THE AQUEOUS CHEMISTRY OF IODINE[*]

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ABSTRACT

The chemistry of iodine has been examined in aqueous solutions of pH 6 to 10 containing 2500 ppm boron as H_3BO_3 at temperatures up to 150°C using absorption spectrophotometry to identify and monitor the iodine species present. Kinetic rate constants for the disproportionation of the HOI intermediate, $3HOI = IO_3^- + 2I^- + 3H^+$, have been measured as a function of pH even though no direct spectral evidence for HOI itself has been observed. An HOI partition coefficient $>10^4$ has been estimated; results of ionic strength tests are consistent with HOI being present as an uncharged triatomic species in solution. Redox and radiation effects on the aqueous iodine chemistry have also been described.

INTRODUCTION

The aqueous chemistry of iodine has been examined over a range of pH levels, concentrations, and temperatures in order to determine the chemical behavior of this fission product under conditions similar to those anticipated in nuclear reactor accidents. The major objectives of this work are: (a) to define the kinetics of the dominant chemical reactions involving iodine in its various forms; (b) to identify and characterize the various species of iodine occurring in these aqueous systems; and (c) to determine the volatilities of these species whenever possible. This work, while still under way, has already progressed through several stages, and the extent of our current understanding is reported

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here. Absorption spectroscopy has been used as the experimental method, primarily because it offers a means by which the various species in solution can be distinguished from one another.

## RESULTS AND DISCUSSION

HYDROLYSIS KINETICS

The kinetics of the I_2 hydrolysis chemistry under nonredox conditions has been examined from 20 to 150°C, and the chemistry can be described by the following reactions:

$$I_2 + H_2O = \text{"HOI"} + I^- + H^+ \ , \tag{1}$$

$$3HOI = IO_3^- + 2I^- + 3H^+ \ , \tag{2}$$

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+ \ , \tag{3}$$

where Eq. (3) is the combination (or overall reaction) of the preceding two with the elimination of the intermediate species, "HOI." (This species is given in quotes to designate that it is not necessarily a triatomic molecule, but only some form of the +1 valence iodine. Without the quotes, however, the triatomic molecule is intended.)

The first-stage reaction, Eq. 1, has been found to reach equilibrium (under most of the conditions of pH, temperature, and iodine concentration studied here) within 1 s, and the chemistry of greatest significance is that of the second-stage reaction, Eq. 2. However, in order to study the kinetics of the second-stage reaction, some measure of the "HOI" concentration must be made. Furthermore, we sought to characterize "HOI" as completely as possible since it had previously [1] been assumed to have considerable volatility.

Numerous attempts to detect the "HOI" species spectrophotometrically in the vapor or in solution have been unsuccessful even though the intermediate has been titrated by the standard thiosulfate method and found to be as high as 10^{-3} $\underline{M}$ in some solutions. These solutions were prepared by the classically accepted methods [2] involving the combination of a metal ion, M^{n+}, such as Ag^+ or Hg^{2+} with I_2 solutions to cause the precipitation of the metal iodide and thereby drive the iodine hydrolysis reaction to the right:

$$M^+ + I_2 + H_2O = MI + H^+ + HOI \ . \tag{4}$$
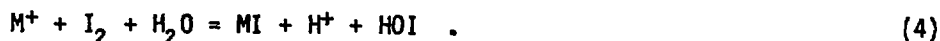
The "HOI" product was then titrated with sodium thiosulfate, or complexed with phenol and then titrated, to demonstrate the presence of the +1 valence iodine. Concentrations of "HOI" as high as 3.7×10^{-3} $\underline{M}$ have been produced in this laboratory and monitored as a function of time by the above thiosulfate titration procedure. From these results, rate constants of 6.39 and 2.95 $\underline{M}^{-1}$ s^{-1} have been obtained for the second-order disproportionation of "HOI" at 22 and 5°C, respectively. The rate at 22°C is in reasonable agreement with that obtained (3) for the +1 valence iodine species in very basic solutions. Although the synthesis of the +1 valence iodine is well known, no spectral or other physical-chemical methods have been used to further characterize the structure of this species in aqueous solutions.

