

Neutron and β/γ Radiolysis of Water up to Supercritical Conditions. 2. SF₆ as a Scavenger for Hydrated Electron

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SF₆ has been used as a specific scavenger to investigate the β/γ radiolysis yield of hydrated electrons in pressurized high temperature sub- and supercritical water. SF₆ is thermally stable in supercritical water, and each scavenging reaction is known to produce six fluoride ions, which can be readily measured using a fluoride-selective electrode. Problems in the application of this method are described, including buildup of acid product and chain reduction of SF₆ in the presence of organic $\cdot\text{H}$ and $\cdot\text{OH}$ radical scavengers. Ultimately we find that the combination of SF₆ and phenol in neutral solution gives reliable results in supercritical water, because the protons and fluoride ions remain associated as HF molecules. The β/γ yields in supercritical water are similar to previous measurements using N₂O scavenger.

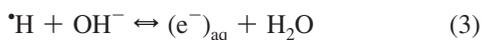
I. Introduction

The radiation-induced breakdown of high temperature water is an important topic in understanding corrosion of structural components in existing nuclear power plants and in predicting corrosion in potentially more efficient reactors operating with supercritical water coolant.^{1–5} In part 1 of this series,⁶ measurements of H₂, $\cdot\text{H}$ atom, and solvated electron yields were presented for the radiolysis of pressurized high temperature water using β/γ radiation generated with a van de Graaff accelerator. An extensive series of measurements were made vs temperature up to 400 °C on a 250 bar isobar, and two series were measured vs density (pressure) for constant temperatures of 380 and 400 °C. (The original report was corrected for a small pressure measurement error in a recent erratum.⁷) These measurements are complementary to similar measurements made in a flow loop⁸ at the University of Wisconsin reactor facility, which will be described in part 3 of this series. The complementary measurements allow separation of radiolysis effects due to β/γ radiation from those due to neutron radiation.

In part 1, hydrated electron yields were determined by the reaction of hydrated electrons (e^-)_{aq} with the scavenger N₂O, which gives the easily measured stable product N₂:



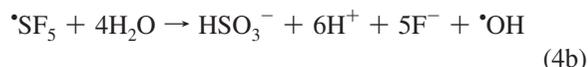
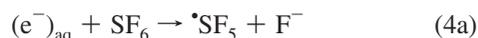
Phenol was added to the water to scavenge $\cdot\text{H}$ atoms, some of which could otherwise convert to solvated electrons (equilibrium reaction 3) and contribute to the observed N₂ yield.



It was found that N₂O decomposes to some extent on the hot metal walls of the flow system at 380 and 400 °C, but it was

possible to subtract this thermal component from the radiolytic yield because the dwell time is quite short—on the order of 1 s. This is not the case for the reactor flow loop,⁸ and the much longer dwell time poses a serious problem for the use of N₂O in that system at supercritical temperatures.

To overcome this problem we explored the use of SF₆ as a specific scavenger for the hydrated electron. SF₆ is thermally stable at the supercritical temperatures, and is known to react with (e^-)_{aq} and then hydrolyze, producing six fluoride ions for every electron:⁹



The fluoride can be conveniently measured with a fluoride-selective electrode. A problem with the SF₆ scavenger is that the acid produced can build up and kinetically compete with the SF₆, leading to an incorrect (low) yield result for (e^-)_{aq}. A simple remedy is to add a small amount of KOH to neutralize the acid. Phenol is added as well to prevent $\cdot\text{H}$ atom contribution to the result.

As we describe below, this system works well in subcritical water. In supercritical water, very strange results were recorded, which have now been understood in terms of a chain reduction of SF₆ in alkaline phenol solutions. Surprisingly, good results are obtained in neutral phenol solutions.

