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The Chemical Behavior of Iodine in Aqueous Solutions up to 150°C.

I. An Experimental Study of Nonredox Conditions

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ABSTRACT

The chemical behavior of iodine, I_2, in (pH = 6 to 10) aqueous solutions containing 2500 ppm boron as H_3BO_3 (0.231 $\underline{M}$) was studied at temperatures up to 150°C. Absorption spectrophotometry was used to identify and monitor the iodine species present. The I_2 hydrolysis chemistry was found to be consistent with the two-stage mechanism:

$$I_2 + H_2O \xrightleftharpoons{} \text{"HOI"} + H^+ + I^- ,$$

$$3\text{"HOI"} \xrightleftharpoons{} IO_3^- + 2I^- + 3H^+ ,$$
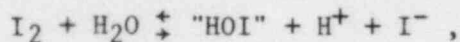
where the intermediate species is designated as "HOI" to emphasize that its exact structure and composition are not defined. Three objectives were considered: (1) species identification, with special attention given to "HOI"; (2) the kinetics of reaction between iodine and water to produce iodide and iodate ions; and (3) partition coefficients between liquid and vapor phases for individual iodine species.

Kinetic rate constants for the disproportionation of the "HOI" intermediate were measured. A typical activation energy for this reaction was found to be 28.4 kJ/mol (6.8 kcal/mol). Although some initial results had suggested an ionic strength dependency, a more detailed examination of the ionic strength effect on this disproportionation reaction suggests that the intermediate in solution throughout the pH 7-10 range is primarily an uncharged species such as the triatomic HOI. No absorption bands can be assigned to the HOI intermediate even though it has been shown, in some cases, to be present at concentrations of $>1 \times 10^{-3}$ $\underline{M}$. A very low molar absorptivity (<10 $\underline{M}^{-1}$ cm^{-1}) is probably responsible for its undetectability. A partition coefficient of $>1 \times 10^4$ has been estimated for HOI.

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L. M. Toth, K. D. Pannell, and O. L. Kirkland

1. INTRODUCTION

Since the accident at the Three Mile Island Unit 2 Nuclear Power Station, there has been a renewed 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 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.

The specific subject of interest during the past 2 years has been the reaction of molecular iodine, I_2, with aqueous solutions in nonredox situations under LWR accident conditions:

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

$$3\ HOI = IO_3^- + 2I^- + 3H^+ . \tag{2}$$
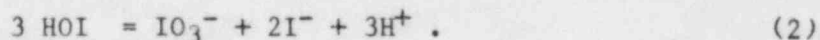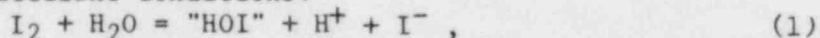
(The quotation marks are used around the HOI intermediate to emphasize that, although the +1 oxidation state of iodine can be readily established, the exact nature of the species in solution has never been clearly characterized. When written as HOI, however, the triatomic molecule itself is being specified.) Admittedly, if the iodine source were NaI instead of I_2 and no additional reactions occurred to alter its oxidation state, Eqs. (1) and (2) would not be pertinent to a reactor accident situation. Nevertheless, the I_2 hydrolysis chemistry as expressed in the above equations must be evaluated to aid in understanding the ultimate fate of I_2 in the event that it should ever be considered as a possible species in a real situation. Subsequent work will involve considerations of redox effects, radiation effects, and organic iodine compounds to complete this understanding of iodine chemistry.

The experimental method selected for this work was mainly visible-ultraviolet (vis-uv) absorption spectrophotometry, largely because it enables the identification of species plus the determination of concentrations in liquid and vapor media. Furthermore, the desire to perform experiments at relatively high temperatures (100-300°C) and pressures (the vapor pressure of water corresponding to those high temperatures) precludes the use of many other analytical techniques, whereas spectrophotometry is well suited to the measurement of species irrespective of the temperature.

Admittedly, much is already known about the aqueous chemistry of iodine since it has been a subject of considerable study over the past hundred years. An evaluation of previously published data was made during the early stages of planning, and the predictions of equilibrium and dynamic concentrations of iodine species according to thermodynamic and kinetic calculations were recently published.[1,2] First, these calculations predict that the equilibrium concentrations at relatively high pH values (e.g., 7-10) and high temperatures favor the occurrence of most of the iodine as nonvolatile iodide and iodate species. Second, since the kinetics of the hydrolysis reaction and ensuing disproportionation reaction of the intermediate "HOI" species can be extremely slow under some circumstances, it is possible for some potentially volatile intermediate to be present in the system for periods of hours, days, or even weeks.

