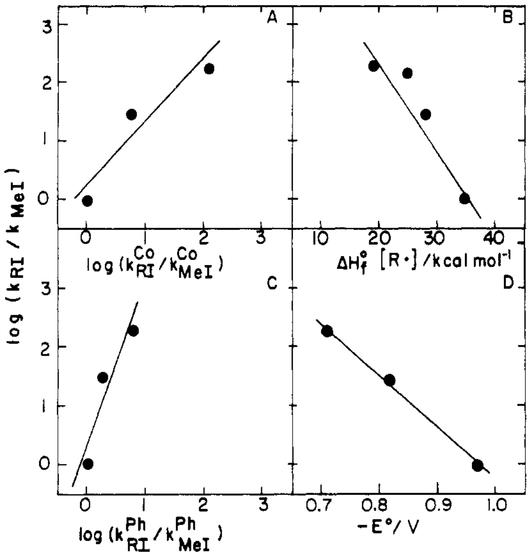

Figure 2. Attempted correlations of k_{RI} with parameters relating to the reductive dissociation of alkyl halides in terms of (A) log $(k_{RI}{}^{Co}/k_{MeI}{}^{Co})$, where k^{Co} is the rate constant for $Co(CN)_5{}^{3-}$, (B) the enthalpy of formation of the alkyl radical, (C) log $(k_{RI}{}^{Ph}/k_{MeI}{}^{Ph})$, where k^{Ph} is the rate constant for iodine atom abstraction by phenyl radicals, and (D) $E°$(estd) for the electrochemical reduction of the alkyl iodide.

kinetics, $-\mathrm{d}\ln[CrC(CH_3)_2OH^{2+}]/\mathrm{d}t = k_{obsd}$, the expression for the experimental rate constant being

$$k_{obsd} = k_A + k_H k_{RI}[RI]/(k_{Cr}[Cr^{2+}] + k_{RI}[RI]) \tag{6}$$

The experimental data were analyzed by a nonlinear least-squares fit of the data to eq 6, with values of k_A and k_H set at values determined under these precise conditions (see Table I), and k_{Cr} taken to be $5.1 \times 10^7\ M^{-1}\ s^{-1}$, the same as in 0.15–1.0 M 2-PrOH at 22 ± 2 °C.[13] The resulting values of k_{RI} are given in Table I. Alternatively, the equation can be recast into a linear form (eq 7) that permits graphical representation of the data, as illustrated in Figure 1.

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_H} + \frac{k_{Cr}}{k_H k_{RI}}\,\frac{[Cr^{2+}]}{[RI]} \tag{7}$$

Products. The identification of CrR^{2+} as the product provides evidence for the reactions given above. The 2-propyl complex was isolated by ion-exchange chromatography and identified by its absorption spectrum and by its reactions with Br_2 and Hg^{2+}. In the latter case, kinetic data were also used to confirm its identity. Other complexes ($CrCH_3{}^{2+}$, $CrCH_2CH_3{}^{2+}$) were identified by their visible/UV spectra and by the rates of their acidolysis reactions.

Interpretation and Discussion

The reactions shown are in complete accord with earlier studies of $CrC(CH_3)_2OH^{2+}$. They are supported in this case by the fit of the kinetic data to eq 6, as illustrated in Figure 1, and by the confirmation that CrR^{2+} is formed from a given RI.

The reaction between $\cdot C(CH_3)_2OH$ and RI is not without precedent, although the slowness of these reactions has precluded earlier kinetic measurements. For example, pulse-radiolysis experiments[16] set $k < 10^5\ M^{-1}\ s^{-1}$ for the reduction of CH_3I by $\cdot C(CH_3)_2OH$ at pH 7. In contrast, the conjugate base of the radical, a more powerful reducing agent, reacts readily (CH_3I, $k = 1.1 \times 10^8\ M^{-1}\ s^{-1}$).[16] The method employed here is applicable to less reactive substrates, which is the case with all of these alkyl iodides (Table I).

It is instructive to examine the factor(s) responsible for the changes in k_{RI} among the series of compounds examined. The variation of the rate constants with certain other kinetic and thermodynamic measures of the electron-transfer properties of alkyl iodides was explored. Each of the following gave approximate correlations: (a) the rates of inner-sphere reduction of RI by $Co(CN)_5{}^{3-}$ [17] (or for $Cr(15aneN_4)^{2+}$,[18] which is not depicted but gives a quite comparable graph); (b) the enthalpy of formation of R·;[19] (c) the rate of iodine atom abstraction from RI by phenyl radicals;[19] (d) the estimated standard reduction potentials of RI.[20] These correlations in a LFER sense are shown in Figure 2. Electron transfer from $\cdot C(CH_3)_2OH$ to RI appears to be governed by factors similar to those found for the several mechanisms (atom abstraction,[21] electron transfer, dissociative reduction) by which RI is known to react. A finer distinction[22] among the mechanisms cannot be made on the basis of the available data.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82.