II. Experimental Section

The flow system used in these experiments is identical to the apparatus used in part 1.⁶ Briefly, using a pair of HPLC pumps, water is pumped at 6 mL/min through a preheater and then into a titanium or Hastelloy 276 tube of ca. 2 mm i.d. in front of a beam port of a 3 MeV van de Graaff electron accelerator. The dwell time of the water in the irradiation zone is approximately 0.6 s. The water then is cooled to room temperature, and pressure is dropped through a small-diameter capillary. The water travels approximately 15 m from the

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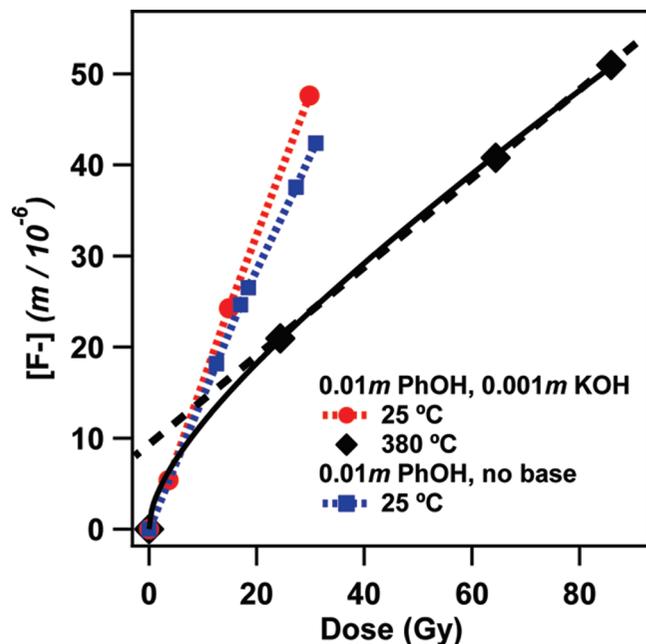


Figure 1. Fluoride production vs dose as a function of temperature in alkaline solutions of SF_6 (0.01 *m* phenol/0.001 *m* KOH/ 2.5×10^{-4} *m* SF_6). (For clarity, the 380 °C dose has not been normalized by multiplying by the density, 0.45 g/cm^3 .) At room temperature slightly nonlinear production of F^- is found in neutral solution due to acid product buildup, but in alkaline solution the signal is linear. In alkaline supercritical water the data appear to be linear (cf. the dashed line), but the intercept is nonzero. The solid line fit is explained in the text.

irradiation vault to the control room for analysis. Rather than collecting 12 mL of solution for gas sparging and mass spectrometry analysis as in part 1, 50 mL of solution was collected in a small beaker for testing with an Accumet fluoride-sensitive electrode. A pH and ionic strength buffer tablet supplied by the manufacturer was added to each beaker, and the SF_6 was briefly sparged from each sample to avoid poisoning of the electrode surface by the SF_6 . The electrode voltage was measured to 0.05 mV precision with a differential voltmeter. With careful measurement practice we are able to obtain ca. 2% precision in repeated measurements of any sample greater than 10 μM concentration.

The continuous electron beam at this accelerator port is poorly focused and varies significantly from day to day. A fiber optic is strung in front of the flow tubing to intercept a small representative fraction of the radiation. Fluorescence and Cerenkov light generated in the fiber is proportional to the dose delivered to the sample. Each day the fluoride concentration generated at room temperature (20 °C) is measured to calibrate the light signal from the fiber. In SF_6 saturated solution containing 0.01 *m* phenol and 0.001 *m* KOH, we take the (scavenged) electron yield to be 2.60×10^{-7} mol/J in order to deduce the actual dose corresponding to a given integrated light intensity. Typical room temperature dose rates generated in this experiment run in the range 10–100 Gy/s. At other temperatures and pressures we assume the absorbed dose is proportional to the water density.

III. Results

Figure 1 compares fluoride concentrations generated vs total dose in SF_6 saturated solutions of 0.01 *m* phenol, for room temperature and for 380 °C at 250 bar pressure. The dwell time is fixed, so total dose is changed via changing the dose rate