Having established that the "HOI" concentration in these solutions was more than 1×10^{-3} $\underline{M}$ and that these solutions were stable enough to attempt spectrophotometric measurements, efforts were made to obtain its absorption spectrum. By correlation with the known spectra of HOCl and HOBr (having bands at 240 and 260 nm, respectively), an absorption band for HOI would be anticipated at approximately 280 nm. However, none of the solutions examined, containing even as much as millimolar concentrations of HOI, ever showed any bands other than those of I^- or I_3^- in solution.

In view of such difficulty in detecting HOI at concentrations as high as 1×10^{-3} $\underline{M}$, it is not surprising that the direct measurement of the "HOI" intermediate cannot be readily made on solutions of lower total iodine concentrations containing strongly absorbing ions such as I^-($\epsilon_{225\ nm}^{I^-} = 13,500$ $\underline{M}^{-1}$ cm^{-1}). Since it was necessary to study the kinetics of the HOI disproportionation reaction (Eq. 2), an alternate way of following the kinetics (to that of monitoring the HOI concentration) was sought.

If one assumes that the reaction of iodine in aqueous solutions can be represented by Eqs. 1-3 and that the first-stage reaction (Eq. 1) goes to completion within 1 s [i.e., prior to the onset of the second-stage reaction (Eq. 2)], then the concentration, [], of the HOI intermediate at any time can be computed from the initial concentration of I_2 and the concentration of I^- measured at that time using the relationship:

$$[HOI] = 5/2[I_2] - 3/2[I^-] \ . \tag{5}$$

This expression has been used to calculate [HOI] at various times and yield second-order rate constants for Eq. 2. These rate constants are shown in Fig. 1 as a function of (kelvin)$^{-1}$ over the temperature range 20 to 150°C and pH range 6 to 10 for 2×10^{-6} $\underline{M}$ I_2 in 0.231 $\underline{M}$ boric acid solutions. Table 1 gives the equation for the least-squares lines through these points, along with the activation energies calculated from the slopes of the lines.
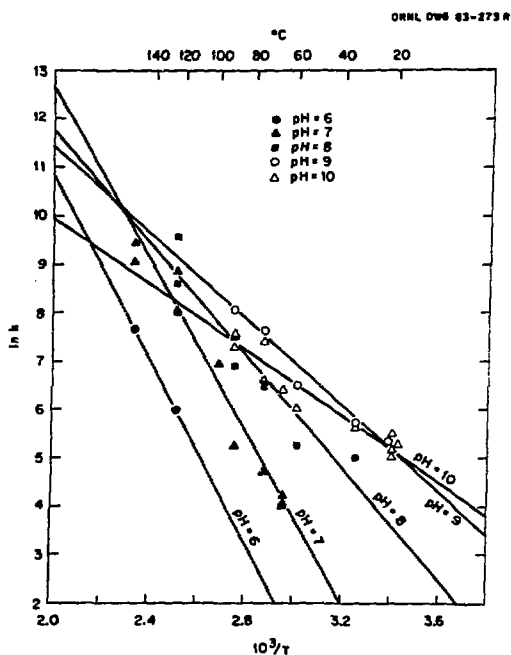

Figure 1. Rate constant for second-stage hydrolysis reaction.

Although we realize that the expression is an oversimplification of the kinetics, more exact computational methods that take into account all of the known interfering reactions prove to be even less satisfactory over the range of parameters examined here. The major reason that the more exact methods fail is that we do not have adequate rate and equilibrium constants for all the elementary iodine reactions above room temperature which must be included in such an exact approach. Since the assumptions made in Eq. 5 become more valid as the temperature increases, it is believed that the rate constants shown in Fig. 1 are the most reliable values currently available. Nevertheless, more rigorous computational methods will eventually be preferred when further data on the ancillary iodine reactions become available.

Table 1

PARAMETERS FOR THE SECOND-STAGE REACTION RATE CONSTANT
AS DETERMINED BY THE LEAST-SQUARES LINES THROUGH THE
RATE CONSTANT DATA SHOWN IN FIG. 1

pH	A*	B*	Activation Energy, E** (kJ/mol)	(kcal/mol)
6	-11.52	34.90	95.7	22.9
7	- 8.90	30.45	73.9	17.7
8	- 5.79	23.34	48.1	11.5
9	- 4.47	20.40	37.2	8.9
10	- 3.42	16.81	28.4	6.8

*Determined from the equation $\ln(k) = A(1000/T) + B$, where k is in $\underline{M}^{-1}$ s^{-1}.