Unfortunately, hydrolysis data above 60°C are not available, and our ability to predict the rates of the above two reactions was limited by the accuracy of estimates for their activation energies. Furthermore, the overall volatility of iodine in aqueous solutions could be dependent largely on the volatility of the intermediate "HOI" species and thus some direct measure of the volatility is highly desirable; but, before the volatility of this or any other species can be measured, some identification and characterization of the species must be made.

This report addresses (1) the identity of the species present in solution and the vapor above — with special attention given to the characterization of the "HOI" species; (2) the kinetics of the iodine reactions with water in pH-adjusted boric acid solutions; and (3) the partition coefficients for each of the identified species. The major parameters that were examined were temperature, pH, and iodine concentration for an aqueous solution containing 2500 ppm boron as boric acid, H_3BO_3 (i.e., 0.231 $\underline{M}$). Boric acid was included not only because it was mandated in NRC program objectives, but also because it afforded a practical buffer for the aqueous solution which would otherwise show a steady decrease in pH due to the acid generated in the reactions of Eqs. (1) and (2). The pH of the boric acid solution was set between 6 and 10 in unit increments by NaOH additions.[3] The sensitivity of the spectrophotometric methods used here has permitted iodine analysis at concentrations as low as 1×10^{-6} M, and the range considered in this study was generally $[I_2] = 10^{-3}$ to 10^{-6} $\underline{M}$. Although some of these data have been presented earlier in an interim report dated November 1981, they are also included here because of the limited distribution which the earlier report received.

2. EXPERIMENTAL METHODS

The initial stages of this work involved the design of a system that was suitable for the study of the iodine hydrolysis reactions shown in Eqs. (1) and (2). Iodine is extremely reactive toward most container materials and, consequently, glass or silica has normally been the

material of choice. However, the use of glass is usually limited to temperatures less than 100°C due to the increasingly high water vapor pressures that must be contained. The most practical systems for containing aqueous iodine solutions at temperatures in excess of the boiling point of water would appear to be unreactive metal containers. Therefore, the development, design, and construction of a suitable container system for the aqueous iodine studies up to 150°C have proceeded along the following sequence: stainless steel vessels, plastic-coated or gold-plated metal vessels, titanium vessels, and ballast-pressured glass cells. Characteristics of each of these are discussed in Appendix A.

As a result of the developmental work, two basic containment systems were selected for the experiments described in this report. The first was a 25.1-cm-pathlength titanium cell (Fig. 1) that was normally filled above the sapphire optical windows with 410 mL of aqueous boric acid solution that had been pH-adjusted with NaOH solution. A small glass capsule containing purified iodine was placed in the cell during assembly and a titanium breaker rod poised above it so that, once the system had equilibrated at a particular temperature, a sharp blow to the exterior end of the rod would cause sudden release of the I_2 into the aqueous medium. For additions to the aqueous medium at temperatures <100°C, aqueous iodine solutions of low pH were loaded in the capsules. Then, when the capsule was broken, the iodine solution could simply mix with the boric acid buffer solution. On other occasions for temperatures <100°C, an aqueous stock solution of I_2 in distilled water was admitted through a separatory funnel attached to the top of the titanium cell. No differences were observed due to the method of addition as long as the contents of the cell were thoroughly mixed after the addition of the iodine solution.

The second system used in this work was a ballast-pressured silica cell (Fig. 2) consisting of two cylindrical chambers connected by silica tubing. The two short sections of tubing that point downward were used to fill the cell, after which they were fused shut prior to inserting the cell in a steel pressure vessel. The steel vessel was ballasted with helium at a pressure equivalent to the water vapor pressure within the silica cell. Windows in the steel vessel matched with those of the silica cell and permitted the passage of the spectrometer light beam when the assembly was placed in the sample compartment.