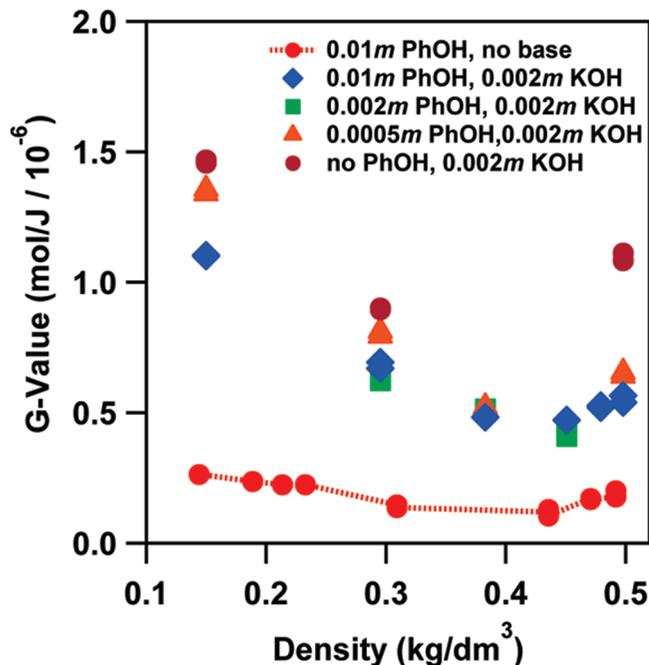


Figure 2. Survey of fluoride production for several KOH and phenol concentrations (2.5×10^{-4} *m* SF_6) as a function of density at 380 °C. The *G* value indicated is fluoride yield divided by 6, to give the $(e^-)_{\text{aq}}$ yield. Neutral solutions of 0.01 *m* phenol agree reasonably well with work conducted by Janik et al.^{6,7}

from the accelerator. In neutral solution the dose response is slightly nonlinear, as predicted, due to acid buildup. In 0.001 *m* KOH solution the fluoride generated is a linear function of the dose (or dose rate), with zero intercept. Similar behavior is found up to 300 °C. At 380 °C, the fluoride concentration in 0.001 *m* KOH appears to be a linear function of dose in the range examined, but the (dashed line) intercept is significantly larger than zero. A blank run with no dose gave no fluoride signal. Indeed, we have never observed breakdown of SF_6 in the absence of radiation. (This zero dose point is omitted from the linear least squares fit here and in the figures discussed below.)

A survey of (apparent) $(e^-)_{\text{aq}}$ yield vs density in supercritical water at 380 °C is displayed in Figure 2 for a constant dose of approximately 50 Gy/s. Contrary to expectation, in neutral solutions of phenol, $G((e^-)_{\text{aq}})$ is nearly equal to the N_2O result from part 1: hydrofluoric acid product buildup appears to be no factor. Also contrary to expectation, in the presence of 0.002 *m* KOH, the $(e^-)_{\text{aq}}$ yield is 3–5 times larger than in neutral solution. (According to the conductivity measurements of Ho et al.,¹⁰ KOH is still fully dissociated up to this concentration.) Possibly some of this additional yield could come from ^1H atom conversion to $(e^-)_{\text{aq}}$, if phenol were a poor scavenger for ^1H atoms at this temperature. We reduced the concentration of the phenol scavenger from 0.01 *m* to 0.002 *m* with little effect (Figure 2). This shows that more than enough phenol is present to scavenge the ^1H atoms. A reduction of phenol concentration to 0.0005 *m* finally led to an increase in the fluoride yield, which we ascribe to this $\text{H} \rightleftharpoons (e^-)_{\text{aq}}$ conversion. By omitting phenol entirely, all ^1H atoms should convert to $(e^-)_{\text{aq}}$ and the yield is in principle due to the sum of $(e^-)_{\text{aq}}$ and ^1H atom yields. The yields found in Figure 2 are larger than the combined $G((e^-)_{\text{aq}})$ and $G(\text{H})$ yields found in part 1.⁶ However, it has since been found that the ^1H atom yield is underestimated in this previous work.¹

More careful measurement of fluoride yield vs unnormalized dose in neutral pH phenol solution is shown in Figure 3 for