**Determined from the slopes of the lines (values of A in column 2).

It is interesting to note that the rate constants in Fig. 1 indicate a very marked change of rate with variation in the pH of the aqueous solutions. This change can be interpreted as being due to variation in pH, the influence of boric acid, or ionic strength effects. (Even though the concentration of boric acid is 0.231 $\underline{M}$, the ionic strength is unusually low at pH 7. It has been calculated to be 0.025 and 0.001 for 0.231 and 0.01 $\underline{M}$ boric acid solutions, respectively, at 25°C from the previously reported equilibrium constants (4). Conductivity measurements of these solutions support these calculations.) The prospect that these changes in the kinetic rate constant could result from variations in ionic strength presented a means of further characterizing the nature of the "HOI" species since the primary salt effect (5) is dependent on the ionic properties of the reacting species.

The effect of ionic strength changes on the kinetics of the disproportionation reaction was determined in a series of experiments where the ionic strength was varied by adding $NaClO_4$ to the reaction mixture and then measuring the rate constants in the fashion described above. The rate constants in Table 2 for two different boric acid concentrations show no systematic variation, within experimental error, as the ionic strength is varied. Although the method of determining the rate constant is an oversimplification, the absence of any effect is still

Table 2

IONIC STRENGTH TESTS ON THE SECOND STAGE DISPROPORTIONATION REACTION:
3 "HOI" $\rightleftharpoons$ IO_3^- + $2I^-$ + $3H^+$, WHERE THE RATE CONSTANT VALUES HAVE
BEEN DETERMINED BY THE SIMPLISTIC MODEL OF EQ. (5)

NaClO$_4$ Conc. (M)	ln (k)	Medium*
0.0	2.56	0.231 M H$_3$BO$_3$
0.05	1.23	
0.50	1.70	
0.0004	0.79	0.01 M H$_3$BO$_3$
0.001	0.71	
0.005	0.95	
0.01	0.43	
0.05	0.73	
0.10	0.48	
0.50	0.33	

*Temperature = 25°C; pH = 7.

evident since ln(k) would have to change by 0.73 in going from 0.0 to 0.10 M
NaClO$_4$ for two interacting uncharged ions. A larger change would be expected
if the charges on the interacting ions were greater. Therefore, we must
conclude that at least one of the interacting species in the disproportionation
reaction is uncharged. With no basis for suspecting the existence of such a
distribution of species other than the OI$^-$ ion (which does not become significant
until pH 10 is reached), both interacting species are assumed to be uncharged;
thus, the triatomic HOI is the most probable intermediate form in the rate-
determining disproportionation reaction.

One other point that should be acknowledged before leaving the ionic strength
subject is also evident in Table 2. The rate constants are noticeably different
between the two boric acid concentrations. There has been some mention of a
catalytic effect from the boric acid solution, and this is perhaps the reason
for the differences in the table. It was, however, beyond the scope of this
work, and consequently the subject was not pursued any further.

A factor of considerable concern in iodine transport predictions has been the volatility of HOI. Much effort has been given to its determination at this laboratory, and all of the attempts to measure it directly with spectrophotometry have been futile. However, an indirect approach was used in which the volatilities of the halogen analogs, HOCl and HOBr, were determined and the volatility of HOI was inferred by correlation with the other two. These data are presented in Table 3 as partition coefficients (liquid concentration divided by vapor concentration), which were measured spectrophotometrically after the solutions had equilibrated. Realizing that partition coefficients increase with increasing atomic weight of the halogen for the diatomic elemental forms, it was assumed that the trend is also prevalent for the hypohalous molecules as well; and therefore, the partition coefficient for HOI would be greater than that determined for HOBr. (Even though HOBr could be reproducibly measured in aqueous solution, no vapor spectrum could be detected in the gas phase above the solution. From the known detection limits of the spectrophotometer, then, the HOI partition coefficient can be rather reliably estimated at $>1 \times 10^4$.)

