very labile. Hence the system takes advantage of a (presumably) relatively rapid electron-transfer reaction, $\mathbf{2} \rightleftharpoons \mathbf{3}$, and the lability of Cr(II) to gain a rapid path to reactants, whereas conversion to products requires slow substitution on Ru(II). The much greater rate of substitution on Cr(II) compared to that on Ru(II) more than compensates for the unfavorable $\mathbf{3} \rightleftharpoons \mathbf{2}$ equilibrium. We believe this is an excellent example of substitution reactions dominating an electron-transfer process.[5c]

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Oxidized Radon in Halogen Fluoride Solutions[1]

Sir:

It has been shown in previous tracer experiments that radon forms a fluoride of very low volatility.[2,3] Solutions of oxidized radon have now been prepared by reaction of microgram amounts of the element with bromine trifluoride, bromine pentafluoride, and chlorine trifluoride. The halogen fluorides can be vacuum distilled from the solutions at room temperature without volatilization of radon. This behavior suggests that radon is present in the solutions as an ionic species, possibly Rn^{2+}. Solids obtained by evaporation of the solutions to dryness have not been identified but appear to be identical with the simple fluoride formed in the reaction of radon and fluorine.[2] The solids liberate elemental radon on hydrolysis, leaving very little activity in the aqueous phase. Since krypton difluoride and xenon difluoride also hydrolyze in this manner, it is probable that the product is radon difluoride in each instance.

Hazeltine and Moser[4] recently reported that nonvolatile, nonextractable radon species could be produced in aqueous solutions through the use of oxidants, such as hydrogen peroxide, potassium permanganate, and potassium persulfate. However, they observed the species only in solutions containing radon and its parent, radium-226, and not in solutions containing radon alone. Flohr and Appelman[5] repeated the experiments and found that the nonvolatile species could be removed from solution by centrifugation. They concluded that no radon compound was present but that radium coprecipitated with suspended matter in the solutions and then produced radon which was mechanically trapped in the solid.

The present experiments were carried out in a shielded cell with gaseous ^{222}Rn, which was collected from a 5-Ci radium chloride solution, passed through a drying tube containing calcium sulfate, and condensed in a trap on a metal vacuum line at $-195°$. The gas was partially purified by distillation at $-78°$ after radiolytic hydrogen and oxygen were pumped off. In the first experiment, approximately 0.25 Ci of radon (1.5 μg) was condensed in a Kel-F tube containing 8 ml of frozen bromine pentafluoride at $-195°$. The mixture was allowed to thaw and warm to room temperature for 1.5 hr, during which time it was shaken several times. At the end of this period, the radon was found to be concentrated in the liquid phase at the bottom of the tube. The position of radon was determined by measuring the β–γ emission of its daughters with a Jordan meter, using a technique similar to that previously described.[2] The solution was then vacuum distilled at room temperature. The bromine pentafluoride distillate was found to be inactive, and the radon was found to be concentrated in the dry residue remaining in the Kel-F tube.

Solutions of approximately 0.12 Ci of radon in 6 ml of bromine trifluoride and 0.32 Ci of radon in 4 ml of chlorine trifluoride were prepared in a similar manner. The reaction of radon with bromine trifluoride was incomplete, probably because of partial condensation of the gas on the test tube walls above the frozen trifluoride. Five per cent of the activity appeared in the first distillate fraction, whereas none appeared in later fractions. All distillate fractions from the chlorine trifluoride solution were found to be inactive.

Aliquots of a solution which contained 15 mCi of radon per ml of bromine trifluoride were removed with Kel-F pipets in a glove box and progressively diluted with inactive bromine trifluoride. The solutions then showed β–γ activities corresponding to the dilution factors. The solutions were centrifuged and decanted from test tube to test tube without loss of activity. To verify that radon was present in the diluted samples as well as the short-lived β–γ emitting daughters, ^{214}Pb and ^{214}Bi, the activity was checked over a period of 22 days and was found to decay with the half-life of ^{222}Rn (3.8 days). Some radiation decomposition of bromine trifluoride was noted in the undiluted stock solution, which changed from a yellow color to a deep orange color within 3 days. The reduction products (Br_2 and BrF) were distilled from the solution without volatilization of radon.

In a comparison of the electronic structures of group VIII elements, it can be noted that 18 electrons are added in completed shells between argon and krypton and 18 between krypton and xenon, whereas 32 electrons are added between xenon and radon. The longer interval between xenon and radon (filling of 4f orbitals as well as 5d, 6s, and 6p orbitals) undoubtedly produces a greater change in the properties of these two elements than that between preceding pairs of elements in the series. It is not surprising, therefore, to find that radon is much more "metallic" than xenon. The first ionization potential of radon is only 10.75 V, comparable to that of iodine (10.45 V) and much lower than ionization potentials of other halogens or hydrogen. The low volatility of radon fluoride has led Weinstock[6] to pro-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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[6] B. Weinstock, ref 3, p 119.

pose an ionic structure for the solid, and the behavior in halogen fluoride solutions is also indicative of the presence of ionic species. Electromigration and coprecipitation experiments are now being planned to determine the charge and chemical characteristics of the oxidized species. It is probable that stable solutions of radon in one or more positive valence states can be prepared in other nonaqueous solvents, such as hydrogen fluoride, antimony pentafluoride, or various metal hexafluorides.

