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**The Chemical Behavior of Iodine in
Aqueous Solutions up to 150°C.
II. Radiation-Redox Conditions**

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THE CHEMICAL BEHAVIOR OF IODINE IN AQUEOUS SOLUTIONS UP TO 150°C.
II. RADIATION-REDOX CONDITIONS

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ABSTRACT

Redox reactions that might alter the volatility of aqueous iodine solutions have been examined experimentally using absorption spectrophotometry. Oxygen and hydrogen atmospheres had no effect on the iodine chemistry at temperatures up to 150°C. However, irradiation of aqueous solutions with a ^{60}Co source, 0.8×10^6 R/h, produced radiolysis products that either oxidized iodide ion or reduced IO_3^- in the pH range 6-9 and generated significant amounts of volatile iodine. The amount of iodine volatilized varied from a few percent for solute concentrations of 10^{-4} M to as much as 10 to 19% for 10^{-6} M CsI or KIO_3 solutes. Silver metal has been shown to provide an effective gettering route for I^- in solution if these ions are first oxidized by $\cdot\text{OH}$ radicals generated during the radiolysis of the solutions.

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THE CHEMICAL BEHAVIOR OF IODINE IN AQUEOUS SOLUTIONS UP TO 150°C.

II. RADIATION-REDOX CONDITIONS

L. M. Toth
K. E. Dodson

1. INTRODUCTION

The accident at the Three Mile Island Unit 2 Nuclear Power Station on March 28, 1979 has regenerated interest in the chemical behavior of aqueous iodine solutions. In response, several research efforts have been initiated in an attempt to answer many unresolved questions. One such endeavor, supported by the U.S. Nuclear Regulatory Commission, was begun at the Oak Ridge National Laboratory (ORNL) in late 1980 to identify the various iodine species present in the primary system and to establish the containment conditions representative of hypothetical accidents in PWRs and BWRs.

Part I of this series¹ dealt with the iodine hydrolysis reaction under nonredox conditions:



and addressed (1) the identities of the species present in solution and in the vapor above, (2) the kinetics of the iodine reactions with water in pH-adjusted boric acid solutions, and (3) the partition coefficient of each of the identified species. It was shown that the first-stage hydrolysis reaction, Eq. (1), reached equilibrium very rapidly and that under most conditions of pertinent interest (namely, pH 6-10, $T > 50^\circ\text{C}$, $\text{I}_2 < 10^{-4} \text{ M}$), the equilibrium is far to the right. In other words, no molecular iodine, I_2 , can be detected since its concentration is $\ll 1\%$ of the total iodine content of the system.² The second-stage reaction, Eq. (2), represents the disproportionation of the intermediate, HOI, and requires anywhere from seconds to days to reach equilibrium, depending on the conditions. It was this latter reaction that was studied in detail and for which kinetic rate constants were measured as a function of temperature and pH.

Although the HOI species was never unequivocally identified as an uncharged triatomic molecule in solution, ionic strength measurements established that it was an uncharged species; therefore, HOI was the simplest and most plausible form that could be present. (Earlier titrimetric procedures using sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, have established that the intermediate contained iodine in the $+1^{2/3}$ valence state.) Efforts to identify an absorption spectrum of HOI whose intensity and wavelength position correlated with the other halogen analogs were not successful. Recently, however, Paquette et al.³ have found such evidence in the form of a weak uv absorption band which is consistent with the triatomic form of the intermediate. By another correlation procedure coupled with

volatility measurements of HOCl and HOBr , we have determined that the partition coefficient for HOI is $>10^4$.

In this report, we have addressed the inclusion of redox reactions in the above chemistry to determine how they alter the effective volatility of iodine. Since I_2 is the only iodine compound that has been found to have any measurable volatility, the current concern has been with reactions that compete in some way with Eqs. (1) and (2) to regenerate I_2 . Three separate topics have been studied: (1) the effect of gases (O_2 and H_2) on iodine chemistry at temperatures up to 150°C ; (2) the effect of silver metal in altering the soluble iodine species; and (3) the effect of ionizing radiation, (1.33- and 1.17-MeV gamma rays from a ^{60}Co source) on the aqueous iodine chemistry. Although the work had progressed through the first two topics, we were not able to complete the experiments on the effects of radiation, largely because of observations during the course of the work that led to further questions and/or an evolution in the experimental procedure. While we have not been able to carry our project to satisfactory completion, the experimental technique and the results obtained thus far provide some interesting considerations for those who might be able to continue this work. We shall indicate in the following paragraphs where the experiments are deficient and where they might be extended.

