Pb^+ with large water clusters. The extent of interaction is significant as seen in the mass spectrum shown in Figure 3. Interestingly, the Pb^+ readily associates with large numbers of waters. Particularly strong interactions are indicated by the magic numbers shown in the mass spectra representing 20, 30, 42 and 68 water molecules, respectively.

Figure 2.

Figure 3

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