A small dam in the larger chamber of the silica cell promoted the pumping of solution around through the smaller chamber when the system was rocked. The 19 mL of solution completely filled the small liquid chamber and connecting tubes, leaving just enough liquid in the larger, vapor-phase chamber to slosh over the dam when the assembly was rocked. Gentle rocking of the cell ensured equilibration of liquid and vapor phases by circulating the solution through the two chambers. Absorption spectra of either liquid or vapor phases could be measured by merely shifting the cell assembly up or down so that the appropriate window intersected the spectrometer light beam. The liquid and vapor pathlengths of this cell were 2.08 and 30.3 cm, respectively. However, for
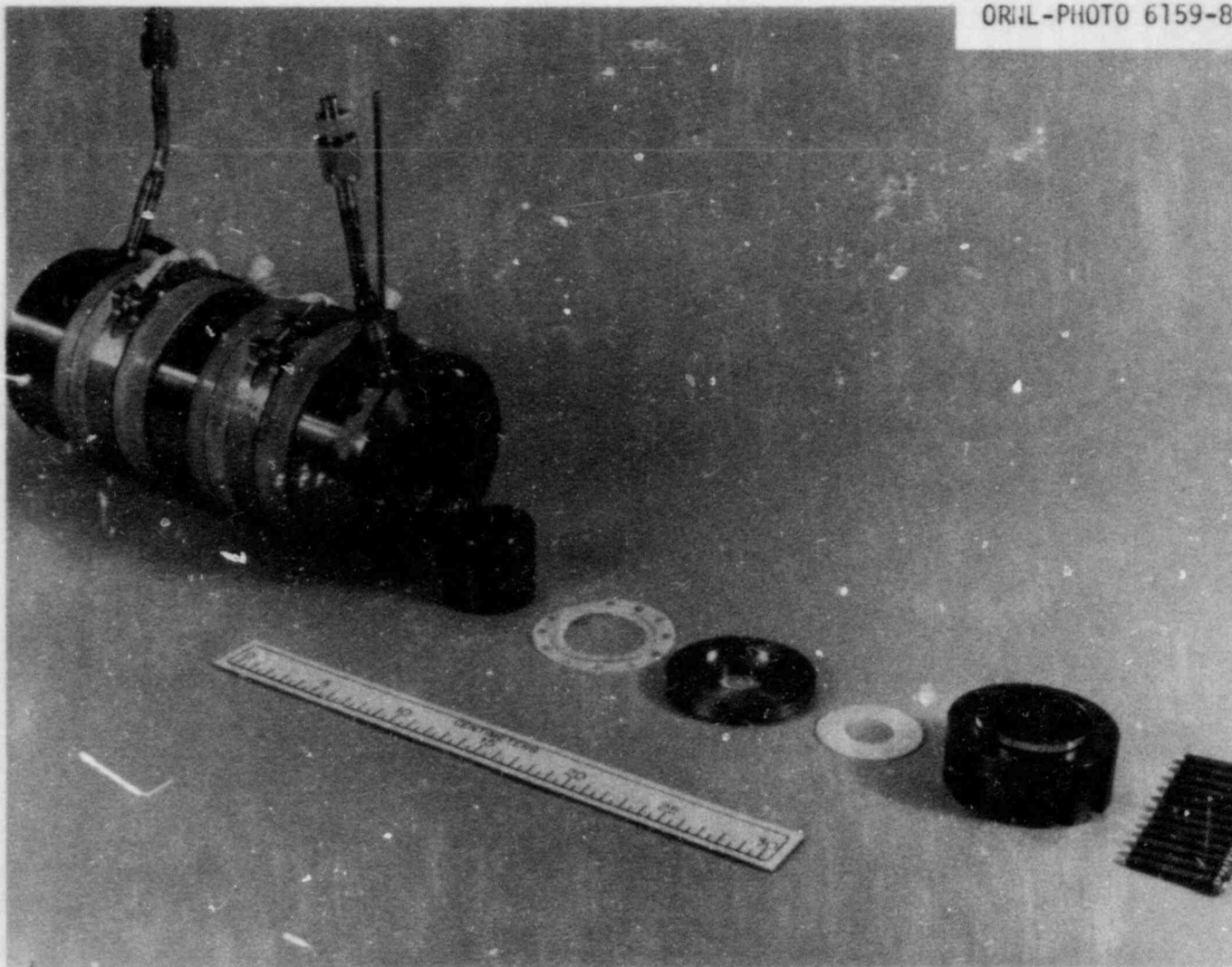
Fig. 1. Exploded view of titanium cell. Two 5-in.-diam band
heaters can be seen around the body of the cylindrical cell.

ORNL-PHOTO 0792-81

Fig. 2. Photograph of a two-chamber ballast-pressured silica cell. A small dam can be seen inside the large chamber at the point where the right connecting tube is attached.

some work (e.g., the HOCl distribution coefficient measurements made on a system analogous to that of HOI) a 0.5- or 0.05-cm-pathlength cell was used for the liquid phase. The system was best suited for long-term equilibration experiments in which distribution coefficients of iodine and absorption spectra of the various species were sought.