2. EXPERIMENTAL METHODS

2.1 REDOX EXPERIMENTS

Solutions of $0.231\text{ M H}_3\text{BO}_3$ that had been pH adjusted with NaOH solution and were contained in a 25.1-cm-pathlength titanium cell were sparged and equilibrated with atmospheres of N_2 , H_2 , or O_2 . The titanium cell and its contents were then heated to temperatures ranging between 65 and 150°C . Iodine, iodate, or iodide was then added to the system either as an aqueous solution of I_2 , KIO_3 , or KI in distilled water for temperatures $<100^\circ\text{C}$ or by breaking a glass capsule containing purified I_2 , KIO_3 , or KI (placed in the titanium cell at the time of assembly) for temperatures $>100^\circ\text{C}$. A detailed description of the cell and the addition of iodine can be found in ref. 1. The system was scanned at 225 nm , where I^- absorbs, to watch for the reduction of I_2 and IO_3^- to I^- or for the oxidation of I^- to IO_3^- where KI was released into the system. The absorption spectra were monitored with a Cary 14 spectrophotometer that had been modified with an enlarged sample-reference compartment.

2.2 IRRADIATION EXPERIMENTS

The iodine or iodate solutions were irradiated with a $0.8 \times 10^6\text{ R/h}$ ^{60}Co source. The solutions were contained in a Pyrex glass circulation system (liquid volume, 260 mL) that consisted of an irradiation cell, a magnetic stir-bar pump, and a pH electrode chamber (see Fig. 1). These components were connected by glass tubing attached with shrinkable Teflon unions. Since all of the glass tubing was butted together, minimal exposure to the Teflon tubing occurred. A gas purge line supplying 40 mL/min

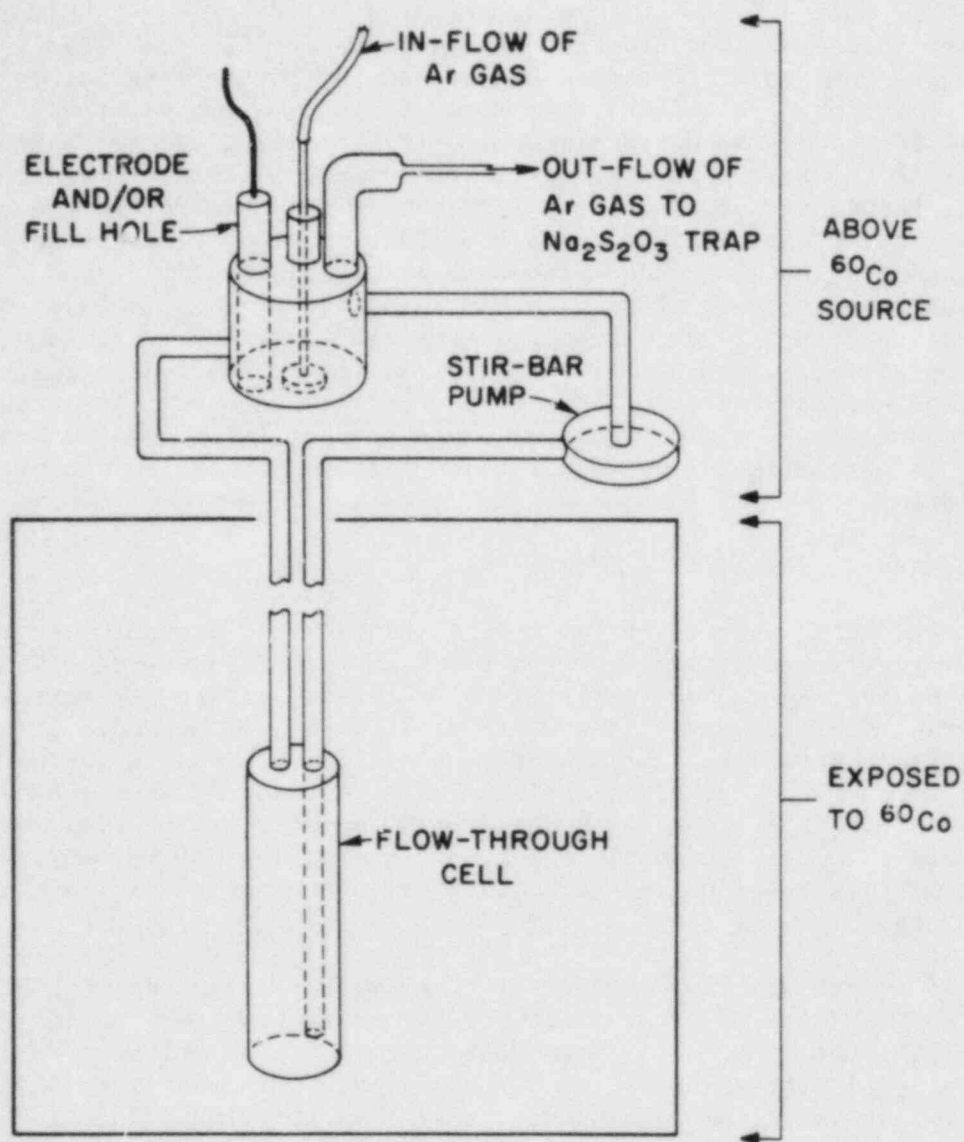


Fig. 1. Glass circulation system used in ^{60}Co irradiations.

argon that had been purified by passage through titanium sponge at 600°C was connected to the pH chamber to exclude air from the system. Only the irradiation cell was exposed to gamma irradiation since the pump and the electrode had to be located outside the irradiation zone.