Table 3

MOLAR ABSORPTIVITIES FOR HYPOHALOUS
ACIDS AND THEIR RELATED IONS

Species	Band (nm)	Molar Absorptivity ($\underline{M}^{-1}$ cm^{-1})
OCl$^-$	290	360
OBr$^-$	331	326
OI$^-$*	365	32
HOCl**	240	90
HOBr**	260	92
HOI	(280)‡	(10-100)‡

*Values taken from ref. (6).

**Value taken from ref. (7).

‡Values are estimated.

REDOX REACTIONS

All of the preceding discussion has been concerned with the fate of molecular iodine, I_2, in aqueous solutions and the iodine products that result from its reaction with water. Thus, the research approached the study of iodine by presuming that the initial form was I_2, the most volatile of the known species; and, from the data described in the preceding paragraphs, it was confirmed that iodine hydrolyzes and converts ultimately to nonvolatile I^- and IO_3^- at pH values greater than 7. Nevertheless, there still exists the possibility that conditions could exist where some redox reactions would be in competition with the normal hydrolysis chemistry of Eqs. 1-3 to produce a steady-state concentration of volatile iodine, namely I_2. It was for this reason that various redox processes have also been considered. In addition, some attention had been given to defining a mechanism whereby the iodine inventory of an aqueous solution could be diminished if it were in contact with some typical reactor components. Finally, the question of radiation effects has been addressed because radiation can initiate a novel array of redox reactions which may alter the volatility of iodine.

Iodine Reaction with Silver

It is well known that I^- can be precipitated by the addition of silver ion (Ag^+):

$$Ag^+ + I^- \rightarrow AgI\downarrow \quad . \tag{6}$$

On the other hand, the reaction of silver metal with the iodide ion does not occur. Since a considerable amount of silver occurs in control rod alloys, a mechanism whereby this silver might serve as a sink for iodine has been developed in which silver metal combines directly with molecular iodine that has been radiolytically produced:

$$Ag^0 + 1/2\ I_2 \rightarrow AgI\downarrow \quad . \tag{7}$$

It has been confirmed in this laboratory that iodide ion is effectively oxidized to I_2 when aqueous solutions are exposed to gamma radiation from a ^{60}Co source. The mechanism presumably involves the oxidation of I^- with hydroxyl radicals produced from the radiolysis of water (8):
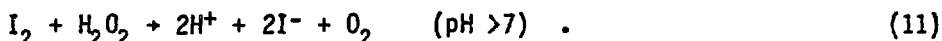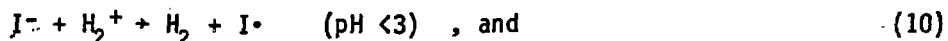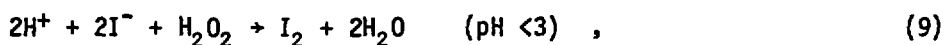
$$I^- + OH \rightarrow I\cdot + OH^- \tag{8}$$

where the I· radicals thus produced combine ultimately to form either I_2 or I_3^-, depending on the I^- concentration. This last reaction is acid dependent and

occurs best at pH <7; but even at pH 7, there is enough oxidation of I- in a 1-MR/h radiation source to effectively oxidize I^- and precipitate iodine through the reaction of Eq. 7. This fact has been demonstrated in our laboratory for irradiation times of 2 h for solutions of pH 7 and with CsI concentrations as high as 1×10^{-4} $\underline{M}$.

Effects of Radiation on Iodine Chemistry

Another cause of redox changes in the chemistry of iodine is that of radiation. Typical reactions between water radialysis products and iodine species (9, 10) are:

$$I^- + \cdot OH \rightarrow I \cdot + OH^- \quad (pH <7) \quad , \tag{8}$$

$$2H^+ + 2I^- + H_2O_2 \rightarrow I_2 + 2H_2O \quad (pH <3) \quad , \tag{9}$$

$$I^- + H_2^+ \rightarrow H_2 + I \cdot \quad (pH <3) \quad , \text{ and} \tag{10}$$

$$I_2 + H_2O_2 \rightarrow 2H^+ + 2I^- + O_2 \quad (pH >7) \quad . \tag{11}$$

The products of aqueous-solution radiolysis are the oxidizing radical $\cdot OH$, its molecular analog, H_2O_2, and the reducing radicals, $H \cdot$ and the hydrated electron, $e^-(H_2O)$ (11). These species participate in the secondary reactions shown above to generate redox products of iodine.