Absorption spectra were monitored with a special Cary 14 recording spectrophotometer that had an enlarged sample-reference compartment area. A cradle in the compartment permitted the rocking of large sample cells between spectral measurements. Because the response time of the spectrometer was of the order of 1 s, it was not possible to monitor very fast kinetic processes with this instrument. Furthermore, the release and mixing of reagents into a previously equilibrated aqueous solution usually required up to 1 min before spectral measurements could begin. Therefore, most well-mixed solutions were not monitored until 1 min after the reagents had been added. In some instances, however, unmixed solutions were monitored throughout the introduction of reagents and here the 1-s response time of the instrumentation governed the time limitations of the measurements. The results of these unmixed solutions vary greatly from those of the homogeneous solutions, mainly because of local concentration gradients that altered the hydrolysis rate of I_2. These unmixed solutions have been studied briefly by high-speed motion picture photography, and the results will be contrasted with those of the homogeneously mixed solutions.

Although the wavelength range of the spectrophotometer extends from 2500 to 190 nm, the interfering absorption bands from water overtones in the near-infrared region reduce the practical spectral range for aqueous solutions to the 800- to 190-nm region. However, when the gas space above the aqueous solutions was examined, it was often possible to cover the full spectral region of the instrument from the infrared to the ultraviolet limits. Iodine species typically absorb in the vis-uv region with molar absorptivities that often permit detection at rather low concentrations. Typical spectra of these iodine species are shown in Appendix B for condensed, as well as volatile, forms. Table 1 gives the wavelengths and molar absorptivities of the various species that were monitored.

3. RESULTS AND DISCUSSION

When molecular iodine is released into water, it is generally accepted[4] that it reacts according to Eqs. (1) and (2). For the purpose of the following discussion, we shall define these two reactions as the first and second stages, respectively, of the overall hydrolysis reaction:

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+ . \tag{3}$$
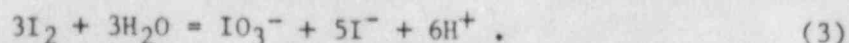
The stoichiometry of the overall reaction provides a useful test by which this reaction can be distinguished from corrosion-related

Table 1. Iodine species, molar absorptivities, and
detection limits currently identified

Species	Molar absorptivity, ε ($\underline{M}^{-1}$ cm^{-1})	Wavelength, λ (nm)	Detection limit $\times 10^6$ ($\underline{M}$)[a]
Liquid			
I_2	748	460	2.2
	17	270	
		205	
I_3^-	26,400	350	0.06
I^-	13,500	225	0.12
IO_3^-	5,332	200	0.3
CH_3I	173	248	9.6
Vapor			
I_2	831	533	2.0
HI	356	258	4.7
CH_3I	2,833	201	0.6

[a]Molarity, as determined from Beer's law, $c = A/\varepsilon l$, where $A = 0.05$, $l = 30$ cm for this system, and the ε values were taken from column 2.

reactions where all of the iodine is expected to be converted to I^-. This will become evident in the kinetics section of the discussion.

It is also generally recognized[2] that the first-stage reaction is very fast, usually reaching equilibrium conditions within 1 s, whereas the second stage is much slower and takes anywhere from seconds to years (depending on the temperature, pH, etc.). If, then, I_2 is released in a system where the detection equipment has a response time of 1 s, the first stage of the hydrolysis would be completed (or at equilibrium) by the time of the first meaningful measurement. This was actually verified in the initial stages of this research by using high-speed motion picture photography to monitor the fate of I_2 released in aqueous boric acid buffer solutions at a pH of 7 and a temperature of 150°C. Even in these unstirred solutions where concentration gradients would permit the pH in the release zone to reach abnormally low values, all the brown (aqueous) I_2 color disappeared within 3 s, thus confirming the fact that the first stage of the hydrolysis reaction is extremely fast.

3.1 KINETICS STUDY

The kinetics of the very rapid first-stage reaction will probably not be of particular significance to any reactor accident considerations, whereas the second stage would determine which of the potentially volatile iodine species would be present in a reactor if molecular iodine should be formed and then contact an aqueous medium. Therefore, a study of the second-stage reaction became the topic of concern, and the absorption spectrophotometer with a 1-s response time was adequately suited for the task.