The system was operated by setting the pH of the deaerated aqueous solutions, containing dissolved CsI or KIO_3 , prior to irradiation and allowing the pH to stabilize. In some of the experiments, the pH changes of the system were monitored using a Ross pH electrode in the pH chamber of the system in Fig. 1. In runs where pH changes were not needed, the electrode was simply left out of the chamber and the opening was sealed off with a glass stopper and shrinkable Teflon. Experiments were conducted both with and without argon purging during irradiation. In later runs where volatile I_2 produced during irradiation was analyzed, the outflow of argon gas was sparged through a sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, solution placed downstream on the exit gas line. The iodine reaching this trap was converted to iodide, which was subsequently measured using spectrophotometry. The iodide or iodate concentrations of the aqueous solutions were measured spectrophotometrically both before and after irradiation.

2.3 SILVER GETTERING EXPERIMENTS

Irradiation experiments on iodine solutions in contact with silver metal were also conducted with the 0.8×10^6 R/h ^{60}Co source. The silver powder, Ag° , used in the experiments was prepared by taking Ag_2O (prepared by method given in Brauer⁴) and passing 4% hydrogen in argon over it in a porcelain boat housed in a silica tube that was plugged with Teflon stoppers and supplied through Teflon lines. A water bubbler at the end of the train ensured a qualitative measure of the flow rate. The brown-black Ag_2O turned matte-silver after reaching 550 to 590°C. The Ag° powder was then cooled and bottled without exposure to the atmosphere.

Before irradiation, iodide solutions with pH adjusted with HCl for $\text{pH} < 7$ and NaOH for $\text{pH} > 7$, were thoroughly contacted with the Ag° powder by stirring the mixture for several minutes. The solutions were then irradiated in a Pyrex beaker that was sealed within a stainless steel vessel. The vessel was equipped with a glass stirring paddle so that the solutions could be agitated during irradiation. The concentrations of iodide in solution before contacting with silver and the irradiated solution, after filtering out silver, were determined by spectrophotometry.

3. RESULTS AND DISCUSSION

Various redox processes which could alter the volatility of the iodine in an aqueous solution have been considered. These include both redox and radiation-induced redox changes. In addition, the effect of silver metal on iodide ion in aqueous solution has been examined in order to determine if there are pathways by which its chemical or physical stability in solution could be altered. Because the role that

silver plays depends on redox reactions caused by radiolysis, this discussion follows the radiation effects section (see Sect. 3.3). Other redox reactions should be considered in addition to these few cited here, for example, those due to Cu^{2+} or Fe^{3+} impurities in solution (both with and without radiation); however, these reactions exceeded the scope of our work plan and therefore were not addressed. A more comprehensive examination of redox effects on aqueous iodine chemistry, as it pertains to LWR and BWR accident scenarios, should also include impurity ion effects such as these.

3.1 REDOX REACTIONS

The purely redox reactions that have been considered have arisen as a result of NRC program guidelines. Although most of these reactions and their rates could have been predicted from data in the open literature, programmatic mandates have made it necessary to address them systematically under conditions of an LWR accident. Comparisons with the literature data will be included when appropriate. Reactions involving either O_2 or H_2 atmospheres in equilibrium with the aqueous solution have been studied — O_2 , because it is an atmospheric component always in contact with the aqueous phase and H_2 , because it is a probable product of the steam reaction with the zirconium metal components of the reactor system. Both of these gases have been examined at pressures up to 1 atm (1 bar).

3.1.1 Effect of O_2 , H_2 , and N_2 on Eq. (2)

The reaction rate of second-stage hydrolysis reaction, Eq. (2), was measured in the presence of O_2 , H_2 and N_2 to determine if these atmospheres had any influence on the previously reported¹ kinetics. Reaction rates for $2 \times 10^{-6} \text{ M I}_2$ in $0.231 \text{ M H}_3\text{BO}_3$ at pH 7 and 65°C have been measured for solutions sparged and equilibrated with atmospheres of O_2 , H_2 and N_2 , respectively. Comparison of these rates with those measured earlier on air-saturated solutions showed no differences, within experimental error. Second-stage reaction rates at 90 and 125°C have also been measured in pH 7 solutions equilibrated with these various sparge gases and have been found to be identical to those measured in solutions that were saturated with air and buffered with boric acid.