Registry No. $(H_2O)_5CrCH(CH_3)_2{}^{2+}$, 60764-48-9; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3; CH_3I, 74-88-4; CH_3CH_2I, 75-03-6; $(CH_3)_2CHI$, 75-30-9; $c\text{-}C_5H_9I$, 1556-18-9.

---

(16) Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2705.

(17) Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2.

(18) Samuels, G. J.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 2587.

(19) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655.

(20) Eberson, L. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 533.

(21) Halogen abstraction reactions by Et_3Si follow the reactivity order $CH_3X \geq C_2H_5X < i\text{-}C_3H_7X$: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123. The absolute rate constants are, however, close to diffusion controlled in these systems, and the selectivity of the radical is diminished.

(22) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; pp 138–168. A detailed discussion of these mechanisms is presented in this reference.

Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Hydrolytic Reactions of Radon Fluorides

Lawrence Stein

Received May 1, 1984

The chemistry of radon has been studied by radioactive-tracer methods, since no stable isotopes of this element are known. It has been shown that radon reacts with fluorine,[1] halogen fluorides,[2] and a number of oxidizing salts.[3,4] By comparing the properties of its products with known properties of krypton and xenon fluorides, it has been possible to deduce that radon forms a difluoride, RnF_2, and derivatives of the difluoride, such as $RnF^+SbF_6{}^-$, $RnF^+TaF_6{}^-$, and $RnF^+BiF_6{}^-$. The trace products are reduced to elemental radon by water in reactions that are analogous to those of KrF_2 and XeF_2 with water:

$$KrF_2 + H_2O \rightarrow Kr + {}^1\!/_2O_2 + 2HF$$

$$XeF_2 + H_2O \rightarrow Xe + {}^1\!/_2O_2 + 2HF$$

$$RnF_2 + H_2O \rightarrow Rn + {}^1\!/_2O_2 + 2HF$$

(In contrast, XeF_4 and XeF_6 form stable solutions of XeO_3.[5,6])

---

(1) Fields, P. R.; Stein, L.; Zirin, M. H. *J. Am. Chem. Soc.* **1962**, *84*, 4164.

(2) Stein, L. *Science (Washington, D.C.)* **1970**, *168*, 362.

(3) Stein, L. *Science (Washington, D.C.)* **1972**, *175*, 1463.

(4) Stein, L. *Radiochim. Acta* **1983**, *32*, 163.

(5) Malm, J. G.; Appelman, E. H. *At. Energy Rev.* **1967**, *7* (3), 3.

(6) Bartlett, N.; Sladky, F. O. In "Comprehensive Inorganic Chemistry"; Trotman-Dickenson, A. F., Ed.; Pergamon Press: Oxford, 1973; Vol. 1, pp 213–330.

0020-1669/84/1323-3670$01.50/0 © 1984 American Chemical Society

The fluoride also coprecipitates from halogen fluoride solutions with XeF_2 and complexes of XeF_2 but not with XeF_4.[7,8]

Recently, Avrorin et al.[9] have reported the preparation of a higher fluoride of radon, either RnF_4 or RnF_6, and a water-soluble oxide, RnO_3, in tracer experiments with isotope ^{222}Rn. They hydrolyzed complex mixtures of products that had been obtained by heating radon, xenon, fluorine, bromine pentafluoride, and either sodium fluoride or nickel fluoride. Part of the radon volatilized on hydrolysis and part remained in the aqueous phase, suggesting the formation of RnO_3. However, Avrorin et al. failed to closely examine the contents of the aqueous phase. In this note we report the results of experiments that we have carried out, using larger amounts of reagents and similar conditions, in an effort to confirm their findings.

Experimental Section

A Monel reactor (9.05-mL volume) attached to a Monel valve was loaded at room temperature with either NiF_2 (16.8–27.7 mmol) or NaF (39.3–42.9 mmol), cooled to −195 °C, and charged with BrF_5 (15.5–46.4 mmol), ^{222}Rn (49–221 μCi), xenon (0.54–0.57 mmol), and fluorine (54.7–57.1 mmol). Each mixture was heated at 250–265 °C for approximately 40 h. The excess fluorine was pumped off at −195 °C, and BrF_5 and uncomplexed XeF_6 were vacuum distilled from the reactor at 0 °C. (The XeF_6 product was complexes by NaF but not by NiF_2). Products remaining in the reactor were then hydrolyzed with 8–15 mL of 0.10 M aqueous XeO_3 solution at 0 °C. Radon in the hydrolysate was analyzed by measuring the γ emissions of its daughters, ^{214}Pb and ^{214}Bi, in equilibrium with their parent.[4] The hydrolysate was centrifuged and the supernate transferred to a separate container; the radon was then analyzed in each fraction. The supernate was flushed with nitrogen for 5–10 min and the residue stirred with 10 mL of either water, 0.10 M XeO_3 solution, or 1 M KI solution; after 4 h, the analyses were repeated.

To determine the behavior of radon in simpler mixtures, several experiments were carried out with only radon, fluorine, and NiF_2 or with only radon, fluorine, and NaF. Each mixture was heated at 335–350 °C for approximately 3 h, excess fluorine was pumped off at −195 °C, and the products were hydrolyzed as before.