Several basic points concerning the nature of the spectrophotometric procedure should first be emphasized. In principle, the progress of this kinetic process could be followed by monitoring the iodine reactant, the intermediates, or the product ions. However, the I_2 reactant either disappears within the response time of the instrument for high pH values or is not present in sufficient concentration to be routinely monitored. An absorption band for the "HOI" intermediate has not been identified as has been done for the OI^- ion in 4 $\underline{M}$ NaOH solutions[5] (one should not be confused by a seldom considered weak I_2 band at 270 nm — see Fig. B.2, Appendix B — which is easily observable in the vapor and may be incorrectly interpreted as an HOI band), and the absorption band for the IO_3^- product occurs at the uv limit of the spectrophotometer (see spectrum in Appendix B) and therefore will be obscured by the extremely intense absorption of I^-. With these considerations in mind, the greatest amount of information can be obtained by monitoring the rate of growth of the I^- band occurring at 225 nm (see Fig. B.5, Appendix B). The rate of formation of I^- typically follows the trend illustrated in Fig. 3. Immediately after release of iodine into the boric acid solution adjusted to a pH of 7-10, the iodine hydrolyzes within 1 s via Eq. (1) to form I^- at a concentration equal to that of the initial iodine. At this point, we must assume (since it cannot be measured spectrophotometrically) that an
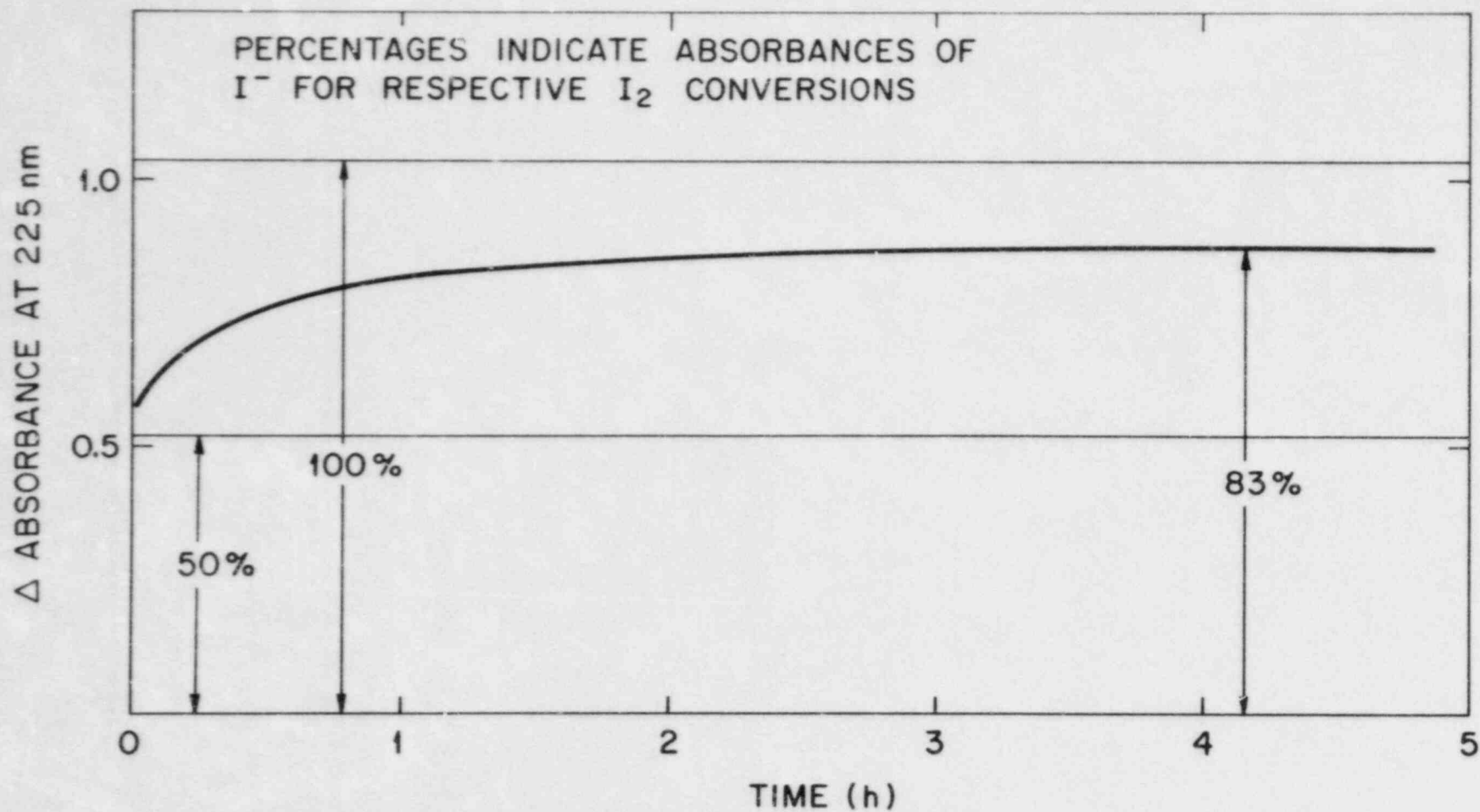
Fig. 3. Growth of the I⁻ band for a typical kinetics experiment. Aqueous solution conditions illustrated here are 2×10^{-6} $\underline{M}$ I_2 in pH 8, 0.231 $\underline{M}$ H_3BO_3 at 65°C.