3.1.2 Other Redox Considerations Regarding O_2 and H_2

Solutions of $0.231 \text{ M H}_3\text{BO}_3$ with pH adjusted to 7 and 10 were sparged and saturated with H_2 at 25°C , heated to 150°C , and equilibrated. Potassium iodate was added by the capsule break method¹ to bring the KIO_3 concentration to $4 \times 10^{-6} \text{ M}$. The system was spectrophotometrically monitored for IO_3^- reduction to I^- , but none was detected even after 14 h at 150°C .

A second series of experiments, performed similarly but with O_2 sparging (in place of H_2) and KI added (instead of KIO_3) showed no indication of I^- oxidation² after 14 h at 150°C .

From the literature,^{5,6} an expression for the rate of I^- oxidation is given (in terms of the I_3^- formed since the I_2 product combines readily with I^- to form triiodide):

$$d[I_3^-]/dt = k[I^-][O_2][H^+], \quad (3)$$

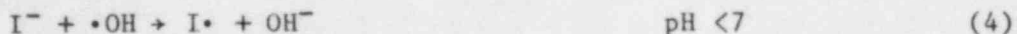
where the k at 25°C can be calculated from the data in ref. 5 and is found to be $8 \times 10^{-3} \text{ min}^{-1} \text{ M}^{-2}$. Likewise from the data in ref. 6, it is found to be $20.9 \times 10^{-3} \text{ min}^{-1} \text{ M}^{-2}$. Aldridge further states⁶ that the rate of oxidation increases by a factor of 2.5 when the temperature is increased to 35°C if the associated decrease in the concentration of dissolved oxygen is taken into account. From these data, we have calculated an activation energy of 16.7 kcal/mol (69.8 kJ/mol) and thereby estimate a rate constant of $86.8 \text{ min}^{-1} \text{ M}^{-2}$ at 150°C.

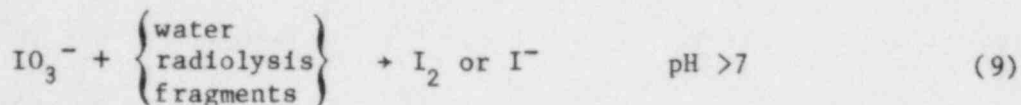
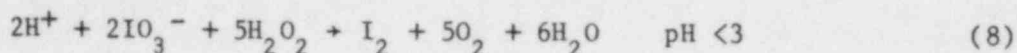
Using Aldridge's value for k at 25°C, the rate of I^- oxidation is $5 \times 10^{-20} \text{ M/min}$ for $[I^-] = 10^{-6} \text{ M}$, $\text{pH} = 8$, and $[O_2] = 0.2 \text{ atm}$ (0.2 bar). Otherwise stated, it would take 4×10^6 years to oxidize 10% of the iodide in solution. At 150°C, the rate is increased to $2.1 \times 10^{-16} \text{ M/min}$ assuming that it is possible to maintain the same $[O_2]$ in solution. It would then take approximately 900 years to oxidize 10% of the iodide in solution. At $\text{pH} = 6$ and $[I^-] = 10^{-4} \text{ M}$, the rate of oxidation would be proportionately higher, that is, $5 \times 10^{-16} \text{ M/min}$.

These data which we have obtained for the O_2 oxidation of I^- at 150°C are therefore consistent with measurements reported in the open literature. We therefore conclude that the dark oxidation (i.e., in the absence of radiation) of I^- is insignificant in terms of reactor accident situations.

3.2 RADIATION EFFECTS

Ionizing radiation affects dilute solutes directly by reacting first with the solvent to generate radical and ion fragments which, in turn, react either with themselves, the parent solvent molecule, or the dissolved solute components. The primary effect of ionizing radiation on water is known⁷ to produce reducing radicals such as the hydrated electron, e_{aq}^- , and the hydrogen atom, $H\cdot$, and oxidizing species such as the hydroxyl radical, $\cdot OH$, the perhydroxyl radical, $HO_2\cdot$, and, by subsequent reaction of these, the molecular compound hydrogen peroxide, H_2O_2 . Some typical reactions of these with various iodine containing molecules and ions are:





Although reaction (9) is known to occur,⁸ no detail regarding its mechanism has been offered.

The peroxide oxidation of I^- has been observed in our laboratory only at very low pH values even though it has been reported to occur at pH 5 or greater.⁹ Since it is prevalent only at very low pH values along with the H_2^+ (formed by the combination of H^+ and $\text{H}\cdot$), oxidation of I^- , Eq. (6), and the peroxide reduction of IO_3^- , Eq. (8), it will henceforth be ignored.

The reactions of significance in our work are those that occur in the pH range 6-10: (1) the oxidation of I^- by hydroxyl radical, Eq. (4); (2) the reduction of I_2 with peroxide, Eq. (7); and (3) the radiolysis products reduction of IO_3^- . Nevertheless, the oxidation of I^- with hydroxyl radical is of greatest concern since it represents a means by which the most probable form of iodine in solution can be oxidized to a volatile species.