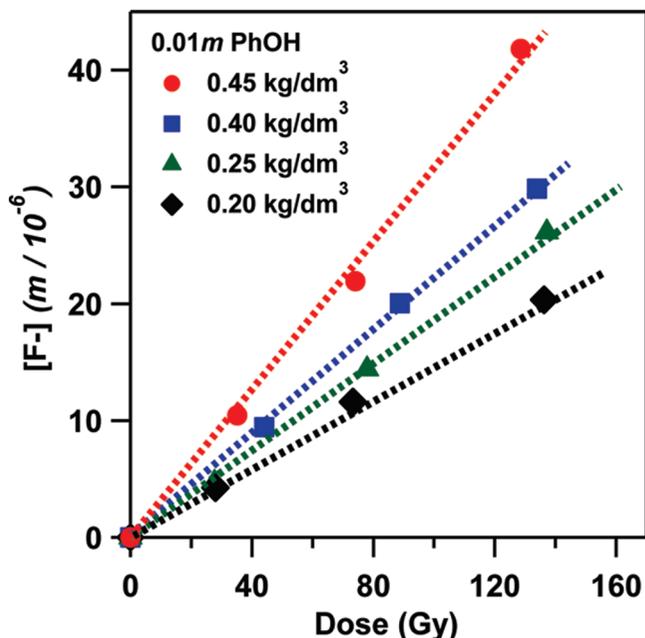


Figure 3. Fluoride production vs (unnormalized) dose in neutral phenol solutions at 380 °C (0.01 *m* phenol/2.5 × 10⁻⁴ *m* SF₆). A zero intercept is visible, indicating no chain reactions are occurring.

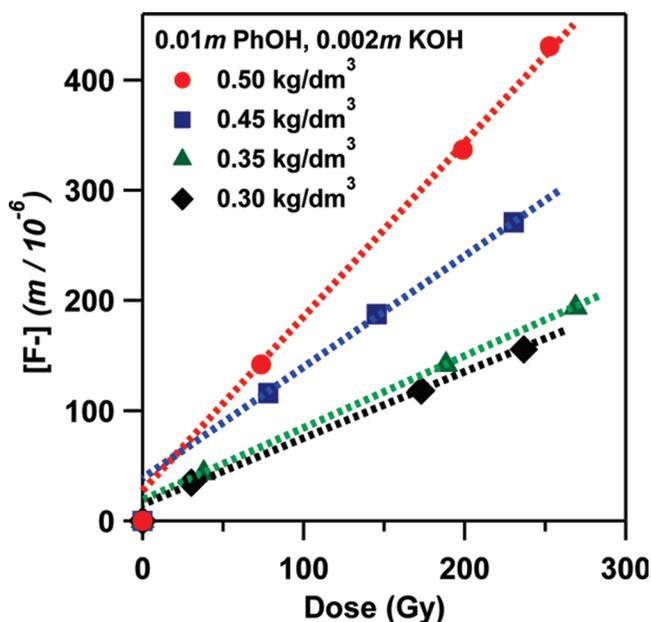


Figure 4. Fluoride production vs (unnormalized) dose in alkaline phenol solutions at 380 °C (0.01 *m* phenol/2.5 × 10⁻⁴ *m* SF₆/0.002 *m* KOH). As opposed to the neutral case, a nonzero intercept is visible, indicating substantial chain reactions are occurring.

several densities at 380 °C, and in Figure 4 similar data are shown for alkaline solutions. (For clarity of display the dose has not been normalized for density.) The neutral solutions of Figure 3 exhibit very linear behavior with zero intercept. The alkaline solutions all exhibit the “nonzero intercept”, which indicates some unanticipated dose-rate-dependent process in the chemistry. (The zero-dose blank experiment gives a zero fluoride result.) In Table 1 we list the (e⁻)_{aq} yields (i.e., $G(\text{F}^-)/6$) in the neutral solutions at 380 and 400 °C. In Figure 5 these yields are compared with the (e⁻)_{aq} yields found for neutral N₂O solutions in part 1.⁶ (Small errors in the pressure measurement of part 1 have been reported in a recent erratum,⁷ and corrected N₂O yields are used in Figure 5.) The results are very similar.

TABLE 1: $G((e^-)_{\text{aq}})$ in Supercritical Water Phenol (0.01 *m*)/SF₆ (2.5 × 10⁻³ *m*) Solutions

| 380 °C | | 400 °C | |
|-------------------------------|---|-------------------------------|---|
| density (kg/dm ³) | 10 ⁻⁷ $G((e^-)_{\text{aq}})$ (mol/J) | density (kg/dm ³) | 10 ⁻⁷ $G((e^-)_{\text{aq}})$ (mol/J) |
| 0.529 | 2.36 | 0.318 8 | 1.62 |
| 0.501 | 2.10 | 0.252 7 | 1.34 |
| 0.469 | 1.76 | 0.212 69 | 1.42 |
| 0.451 | 1.19 | 0.185 81 | 1.49 |
| 0.400 | 0.80 | 0.163 16 | 1.65 |
| 0.350 | 1.22 | 0.138 14 | 1.80 |
| 0.347 | 1.01 | 0.106 86 | 2.06 |
| 0.300 | 1.26 | — | — |
| 0.250 | 1.29 | — | — |
| 0.200 | 1.23 | — | — |
| 0.159 | 1.62 | — | — |
| 0.150 | 1.61 | — | — |

Based on the scatter observed, these yields based on SF₆ are probably uncertain by 20–30% in supercritical water. At 380 °C, the SF₆ scavenging yields appear slightly lower on average than the N₂O result, possibly because the scavenging power of 2.5 × 10⁻⁴ *m* SF₆ is less than that of 2.5 × 10⁻³ *m* N₂O.