equivalent amount of the intermediate "HOI" is formed according to the first-stage reaction. Thus, on monitoring the I^- band, one observes an immediate increase in its absorbance to the 50% value as shown in the figure. Subsequently, a gradual increase in the intensity of the I^- band occurs [which is believed to be due to the second-stage mechanism of Eq. (2)] until the final concentration of I^- is equal to five-sixths that of the original gram-atoms of iodine added. [Note that the stoichiometry of Eq. (3) predicts this.]

In order to study the kinetics of the iodine hydrolysis reaction, two approaches were used. First, a general examination of the kinetics was made by following the growth of the I^- band spectrophotometrically (as described in the previous paragraph) until no further change was observed. This indicated that the hydrolysis reaction of Eq. (3) had reached equilibrium; and, in view of the magnitude of the equilibrium constant as described in ref. 1, we describe it as "reaching completion." Because of the nature of the spectrophotometric method, this represented a point where most (>98%) of the product iodide had been formed. These times to reach completion were then tabulated as described below. Second, during the course of the general study, it became apparent that more detailed information (e.g., rate constants) could be derived if some simple and rather obvious assumptions were made. This analysis led to a study of the elementary aspects of the second-stage hydrolysis reaction and will be presented following the general study.

3.1.1 General Kinetics Observations

The first attempts at measuring rates of reaction were made at 150°C in response to programmatic guidelines, but inconsistencies in the data occurred because of the speed of the overall reaction and of our failure to mix the solution adequately after release of the iodine. It was therefore reasoned that the kinetics at lower temperatures would be slow enough to enable accurate determination of the kinetic parameters and that the experience gained therein would make subsequent attempts at the high-temperature regimes considerably easier. First, 65°C was selected because it represented one point of interest in the program guidelines; it was then followed by measurements at progressively higher temperatures. The results of these experiments are given in Table 2.

Some of the entries in the table are preceded by a < or > sign, and some with the < are enclosed in parentheses. The < and > notations imply that the reaction reached completion before and after, respectively, the time reported for the measurement, while the parentheses designate values that were assumed (instead of being measured) since the trend in the overall series of values indicated that the outcome of the experiment was obvious.

The results of this study show that at a pH of 6 the reaction never reached equilibrium during the time of the experiment. For example, at 65°C and 1×10^{-4} $\underline{M}$ I_2, 25% of the initial iodine still remained after 68 h. As the pH increased, however, the rate of reaction also increased

Table 2. Effects of pH and temperature on the time required for the second-stage reaction of Eq. (2) to achieve completion [a]

Temperature ($^\circ$C)	pH				
	6	7	8	9	10
$[I_2] = 1 \times 10^{-4}$ $\underline{M}$					
65	25% I_2 remains at 68 h	>2 h	1.2 h	0.85 h	0.75 h
100	22 h	21 min	26 min	2-20 min	1-11 min
125	30 min	10 min	<1 min	<1 min	<1 min
150	11 min	1 min	<1 min	<1 min	(<1 min)
$[I_2] = 2 \times 10^{-6}$ $\underline{M}$					
65	>10 h	16 h	4 h	1.9 h	1.4 h
100	132 min	25 min	20 min	7 min	1-7 min
125	76 min	15 min	10-20 min	1 min	<1 min
150	26 min	7 min	<1 min	<1 min	(<1 min)

[a]As measured by the method indicated in Fig. 3.

to the extent that at a pH of 10 the iodide concentration reached 83% of the total iodine added at 0.75 h and then ceased to change.