3.2.1 Oxidation of Iodide Ion

When aqueous solutions containing 10^{-3} M CsI were irradiated in the glass circulation system of Fig. 1, the pH of the solution varied as shown in Fig. 2. Immediately upon exposure of a solution preset to approximately pH 6, the pH jumped by more than a unit to 7.4 and then either stayed at this value or fell gradually with time, depending on whether the solution was being purged with argon gas. At the end of the irradiation, the pH decreased to a lower value — but not as low as that originally set. The final pH of the argon purged solution was greater than that of the unpurged one.

These detailed pH-time profiles (depicted in Fig. 2) emphasize the advantage of monitoring the system throughout the irradiation since, otherwise, nothing but the initial and final pH values would be known. The pH changes that occur throughout the irradiation and thereafter reveal much about the iodine radiation chemistry which is described in the following paragraphs.

The abrupt jump in the pH on irradiation is undoubtedly due to the effects of the OH radical reaction with I^- , Eq. (4), to produce hydroxyl ions and thus an increase in pH. The iodine radical is believed to combine with an unreacted I^- to form I_2^- , which eventually disproportionates to I^- and either I_2 or I_3^- . It is the I_2 molecule, in equilibrium with triiodide ion,



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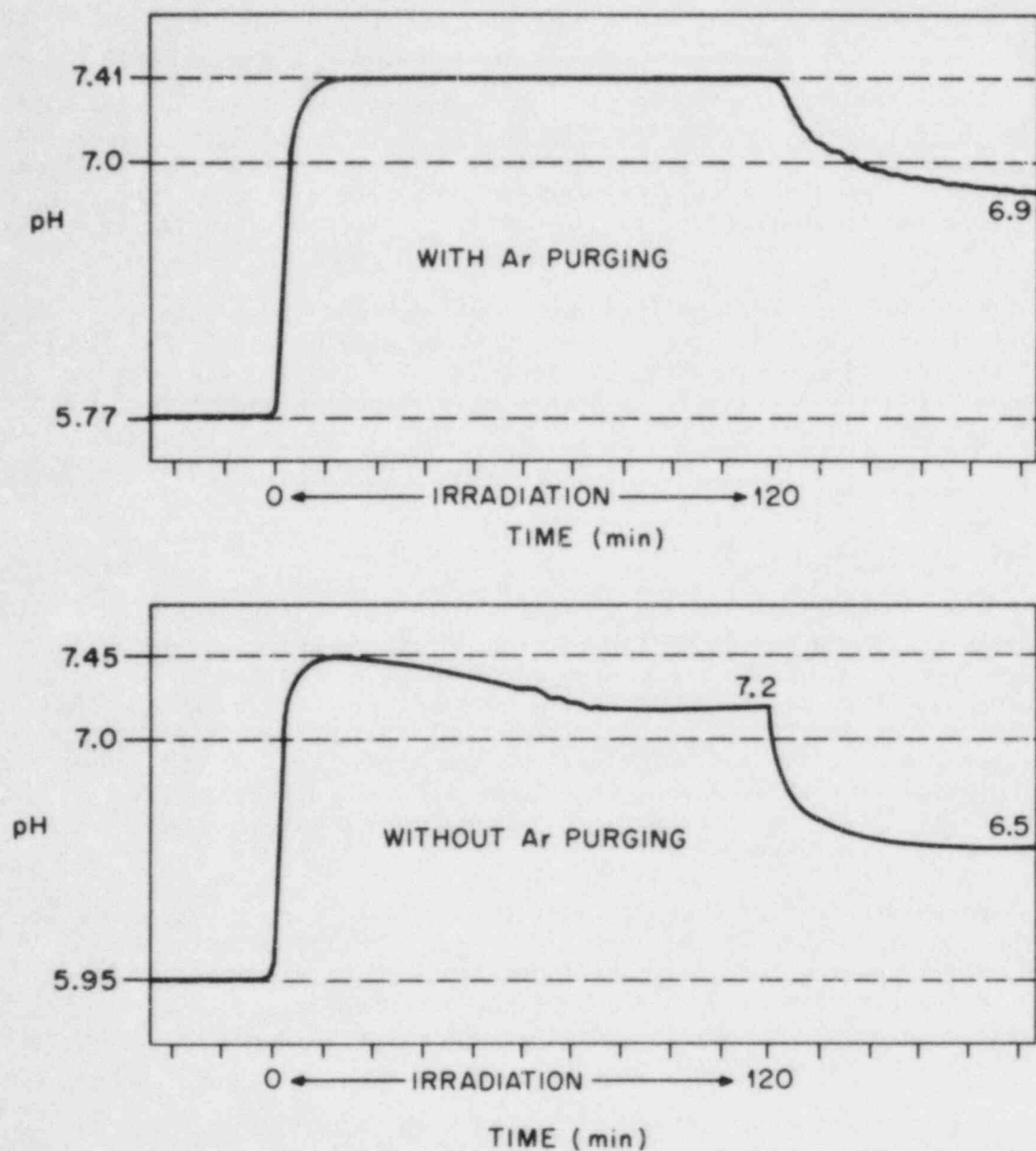