The success of the neutral solution scavenging in supercritical water can be rationalized in terms of the large shift in p*K*_a that all acids exhibit on going from room temperature water to supercritical water. For example, the p*K*_a of HCl near room temperature is -7, whereas in 380 °C supercritical water, the p*K*_a is greater than 3.^{11,12} Similar behavior is known for all acids.¹³ The room temperature p*K*_a of HF is already¹⁴ 3.5, and it can also be expected to shift many p*K* units in the transition to supercritical water. Therefore, in our supercritical water experiment the species present in the irradiation zone is the hydrofluoric acid molecule, not separated H⁺ and F⁻ ions. The reaction of (e⁻)_{aq} with HF molecule is much slower than that with hydrated proton even at room temperature.¹⁵ In earlier work we found a very large rate constant decrease for the reaction of (e⁻)_{aq} with perchloric acid in supercritical water¹⁶ compared to

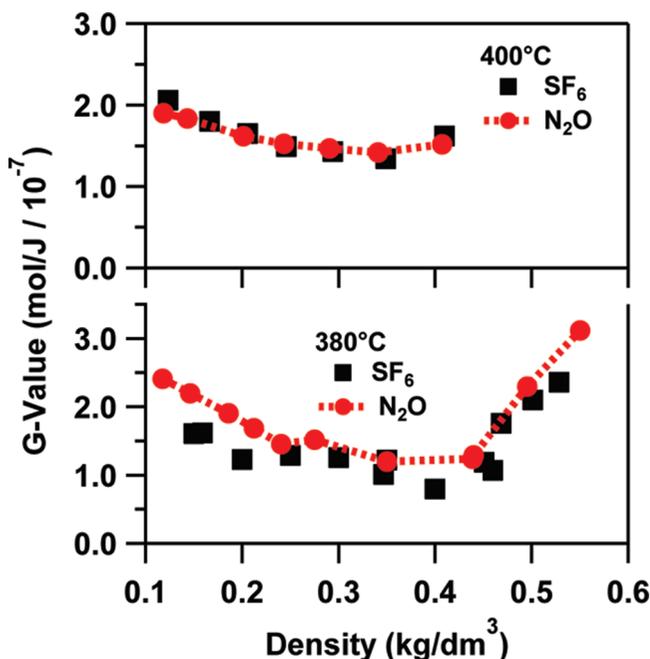


Figure 5. Radiation yields of the solvated electron, (e⁻)_{aq}, during radiolysis of 0.01 *m* phenol/2.5 × 10⁻⁴ *m* SF₆ neutral solution compared to work by Janik et al.^{6,7} (0.01 *m* phenol/2.5 × 10⁻³ *m* N₂O solution) as a function of density at 380 and 400 °C.

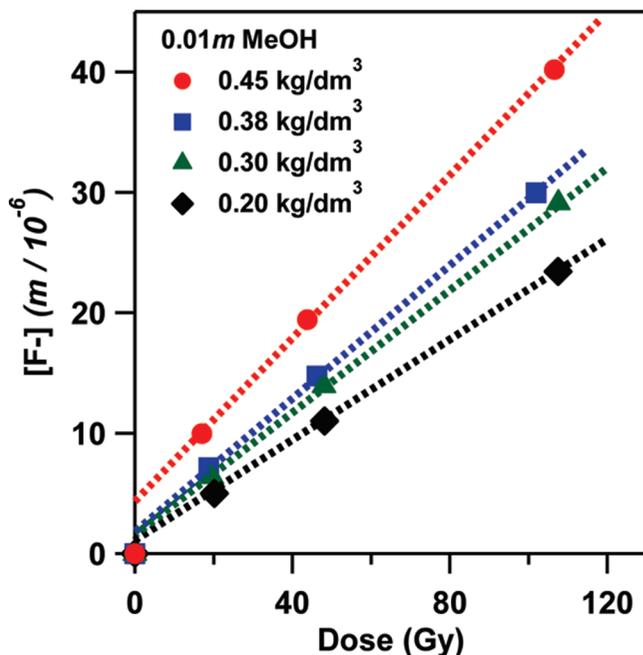


Figure 6. Fluoride production vs (unnormalized) dose in neutral methanol solutions at 380 °C (0.01 *m* methanol/ 2.5×10^{-4} *m* SF₆). A nonzero intercept is visible, indicating a chain reaction.

