New Evidence that Radon is a Metalloid Element: Ion-exchange Reactions of Cationic Radon

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Cationic radon in 1,1,2-trichlorotrifluoroethane displaces hydrogen, sodium, and potassium ions in solid materials, such as Nafion resins (H⁺ and K⁺ forms), potassium hexafluorophosphate, and sodium hexafluoroantimonate; radon in this state can be quantitatively collected by ion-exchange and eluted with bromine trifluoride in sulphuryl chloride.

Rochow¹ and other authors have classified as 'metalloids' a small group of elements which lie between the true metals and nonmetals in the Periodic Table and which have some of the characteristics of both. This group includes boron, silicon, germanium, arsenic, antimony, tellurium, polonium, and astatine. Radon is clearly a member of the group, since it lies on the diagonal of the Table with these elements and forms a series of ionic compounds.^{2,3} Recently, we have found that solutions of cationic radon can be prepared by oxidizing elemental radon with halogen fluorides in 1,1,2-trichlorotrifluoroethane or sulphuryl chloride, solvents which are strongly oxidation-resistant. We report here some ion-exchange reactions of the cationic species which demonstrate their similarity to metal ions.

In our procedure, $10-200 \ \mu\text{Ci}$ of isotope $^{222}\text{Rn}(\text{half-life} 3.82 \text{ days})$ is shaken for ~1 h at room temperature with a solution of $0.10-0.68 \ Mmmm BrF_3$ or $0.10-2.0 \ Mmmmm BrF_5$ in 1,1,2-trichlorotrifluoroethane (5-20 ml). (A $0.68 \ Mmmmm mmmm solution$ is saturated with BrF₃ at 23 °C, but BrF₅ has a higher solubility.) At the end of this period, the radon is in a nonvolatile, oxidized state; the solution can then be flushed with nitrogen or distilled to dryness without loss of the radon. Similar

solutions can be prepared with sulphuryl chloride as the solvent in place of 1,1,2-trichlorotrifluoroethane. The amount of ²²²Rn in each solution can be determined by measuring the γ emissions of daughters ²¹⁴Pb and ²¹⁴Bi in equilibrium with their parent.² We have found that these solutions can be stored in capped FEP Teflon bottles at room temperature for several weeks. By analogy with known products of krypton and xenon, it has been deduced that radon forms a difluoride, RnF₂, in reactions with halogen fluorides;³ the most probable cations in the solutions are therefore RnF⁺ and Rn²⁺.

When a solution of the cations in trichlorotrifluoroethane is passed through a Kel-F plastic column packed with either KPF₆, NaSbF₆, Na₃AlF₆, or thoroughly dried Nafion resin (H⁺ or K⁺ form), the radon displaces the H⁺, Na⁺, and K⁺ ions in these materials and adheres in a narrow band at the top of the column. It can be washed repeatedly with 0.10 M BrF_3 in the halocarbon solvent, then eluted with 1.0 M BrF_3 in SO₂Cl₂. The radon daughters remain on the column during elution and decay *in situ*; new daughters are generated in the radoncontaining eluant fractions.

Sulphuryl chloride has a dielectric constant of 9.15, higher than that of 1,1,2-trichlorotrifluoroethane (2.41), and hence

promotes the ionization of BrF₃. Since sulphuryl chloride alone has little eluting power, we postulate that BrF_2^+ cation is the moiety that displaces radon from the column. The most probable sequence of reactions in the collection and elution of radon from a column packed with Nafion resin (K⁺ form), for example, is that shown by equations (1)—(3). In these equations, R_F represents the fluorocarbon portion of the resin.

$$Rn^{2+} + 2K^{+}R_{F}SO_{3}^{-} \rightleftharpoons Rn^{2+}(R_{F}SO_{3}^{-})_{2} + 2K^{+}$$
 (1)

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^- \tag{2}$$

 $2BrF_{2}^{+} + Rn^{2+}(R_{F}SO_{3}^{-})_{2} \rightleftharpoons 2BrF_{2}^{+}R_{F}^{+}SO_{3}^{-} + Rn^{2+}$ (3)

Although many finely divided solids will partly remove trace amounts of radon from solution by physical adsorption, we have found that removal by ion-exchange is much more efficient. The distribution coefficient, K_d , of cationic radon on the potassium form of Nafion resin is 290 ml/g in 0.10 M BrF₃-trichlorotrifluoroethane; on the hydrogen form of the resin it is approximately 3100 ml/g. In contrast, the distribu-

tion coefficient is less than 10 ml/g on materials which do not undergo exchange with the radon species, such as LiF, MgF_2 , and PbF_2 .

The discovery that radon can be oxidized to the cationic form in these solvents has opened new paths for exploring its chemistry. Among the many questions remaining to be answered are the oxidation states that can be produced in these solutions; the effect of neutral and negatively charged complexing agents upon radon ions; and the ability of the ions to displace heavy alkali metal ions and divalent metal ions which are more firmly bound than hydrogen, sodium, and potassium ions.

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References

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