Fig. 2. Variation of pH with irradiation of 10^{-3} M CsI solutions at 0.8×10^6 R/h ^{60}Co gamma radiation for 120 min.

which is swept from the solution during the argon purge. The rate of removal through purging is such that what I_2 remains in solution and hydrolyzes by Eqs. (1) and (2) is balanced by the hydroxyl ion generated by Eq. (4). Therefore, the pH shows no further change and appears to remain constant at 7.41. If, however, there is no purging, I_2 accumulates in solution and hydrolyzes to a greater extent, with a concomitant increase in the rate of H^+ production. As a result, the pH of the unpurged system peaks and then falls to a lower steady-state value than in the purged system. At the end of the irradiation period, the pH of the solution drops in each case due to hydrolysis of the remaining I_2 in solution. In the unpurged case, it falls to a lower value and at a faster rate because the quantity of I_2 in solution is greater.

The pH measurements alone indicate a difference between purged and unpurged solutions that obviously arises because of the removal (volatilization) of I_2 from the solution during purging. In later studies it was observed that the amount of iodine volatilized was influenced by the presence of the pH electrode itself, which had a tendency to leak KCl into the CsI aqueous solution. The resulting oxidation of Cl^- ions and volatilization of ICl increases the apparent volatility of the iodine solution somewhat as indicated in Tables 1 and 2. Regardless of this complication, the influence of impurity ions such as Cl^- is worth considering since they play a measurable role in the iodine volatility question.

The results of the irradiations of the CsI solutions at various concentrations under argon purge conditions are given in Table 1. (Very few experiments under unpurged conditions were run because the increase in iodine volatility as a result of radiation was the factor of interest, and because purging gave the best test of the amount volatilized.) The table is arranged in order of decreasing CsI concentration, from 10^{-3} M to 10^{-6} M, with individual groups of a particular concentration arranged according to increasing initial pH. Where various times of irradiation were investigated, the shorter irradiation periods appear first.

Table 1 shows that the final pH is invariably greater than the initial pH except in run 567, where there was a slight apparent decrease in pH. The typical irradiation period was 120 min; but when longer irradiation times were examined, the expected increase in volatile iodine occurred. Initially, not all runs were examined for volatile iodine. This apparent oversight arose through the evolution of an experimental procedure where it became obvious that, after seeing a loss of iodine from solution, the suspected pathways had to be examined. Consequently, the later runs were monitored for volatile iodine. Since pH adjustments were made by adding either HCl or NaOH, those runs in which HCl was added contained Cl^- ion and therefore could indicate greater volatility than might be attributable to I_2 alone; however, the amount of Cl^- added as HCl for pH adjustment was extremely small. (See the earlier discussion on leakage of KCl from the pH electrode.) Some experiments were then performed without pH adjustment, and these have been identified by the notation "n.a." following the initial pH value. In addition, run 550 was

Table 1. Effect of ^{60}Co radiation on CsI aqueous solutions for various irradiation times

(Initial, o, and final, f, conditions are given; samples were purged with argon gas at 40 mL/min during runs.)

Run	Time (min)	pH _o	pH _f	$[\text{I}^-]_f/[\text{I}^-]_o$	Volatile iodine (%)
<u>10^{-3} M CsI</u>					
515	120	5.77	8.48	0.95	
519	120	5.95	8.43	0.31	
537	120	6.16(n.a.) ^a	8.86	1.0	0.3
526	120	7.14	8.37	1.0	
521	120	7.20	9.00	1.0	
520	120	8.26	8.66	1.0	
<u>10^{-4} M CsI</u>					
523	10	5.93	7.94	0.96	
539	10	6.16	8.67	1.0	0.59
509	120	5.14		0.99	
538	120	5.19	8.14	0.98	2.58
507	120	6.0	9.1	0.96	
517	120	6.01	8.30	0.99	
516	120	6.04	8.37	0.98	
546	120	7.0(n.a.)	9.02	1.0	0.43
522	120	7.3	8.62	1.0	
506	120	7.65(n.a.)	7.53	1.0	
567	120	8.90	8.70	0.99	0.13
525	777	5.95	8.40	1.0	
540	1440	5.20	8.59	0.95	4.90
509-2	970	6.1		1.0	
547	1080	6.80(n.a.)	8.64	0.98	2.0
<u>2×10^{-5} M CsI</u>					
529	10	5.72	7.69	0.92	
<u>10^{-6} M CsI</u>					
527	10	5.72	8.22		
530	10	5.95	7.33	0.99	
531	10	6.01	8.28	0.98	
536	10	6.02	9.11	0.90	
518	120	5.77	8.20	0.31	
542	120	6.04	8.15	0.07	8.8
543	120	6.05	8.80	0.17	12.7
534	120	6.07	9.39	0.37	
553	120	6.88(n.a.)	9.54	0.16	6.4
550 ^b	120	6.85	8.30	0.16	10.
545	1440	6.03	7.74	0.17	
544 ^c	1000	6.78(n.a.)	8.96	0.25	0
556	998	7.14(n.a.)	8.95	0.8	11.8
551	932	7.62(n.a.)	8.05	0.23	0.31

^a(n.a.) = no pH adjustment.