Results and Discussion

In the experiments with quinary mixtures, we found that 70% or more of the radon initially bound as a nonvolatile fluoride was released as gas during the hydrolysis. However, the remainder was not in solution, as reported by Avrorin et al., but was trapped in undissolved solid. After the centrifugation and purge with nitrogen, less than 0.2% of the radon remained in the liquid phase. Approximately 11–29% (corrected for decay) stayed in the NiF_2 residue and 5–24% in the NaF residue during the course of these experiments. Stirring the solid with water, XeO_3 solution, or KI solution released a further amount of radon as gas but yielded no solution containing a soluble radon compound. Iodine was liberated when KI solution was added to the supernate, showing that XeO_3 was not removed by the purge.

In each experiment with radon, fluorine, and NiF_2, a complex fluoride was formed [probably $(RnF^+)_2NiF_6^{2-}$, a noble-gas analogue of K_2NiF_6 and Cs_2NiF_6]. The radon was found to be concentrated in the NiF_2 powder at the end of the fluorination. In experiments with radon, fluorine, and NaF, the radon was found to be distributed throughout the reactor, suggesting that the simple fluoride RnF_2 was formed. During the hydrolysis of each product, part of the radon was released as gas and part trapped in the solid, as before.

We conclude from this study that no higher fluoride or oxide of radon is formed in the procedure of Avrorin et al. but that, instead, the radon is carried by solids. Other workers have also been misled by this phenomenon. In 1967, Haseltine and Moser[10] reported the oxidation of radon in aqueous solutions with hydrogen peroxide, potassium permanganate, potassium persulfate, and other reagents, but Flohr and Appelman[11] showed that the radon had not been oxidized but merely trapped in suspended solids. Gusev and Kirin[12] later confirmed Flohr and Appelman's results, using barium as a carrier.

Thus far, we have seen no evidence for the existence of radon compounds or ions in aqueous solutions. We have found that solutions of cationic radon can be prepared very readily, however, in nonaqueous solvents, such as hydrogen fluoride and halogen fluorides.[2,4]

Acknowledgment. This work was performed under the auspices of the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38.

Registry No. RnF_4, 18976-86-8; RnF_6, 80948-45-4; RnO_3, 80948-46-5; NiF_2, 10028-18-9; NaF, 7681-49-4; BrF_5, 7789-30-2; ^{222}Rn, 14859-67-7; Xe, 7440-63-3; F_2, 7782-41-4.

---

(7) Nefedov, V. D.; Toropova, M. A.; Avrorin, V. V.; Dudkin, B. N. *Radiokhimiya* **1971**, *13*, 916.

(8) Avrorin, V. V.; Nefedov, V. D.; Toropova, M. A. *Radiokhimiya* **1974**, *16*, 261.

(9) Avrorin V. V.; Krasikova, R. N.; Nefedov, V. D.; Toropova, M. A. *Radiokhimiya* **1981**, *23*, 879.

(10) Haseltine, M. W.; Moser, H. C. *J. Am. Chem. Soc.* **1967**, *89*, 2498.

(11) Flohr, K.; Appelman, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 3584.

(12) Gusev, Yu. K.; Kirin, I. S. *Radiokhimiya* **1971**, *13*, 916.

Contribution from the Department of Chemistry
and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

New Routes to the Preparation of the Aquomolybdenum(IV) Ion by Comproportionation Reactions

F. Albert Cotton,* David O. Marler, and Willi Schwotzer

Received December 16, 1983

The existence of an aquomolybdenum(IV) ion was first demonstrated by Souchay and co-workers[1] in 1966. Beginning in 1975, efforts to establish the nuclearity of the aquo ion in solution produced proposals of both mononuclear[2,3] and binuclear[4–7] structures. These conclusions were based on kinetic, electrochemical and cryoscopic measurements. However, the likelihood of a trinuclear structure of the sort shown in Figure 1., e.g., $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$, was suggested by the fact that merely by addition under mild conditions of certain ligands to a solution of the aquo ion crystalline products were isolated in which an $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3L_9$ structure was found.[8–10] Direct evidence of the trinuclear character of the

---

(1) Souchay, P.; Cadiot, M.; Duhameaux, M. *C. R. Hebd. Seances Acad. Sci.* **1966**, *262*, 1524.

(2) Ramasami, T.; Taylor, R. S.; Sykes, A. G. *J. Am. Chem. Soc.* **1975**, *97*, 5918.

(3) Ojo, S. F.; Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 1006.

(4) Ardon, M.; Pernick. A. *J. Am. Chem. Soc.* **1973**, *95*, 6871.

(5) Ardon, M.; Bino, A.; Yahaw, G. *J. Am. Chem. Soc.* **1976**, *98*, 2338.

(6) Chalilpoyil, P.; Anson, F. C. *Inorg. Chem.* **1978**, *17*, 2418.

(7) Cramer, S. P.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2770.

(8) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.

(9) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3842.

(10) Schlemper, E. O.; Hussian, M. S.; Murmann, R. K. *Cryst. Struct. Commun.* **1982**, *11*, 89.