subcritical temperatures (e.g., the rate constant is $2 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ at 350 °C but reduced to $2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 380 °C, 250 bar). It was ascribed to the same phenomenon; i.e., if perchloric acid is associated, even in the form of ion pairs, the coulomb attraction between $(\text{e}^-)_{\text{aq}}$ and $(\text{H}^+)_{\text{aq}}$ is greatly attenuated and the reaction rate is reduced.

Then how can we understand the results of SF₆ scavenging in alkaline supercritical water? One possibility which concerned us is that radiation deposited in the titanium flow tubing might stimulate chemistry at the (TiO₂) surface, and this process might be sensitive to the pH and the dose rate. For a given length of tubing with inner diameter of $2r$, the near surface volume scales as $2\pi r$ times an effective surface thickness, while the total solution volume scales as πr^2 . If we generously assume the effective thickness at the interface is as great as 1 μm , then for 1.0 mm radius tubing the surface/volume ratio is 2.0×10^{-3} . The density of titanium dioxide is roughly 4 times that of water, so we may expect roughly 4 times more energy deposition in the interface, but even so, efficiency for production of F⁻ would need to be several hundred times higher for a postulated surface process to compete with the bulk chemistry. It should not be possible to observe such a process in this experiment. Ultimately we found similar behavior of alkaline solutions for both titanium tubing and Hastelloy 276C. It seems very unlikely that both oxide surfaces could be so active.

It was decided to try 0.01 *m* methanol as the [•]H atom scavenger in case the phenol was causing the unexpected chemistry. Fluoride production vs dose is plotted for several densities at 380 °C in Figure 6 for neutral methanol solutions and in Figure 7 for alkaline methanol solutions. With methanol as scavenger of [•]H and [•]OH radicals, the intercept of the fluoride production plot is nonzero both with and without the presence of KOH.

Large F⁻ yields and “nonzero intercept” in both neutral and alkaline methanol solutions suggest that high pH is not fundamentally responsible for the behavior. We are led to conclude that a chain reaction is responsible for the unexpected results. We postulate that at high temperature the carbon-

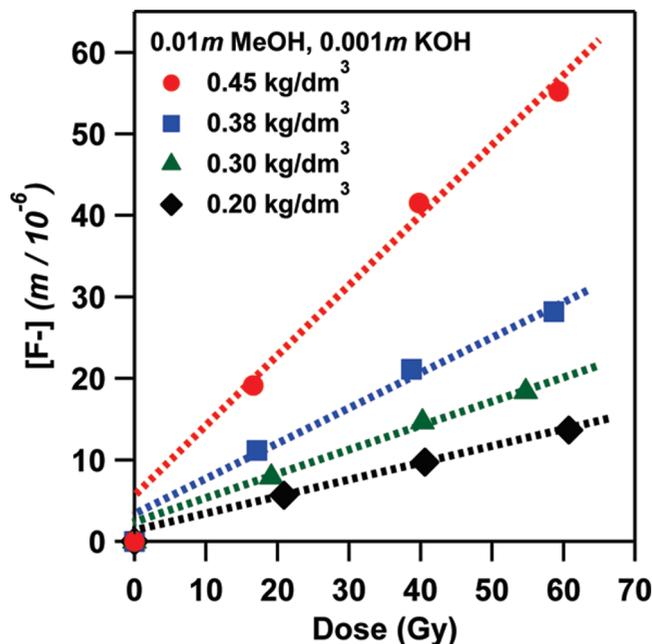


Figure 7. Fluoride production vs (unnormalized) dose in alkaline methanol solutions at 380 °C (0.01 *m* methanol/ 2.5×10^{-4} *m* SF₆/0.001 *m* KOH). A nonzero intercept is visible, indicating a chain reaction.

centered radicals formed from [•]OH and [•]H reaction with methanol (reaction 5) may reduce SF₆, giving initially an [•]SF₅ radical (reaction 6).