^b0.1 M KCl was added to solution.

^c IO_3^- was indicated in test of solution after irradiation.

Table 2. Effect of ^{60}Co radiation on KIO_3 aqueous solutions for various irradiation times

(Initial, o, and final, f, conditions are given; samples were purged with argon gas at 40 mL/min during runs)

Run	Time (min)	pH _o	pH _f	I ⁻ found (%)	Volatile iodine (%)
<u>10^{-4} M KIO_3</u>					
557	120	6.01	9.4	3.1	0.28
571	120	6.0	8.2	3.1	0.13
561	120	6.6 (n.a.) ^a	8.5	12.3	0.34
559	120	8.53	9.4	78.6	
569	120	9.0	7.9	88.6	0.27
570	3900	6.0	7.9	13.0	3.0
560	5270	6.8 (n.a.)	8.9	99.5	2.6
<u>10^{-5} M KIO_3</u>					
587	120	6.9	7.8	0	
586	120	7.8	7.9	0	0.1
585	120	9.1	8.7	65.6	1.2
<u>$2 \times 10^{-6} \text{ M KIO}_3$</u>					
564	120	6.0	8.9	0.0	8.1
563	120	6.7 (n.a.)	8.5	0.0	5.7
584	120	7.2 (e) ^b	8.4	12	2.7
565	120	8.8	9.1		7.9
566	120	9.0 (e)	9.1	100	5.1
<u>10^{-6} M KIO_3</u>					
576	120	5.8	7.3	0.0	3.2
582	120	6.0 (e)	8.1	16.9	9.1
577	120	6.5	8.4	8.6	3.7
583	120	6.7 (e)	8.6	6.8	9.3
579	120	8.1	8.1	4.5	19.0
578	120	8.9	8.6		18.3
568	120	9.0	8.7		2.5
573	7223	5.9	8.6	0	10.4
575	1587	7.1 (n.a.)	8.3	19.8	8.4
574	1608	9.2	8.1	11.2	6.3

^a(n.a.) = no pH adjustment.

^b(e) = pH electrode in solution throughout the run.

made with 0.1 M KCl added to the solution to verify the increased iodine volatility in the presence of chloride ion impurities.

Volatile iodine was detected in every case where the thiosulfate trap was used. The percentage volatilized, as well as the amount of iodide lost, decreased with increasing pH. Nevertheless, even at the high pH values some volatile iodine was detected in the thiosulfate trap. Another significant occurrence was that the increase in iodine volatilization with decreasing iodine concentration, going from a few tenths of a percent in the 10^{-3} M CsI solutions to as much as 12.7% in the 10^{-6} M solutions. In an effort to unequivocally establish the appearance of volatile iodine, long-term irradiations were performed. The runs made with 10^{-4} M CsI solutions were, by far, the easiest to study since the conversion of 2 to 4.9% of the I^- to volatile iodine resulted in an unmistakable amount of iodine in the thiosulfate trap (i.e., a well-pronounced I^- band with peak at 225 nm). Again, the trend with initial pH of the solution was consistent with that expected from Eq. (4), going from the larger amounts of volatile iodine at lower pH values to lesser quantities at the higher pHs.

A problem with the 10^{-6} M CsI experiments was that the total amount of volatile iodine produced as a result of irradiation was rather small and subject to many experimental uncertainties. Consequently, the trends in the data seen in the solutions with higher CsI concentrations are not evident here because of the scatter in the data. On the other hand, the amount of I^- converted (as represented by the $I(\text{final})/I(\text{initial})$ values, I_f/I_o) is definitely greater than that for the higher-concentration runs. Iodate was indicated in run 544, suggesting that the balance of I^- lost does not appear as volatile I_2 but occurs, instead, as IO_3^- . (Compare, for example, the mass balance discrepancies for runs 542, 543, 553, 550, 544, 556, and 551.) Further testing of this latter point would be highly desirable.

The most significant conclusion drawn from these results is that iodine is volatilized as a result of irradiation, with the volatile percentage increasing with decreasing CsI concentration and pH. The most interesting observation is that volatile iodine occurs even at pH values as high as 8.9 (cf. run 567).