Hydrogen peroxide is the molecular product that can act either as an oxidant (Eq. 9) or a reductant (Eq. 11), depending on the pH. It has been shown in this laboratory that Eq. 9 is not significant above pH 3 and, therefore, the only influence of H_2O_2 is that of a reductant (Eq. 11), providing the pH is high enough. The H_2^+ radical is formed by reaction of the hydrogen radical with a proton; but since a high H^+ concentration is required to generate it, the subsequent reaction between H_2^+ and I- occurs only at pH <3. The most significant reaction in the pH range 6 to 8 is that of the $\cdot OH$ radical oxidation of I- even though it has customarily been utilized with other halogens (8) as a means of trapping $\cdot OH$ radicals at very low pH values.

The current research effort has focused on I- radiolysis in unbuffered solutions at near-neutral pH values in order to assess the extent to which I- might change and become volatilized through $\cdot OH$ oxidation. Typical experiments are illustrated in Fig. 2, which shows the pH of the aqueous solution with 10^{-3} $\underline{M}$ CsI as a function of time before, during, and after irradiation. Conditions, with and without argon
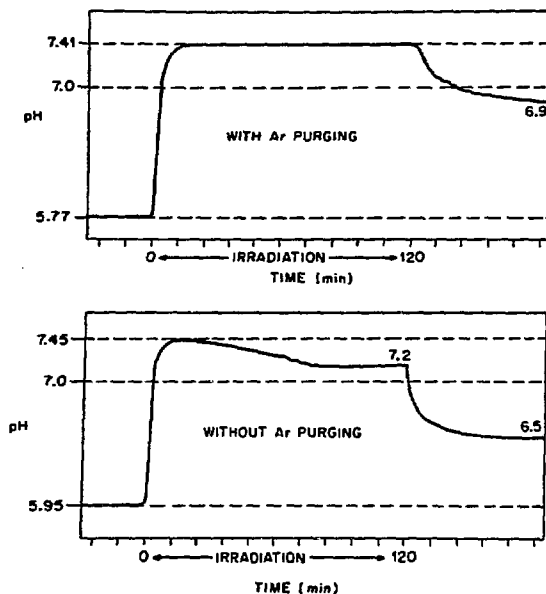
Figure 2. Irradiation of 1 x 10^{-3} M CsI,
pH = 6, in an all-glass flow system for
120 min.

purging, are shown for solutions that had been thoroughly outgassed prior to
irradiation with the gas purge and that were adjusted prior to irradiation to
approximately pH 6 with HCl. Immediately on irradiation of the solution, the
pH jumps by more than a pH unit, presumably from the reaction in Eq. 8. This
pH value remains constant (7.4) if there is argon purging because the I_2 that
ultimately forms is sparged from the solution and caught in the thiosulfate trap.
On cessation of the irradiation, the pH decreases gradually from what is believed
to be hydrolysis of the I_2 remaining in solution. Approximately 0.3% of the
iodine inventory in the system is volatilized and appears in the thiosulfate trap.

If there is no gas sparge during the irradiation, the pH behavior of the system is
somewhat different. The pH of the system rises abruptly, as before, due to the
reaction of Eq. 8; but as the concentration of I_2 builds up, its hydrolysis rate
also increases to the point that it can compete with the oxidation of I$^-$ by $\cdot$OH
radicals. Thus, the pH decreases until a steady-state value is reached (pH 7.2).
On cessation of irradiation, the pH again drops, but this time more rapidly than
in the experiment with gas sparging because there is more I_2 left in solution to
hydrolyze.

When 1×10^{-6} $\underline{M}$ CsI solutions are irradiated in a similar fashion, all of the iodide is oxidized, but only approximately 10% of the iodine inventory appears in the thiosulfate trap. The remainder is believed to be converted to IO_3^- and stays in the solution in accordance with some aspects of previously reported experiments (9). Tests are currently in progress to establish the ultimate fate of the iodine when exposed to irradiation.

The results of these flow experiments demonstrate that iodine can be volatilized when aqueous solutions containing CsI are irradiated. A controlling factor in the rate of volatilization is, again, the pH of the solution because the chemistry described above is a steady-state process and the faster the rate of hydrolysis after formation of I_2, the lower the rate of transport into the vapor.

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