Hydrolysis of this radical is known to give an [•]OH radical in reaction 4b. The [•]OH radical can then react with methanol, completing the chain for reduction of SF₆. A similar chain reduction of N₂O by α -hydroxy radicals has been reported in the literature^{17,18} and was encountered in our previous work.⁶

A simple qualitative model of the kinetics in our experiment can be constructed by assuming plug flow of the solution through a uniformly irradiated zone. In this model the irradiation of a given volume “turns on” as the solution enters the zone, and “turns off” as the solution exits. We postulate that the alcohol radical concentration quickly reaches a steady state $[\text{R}]_{\text{ss}}$, given by

$$\frac{d[\text{R}]}{dt} = 0 = \delta(G(\text{R})) - 2k_2[\text{R}]^2 \quad (7)$$

$$[\text{R}]_{\text{ss}} = \sqrt{\frac{\delta(G(\text{R}))}{2k_2}} \quad (8)$$

where δ is the dose rate, $2k_2$ is the second order recombination rate of the alcohol radicals [•]R, and $G(\text{R})$ corresponds to the yield of all radicals (note that $(\text{e}^-)_{\text{aq}}$ and [•]H atoms convert to [•]OH and then to alcohol radicals [•]R via the postulated reactions 4a, 4b, and 5). The production of fluoride ions is then given by the desired scavenging of hydrated electrons and by the additional chain reaction (with rate constant k_c):

$$\frac{d[F^-]}{dt} = 6\delta(G(e^-)_{aq}) + 6k_c[SF_6][\cdot R]_{ss} \quad (9)$$

Integrating over the time of flow through the irradiation zone, we find a term proportional to the dose rate (the desired scavenging) plus a term proportional to the square root of the dose rate (the chain reaction). When plotted vs dose rate as in our experiment, the fluoride production appears to be quite linear except at very low dose, which accounts for the apparent “nonzero intercept”.

Turning now to the alkaline phenol solutions, a “linear plus square root” function of dose is shown to fit the “nonzero intercept” data in Figure 1 (solid line), using the $G((e^-)_{aq})$ from Table 1 for the linear term. (We have insufficient yield and rate constant information to interpret the square root term, which also shows 50% run-to-run variation, possibly due to the poorly defined electron beam focus. The experiment was not designed to investigate this phenomenon.) The scavenging of $\cdot H$ atoms and $\cdot OH$ radicals by phenol will give the immediate free radical adduct products $\cdot HPhOH$ and $\cdot HOPhOH$, where we make no distinction between ortho, meta, para, or ipso additions to the ring. The $\cdot HPhOH$ adduct radical cannot be responsible for a chain process because the $\cdot OH$ radical formed from SF₆ hydrolysis must carry the chain. Moreover, product measurements in γ radiolysis of phenol solution at high temperature show a large yield of benzene,¹⁹ which presumably comes from substitution of $-H$ for $-OH$ in the phenol ring and the effective conversion of $\cdot H$ radicals to $\cdot OH$ radicals. Apparently the neutral $\cdot OH$ adduct radical $\cdot HOPhOH$ cannot reduce SF₆, because we find no chain reaction in neutral solutions. At room temperature, it is known that the pK_a of $\cdot HOPhOH$ is approximately 9.6.²⁰ It is reasonable to suggest that the weak acid can be neutralized by KOH in supercritical water, giving $\cdot HOPhO^-$. If $\cdot HOPhO^-$ were to reduce SF₆, then we would have a simple explanation for the effect of base in the phenol/SF₆ scavenging system. However, $\cdot HOPhO^-$ is known to dissociate within some nanoseconds at room temperature, producing OH⁻ and a neutral phenoxyl radical.²⁰ This probably happens even faster in supercritical water. Phenoxyl radical itself is not a reducing radical. In order for this chemistry to be responsible for the chain reduction of SF₆ in alkaline solutions, it seems that a product radical of the phenoxyl must be invoked.

Room temperature studies of the products for phenoxyl radical recombination show that the initial product is dominated by C–C coupling and the formation of dihydroxybiphenyls.²¹ In relatively low-dose γ experiments, the subsequent reaction of these products with phenoxyl radical becomes by far the most probable recombination pathway. Thus there are many potential polyaromatic radical products of phenoxyl recombination in alkaline solutions. One of them may be able to reduce SF₆. The $\cdot OH$ radical is actually known to be in equilibrium with the $\cdot HOPhOH$ adduct at supercritical temperatures.²² Thus an OH adduct to one of the product polyaromatic molecules might be able to reduce SF₆. We are unable to identify a particular product which is most likely to reduce SF₆, but the existence of such a reducing radical product seems to be the only explanation for our results in alkaline phenol solution.