3.2.2 Reduction of IO_3^-

When aqueous solutions containing KIO_3 are irradiated at near-neutral or higher pH values, the iodate ion is typically reduced to I^- . In addition, some I_2 occurs as an intermediate in the reduction process and can be volatilized from solution. The results of the KIO_3 solution irradiations are given in Table 2, which is arranged in much the same way as Table 1 for the CsI experiments. In Table 2, however, a " I^- found" is given instead of the $[I^-]_f/[I^-]_o$ ratio because iodide occurs only as a result of the IO_3^- reduction process.

As seen in Table 2 for the 10^{-4} M KIO_3 , the percent of I^- formed by reduction increases with increasing pH, ranging from a few percent to as much as 88.6% for run 569 at pH 9. Longer irradiation times produced much more reduction, 99.5% for run 560, and showed pH trends similar to those found in samples subjected to much shorter irradiation periods. This result should be compared with run 561, where only 12.3% was reduced after 120 min. The longer runs were particularly significant in testing for volatilized I_2 because the shorter irradiation times produced amounts that were at the experimental limits. The 2.6 and 3.0% values reported for runs 560 and 570, respectively, clearly demonstrate that iodine was volatilized from the IO_3^- solutions. (The mass balance error in run 560 is indicative of the experimental uncertainties involved in these measurements.)

Lower concentrations of IO_3^- produced similar results, but as in the I^- irradiation experiments, the scatter of the data became more pronounced. Also, like the I^- irradiation experiments, the percentages of IO_3^- reduced and I_2 volatilized were greater for the lower concentrations. The scatter in these data left much room for improvement, and it was in this area that additional work was considered necessary. Experiments with an "(e)" beside the initial pH value indicate that the pH was monitored continuously throughout the experiment as was done for the I^- irradiations (Fig. 2). In the IO_3^- case, however, the pH fell abruptly on exposure and then rose slowly throughout the irradiation. At the end of the irradiation, the pH increased further and then leveled out at a constant value higher than the original pH of the solution. Presently, we can give no satisfactory description of the mechanism that would explain the changes in the pH seen here.

These measurements show that iodate ion is reduced in the presence of a radiation field even at initial pH values as low as 6.0. It was originally believed that there might be a set of parameters — pH, concentration, etc. — where there would be no net change in the distribution of iodine species as a result of irradiation. Instead, the data indicate that iodate is reduced at pH values as low as 6 and iodide is oxidized at pH values as high as 8. Further examination of the behavior of these solutions to determine the steady-state distribution of species in solution during irradiation appears to be essential in developing a predictive ability regarding the effects of radiation on iodine chemistry.

3.3 REACTION OF Ag° WITH I^-

Other redox agents with iodine-containing solutions were also of concern in this work; metallic silver was of foremost interest because of the large amount of silver that occurs in LWR control rods and could interact with solutions containing iodine. It was realized that I^- does not react with Ag° , but I_2 combines directly to form an insoluble precipitate:



This reaction can be easily demonstrated by adding silver powder to an aqueous iodine solution and agitating the mixture until the yellow color of the soluble iodine species disappears. Analyses of the resulting solution indicate that no iodine species are present except for some residual iodide ion.

Therefore, the reaction of silver with I^- requires some mechanism by which I^- can be oxidized to I_2 . Radiation chemistry presents the most direct route since we have already shown that the $\cdot OH$ oxidation of I^- occurs readily via Eq. (4) to form, ultimately, I_2 . We have demonstrated this silver gettering of iodide in aqueous solutions of 3×10^{-6} M CsI solutions at pH 5 where complete loss of I^- occurs after 1 h of irradiation. On the other hand, higher concentrations (6×10^{-5} M) at the same pH show only approximately 10% loss of I^- after 1 h. The loss of I^- from is diminished at high pH values, which is entirely consistent with the pH effects on I^- oxidation described in the previous section. The effects of I^- concentration on the amount of iodide lost in the silver gettering experiments are also consistent with this mechanism since the rate of reaction is a function of the product, $[I^-][\cdot OH]$; and although the $[I^-]$ is greater, the $[\cdot OH]$ is dependent only on the water concentration and the radiation flux.

4. CONCLUSIONS

Redox reactions have been shown to have a considerable effect on iodine volatility in aqueous solutions. However, the presence of O_2 or H_2 atmospheres alone is not sufficient to produce these changes in the aqueous chemistry. The most significant influence found thus far has been that of radiation, which generates solvent (water) radical fragments that either oxidize I^- or reduce IO_3^- . Although these reactions are greatly affected by the pH of the solution, we have not found a pH, in the near-neutral conditions examined, where volatilization does not occur. This work was interrupted before many of the details of this radiation-induced redox chemistry could be examined. Further work in this area should be performed with in situ detection of the reaction products.

Silver metal has been shown to provide a sink for iodine by reacting with I_2 (produced by radiation effects on iodide ions) to form insoluble AgI. Other redox reactions involving soluble impurity ions such as Cu^{2+} , Fe^{3+} , or Cl^- should be considered in subsequent studies.

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