Reactions with the lower concentrations of iodine (e.g., 2×10^{-6} M) invariably took longer to reach the same degree of completion than did the corresponding 1×10^{-4} M run. (The only exception to this trend was found with the 100°C data. Experimental difficulties with the procedure at 100° made this data very difficult to reproduce.) Since the second-stage reaction is a disproportionation process where two intermediates must interact with each other, the rate of product formation would be proportional to the square of the intermediate concentration, $d["HOI"]/dt = -k["HOI"]^2$; therefore, the lower the concentration of the intermediate, the longer the reaction would require for completion. Calculations based on this type of a rate expression have been made,[1,2] and plots of the intermediate concentration as a function of time for various total concentration of iodine have substantiated this fact.

Especially significant is the effect of temperature on the hydrolysis reaction because in going from 65 to 150 C, the time to reach completion decreases dramatically from hours to <1 min. At 150 C, the reaction reaches completion by the time of the first measurement, namely, 1 min; and therefore the time to achieve completion is indicated as "less than" 1 min. The data at 150°C made it obvious that a study of the kinetics of the reaction at still higher temperatures would be pointless; instead, a careful examination of the kinetics at temperatures up to 150 C would be more appropriate.

Before leaving the discussion of the general studies, it should be emphasized that the ultimate question of interest lies with iodine volatility. The attention given to iodine hydrolysis reactions is only of importance to the extent that the aqueous chemistry would control the amount of volatile iodine over the solution. In two separate experiments, the vapor phase was examined over the same interval as that followed in the liquid studies in order to validate the assumption that the liquid phase governs the vapor chemistry. These two experiments were performed at 65°C with an initial I_2 concentration of 1×10^{-4} M. In one case, the 0.231 M boric acid solution was adjusted to pH 6 prior to the release of the iodine. After 2.2 h, 82% of the iodine initially seen in the vapor immediately after release of the I_2 into the aqueous solution was still present there. (The data in Table 2 indicate that 25% of the iodine in the aqueous solution remained after 68 h; therefore, the presence of iodine in the vapor after 2.2 h would be entirely reasonable.) In the other case, the 0.231 M boric acid solution was adjusted to pH 8 prior to the release of the iodine. Here, the first measurement (at 1 min) showed no iodine in the vapor, but by this time the first-stage reaction had already gone to completion. (Note that the second-stage reaction required 1.2 h for completion in the aqueous phase.)

The results of this general study show that the kinetics of the iodine hydrolysis reaction are indeed rapid, especially at the higher

temperatures, in agreement with the kinetics calculations that were made based on earlier data given in the literature. However, the effect of temperature has never been quantified and a more detailed analysis of the data is needed (see Sect. 3.1.2). Finally, the experiments described in the preceding paragraph demonstrate that there is rapid equilibration between liquid and vapor phases; therefore, the aqueous solution should control the chemistry occurring in the vapor phase if there is sufficient interface between them.

3.1.2 Detailed Analysis of Kinetics Experiments

If the first stage of the hydrolysis reaction goes to completion within 1 s and 50% of the iodine appears as iodide, with the remainder occurring as the "HOI" intermediate (which does not absorb in the uv region), the "HOI" concentration at any instant can be expressed in terms of the iodide ion concentration measured at that instant as follows:

$$["HOI"] = 5/2 \ [I_2]_o - 3/2 \ [I^-] \ , \tag{4}$$

where $[I_2]_o$ is the concentration of I_2 initially released in the system. Although this method of calculation is an oversimplification of the actual kinetics and is subject to some error under conditions where the iodine concentration is high and the pH and temperatures are low,[11] we have found it is the only model which is generally satisfactory over the full range of parameters explored here.

By using data obtained from runs such as those described in the previous section, the concentration of the ["HOI"] intermediate can be calculated. When the reciprocals of these calculated ["HOI"] values are plotted as a function of time (a classical second-order kinetic reaction plot), the slopes of the lines then define the second-order rate constant. A typical plot at 35°C is shown in Fig. 4. Similar plots have been made for data taken at $2 \times 10^{-6} \ \underline{M} \ I_2$ from 20 to 150°C in 0.231 $\underline{M}$ boric acid solutions where the pH had been adjusted in increments from 6 to 10; rate constants were determined from plots such as that given in Fig. 4 and then collected in the Arrhenius activation energy plot of Fig. 5.