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Spectroscopic Observation of the Triplet Excited State of Uracil in Solution

Sir:

Considerable work has recently been published on the effect of ultraviolet irradiation on the basic pyrimidines and purines in DNA and RNA, and on DNA itself (for recent reviews see ref 1–3). Various studies,[1–5] including photosensitization studies, have shown that dimerization of thymine and uracil occurs primarily from an excited triplet level, while an excited singlet state has also been invoked as the precursor under certain experimental conditions. Low-temperature (ethylene glycol–water glasses at 77°K) phosphorescence spectra of various nucleotides and dinucleotides have been observed,[1] but no triplet–triplet absorption spectra have been reported. Attempts[6] to determine triplet absorption spectra on flash photolysis of aqueous solutions of uracil, 5-bromouracil, and thymine at 20° were negative, using flash-duration resolution of ~20 μsec. Such a failure was accounted as due to the short lifetimes of these triplets (estimated as 0.5–5.0 μsec) and the relatively low quantum yield.

A different approach to produce and study such triplets is presented here, using the much higher time-resolution available in the pulse radiolysis technique. The radiolysis of organic liquids is known to produce excited singlets and triplets which can transfer their energy to solutes. Naphthalene (N) and anthracene (A) triplets have, for example, been observed[7] on pulse radiolysis of solutions of N and A in various polar protic and aprotic solvents. Figure 1 shows the transient optical absorption spectra produced on pulse radiolysis of uracil in acetonitrile (AN), dimethylformamide (DMF), and isopropyl alcohol (*i*-PrOH). Single pulses of 2.3-MeV electrons, 30-nsec duration, were used;[8] the monitoring light entered a double monochromator and an EMI 9558 QB photomultiplier was employed.

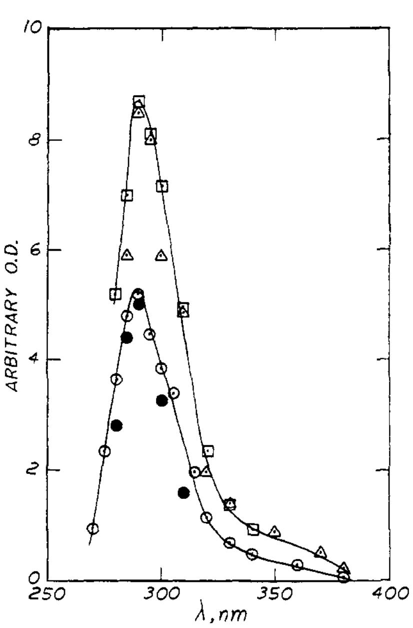

Figure 1. Transient optical spectra obtained on pulse radiolysis of oxygen-free solutions of uracil in acetonitrile (⊙, 2×10^{-4} *M*), in dimethylformamide (⊡, 7×10^{-4} *M*), and in isopropyl alcohol (◬, 2×10^{-4} *M*). The OD was measured at ≤ 0.2 μsec after a 30-nsec pulse of electrons, dose per pulse ~28 krads. Filled circles (●) obtained from flash photolysis of oxygen-free 2×10^{-5} *M* uracil in acetonitrile, OD normalized to pulse data.

The following observations and considerations support the assignment of this transient spectrum to the T–T absorption of uracil. (1) An identical transient absorption with $\lambda_{\max}$ 289 ± 1 nm has been obtained in the pulse radiolysis of uracil in five different organic liquids. (2) The amount of transient observed is directly proportional to the *G* value of N^T or A^T produced[7] in that solvent; *e.g.*, G_{N^T} is 0.11, 0.19, and 0.20 in AN, DMF, and *i*-PrOH, respectively. (3) The flash photolysis[9] of 2×10^{-5} *M* uracil in AN and 1×10^{-5} *M* uracil in water at pH 5.0 in carefully degassed solutions is found to produce a similar spectrum with $\lambda_{\max}$ ~290 nm (see Figure 1). (4) The transient is not due to an electron adduct of uracil since it differs from the absorption spectrum of such an adduct[8b] and is formed in N_2O-saturated solutions; furthermore, the extent of its formation does not correlate with the $G_{e^-_{\text{solv}}}$ produced[7] in these solvents. $G_{e^-_{\text{solv}}}$ is 0.44, 1.62, and 0.92 in AN, DMF, and *i*-PrOH, respectively. (5) The transient decays by a first-order process in the three solvents with a half-life, $t_{1/2} = 0.693/k$, of 6.0 ± 0.4, 10.0 ± 1.0, and 5.0 ± 1.0 μsec in AN, DMF, and *i*-PrOH, respectively, under the particular experimental conditions and uracil concentrations. (6) The absorption maxima of other pyrimidines and purines examined are shifted to higher or lower wavelengths; *e.g.*, thymine triplet has $\lambda_{\max}$ ~300 nm. (7) Taking[10] the T–T extinction coefficient of naphthalene as 22,600 M^{-1} cm^{-1}, the T–T extinction coefficient of uracil at 289 nm is determined to be $\geq$91,000 M^{-1} cm^{-1} (± 10%), assuming equal formation of triplet states.

Full details on the nature of triplet excited states of various pyrimidines, purines, and dinucleotides and the effect of solute concentration, pH, O_2, and energy-trans-

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