IV. Discussion

The results of the present study for neutral supercritical water solutions confirm the measurements of electron scavenging carried out in part 1 using the N₂O scavenger.⁶ At the same time it becomes very clear that the scavenging results are very sensitive to the concentration of added base, due to the very

fast reaction of (H⁺)_{aq} with either base or (e⁻)_{aq} in the low dielectric supercritical water solvent. This was already observed in nanosecond radiolysis experiments at Argonne National Laboratory, where the addition of 0.001 *m* KOH was used to greatly extend the electron lifetime.²³ Recent picosecond radiolysis measurements of hydrated electron in supercritical water show that this recombination is indeed very fast in neutral water spurs.²⁴ Therefore, “the yield” of hydrated electrons (and H atoms) inferred from scavenging experiments in supercritical water is a very strong function of the pH and the scavenger used.

In our previous work,⁶ we noted the strong difference between our N₂O scavenging yields and the methyl viologen scavenging results from the University of Tokyo.²⁵ While the two laboratories agreed at 380 °C near 0.5 g/cm³, as the density decreased the methyl viologen scavenging produced a much stronger increase in yield, reaching $G(MV^+) = 5.1 \times 10^{-7}$ mol/J at 0.2g/cm³ in comparison with $G(N_2) = 1.8 \times 10^{-7}$ mol/J from N₂O. Despite careful scrutiny, we are unable to suggest any particular flaw in the experiments at either laboratory which might explain the discrepancy. It seems reasonable to think that both laboratories are correct and the primary difference lies in the chemistry. Both the SF₆ and N₂O scavenging systems in our work are entirely neutral. The scavenging rate constants for both scavengers are approximately $2 \times 10^{11} M^{-1} s^{-1}$ and depend somewhat on density as shown in previous work.²³ The scavenging power, or rate constant times scavenger concentration, is on the order of $10^7 s^{-1}$ for SF₆ and $10^8 s^{-1}$ for N₂O at the concentrations employed. The methyl viologen scavenger used at the University of Tokyo is a dication, MV²⁺. Unfortunately, its scavenging rate constant in supercritical water is not reported, but the rate constant at 350 °C is greater than $10^{12} M^{-1} s^{-1}$.²⁵ One assumes that it is typically ion paired in the low-dielectric supercritical water, but perhaps a large fraction of the MV²⁺ is only paired with one counterion, so that scavenging of (e⁻)_{aq} is very fast with the singly charged scavenger.¹⁶ If the rate constant remains in the $10^{12} M^{-1} s^{-1}$ range or higher, then the scavenging power of $5 \times 10^{-4} m$ methyl viologen in the University of Tokyo experiment will be greater than the scavenging power in our experiments, and scavenging will occur at earlier time, perhaps competing effectively with the charge recombination of (e⁻)_{aq} with (H⁺)_{aq}. The University of Tokyo data may approach the (e⁻)_{aq} yields at “time zero” in the spurs, whereas our experiments probe something closer to an “escape yield”. The escape yields of all radical species are important for applications such as modeling of nuclear reactors cooled by supercritical water.¹ Given the fast recombination of (e⁻)_{aq} and (H⁺)_{aq} in supercritical water, it may only be meaningful to report the sum of reducing radicals $G((e^-)_{aq} + \cdot H)$ for the escape yields in this application.

V. Summary

The use of SF₆ as scavenger for hydrated electron is shown to give reasonable “escape” yields in radiolysis of supercritical water–phenol solutions at neutral pH. This success must be due to the strong association of the HF acid product in the low-dielectric supercritical fluid. Addition of base was shown to give anomalously high results, which is interpreted as a chain reaction carried by the $\cdot OH$ radical product of the SF₆ decomposition. $\cdot OH$ radical must react with phenol or a secondary radiolytic product, to give a radical which can reduce the SF₆, but only in alkaline solutions. Use of methanol scavenger in place of phenol showed a similar chain reaction in both neutral and alkaline supercritical water solutions.

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