The parameters for the least-squares lines through these data are given in Table 3 along with activation energies calculated from the slopes of the lines. It should be noted in Fig. 5 that the slopes of the lines, and hence the activation energies, decrease with increasing pH (see also Table 3). The decrease in the activation energy can be interpreted as being due to pH, boric acid, or ionic strength effects. (It should be noted that even though the concentration of boric acid is 0.231 $\underline{M}$, the ionic strength is unusually low[3] and is calculated to vary beween 0.025 and 0.222 in going from pH 7 to pH 10.)

The interesting prospect that these changes in the kinetic rate constant could be due to changes in the ionic strength presents a means of further characterizing the nature of the "HOI" species.

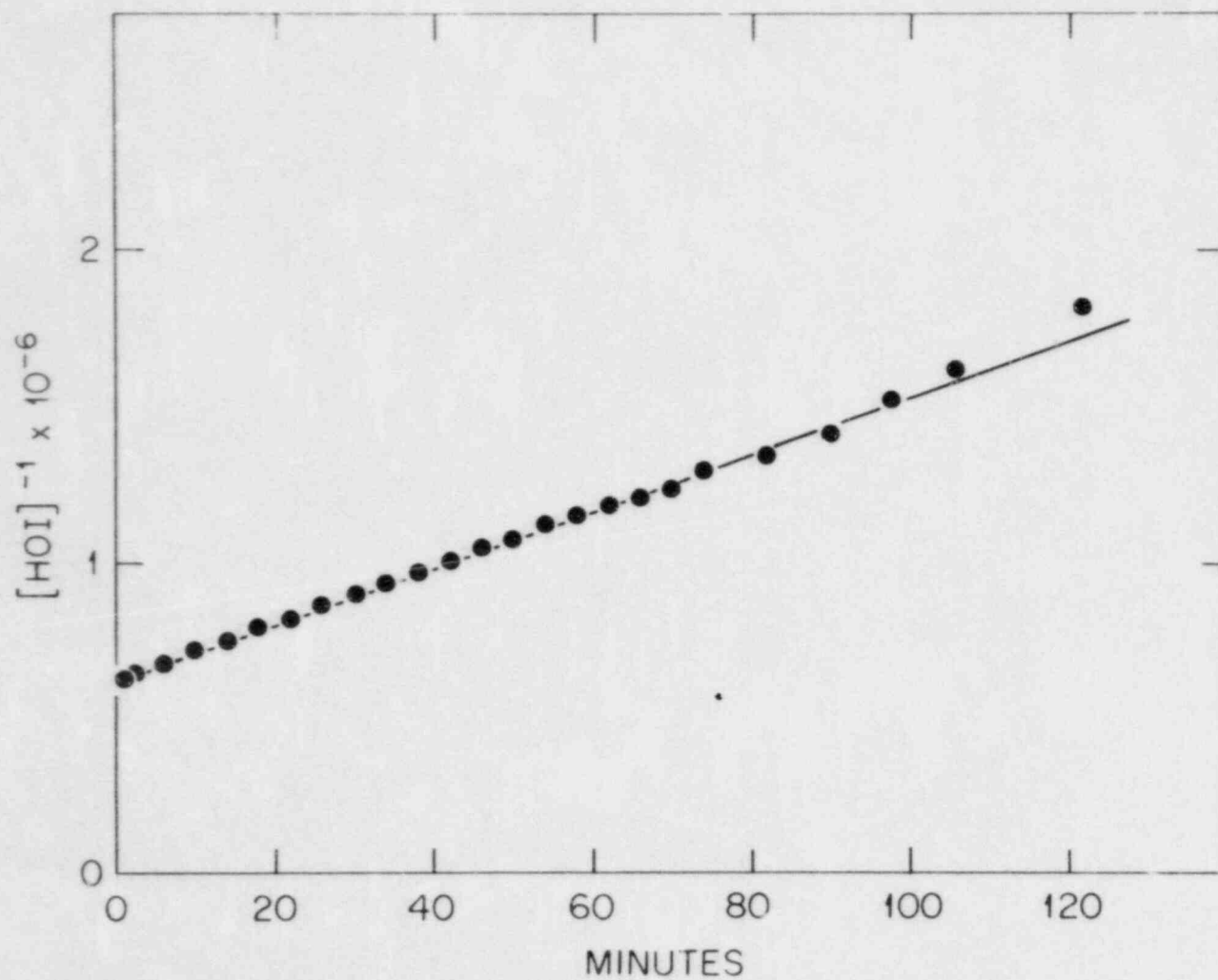Fig. 4. Typical second-order plot of data obtained from Eq. (4) using measured values of $[I^-]$ and $[I_2]_o$. Temperature, 35°C.

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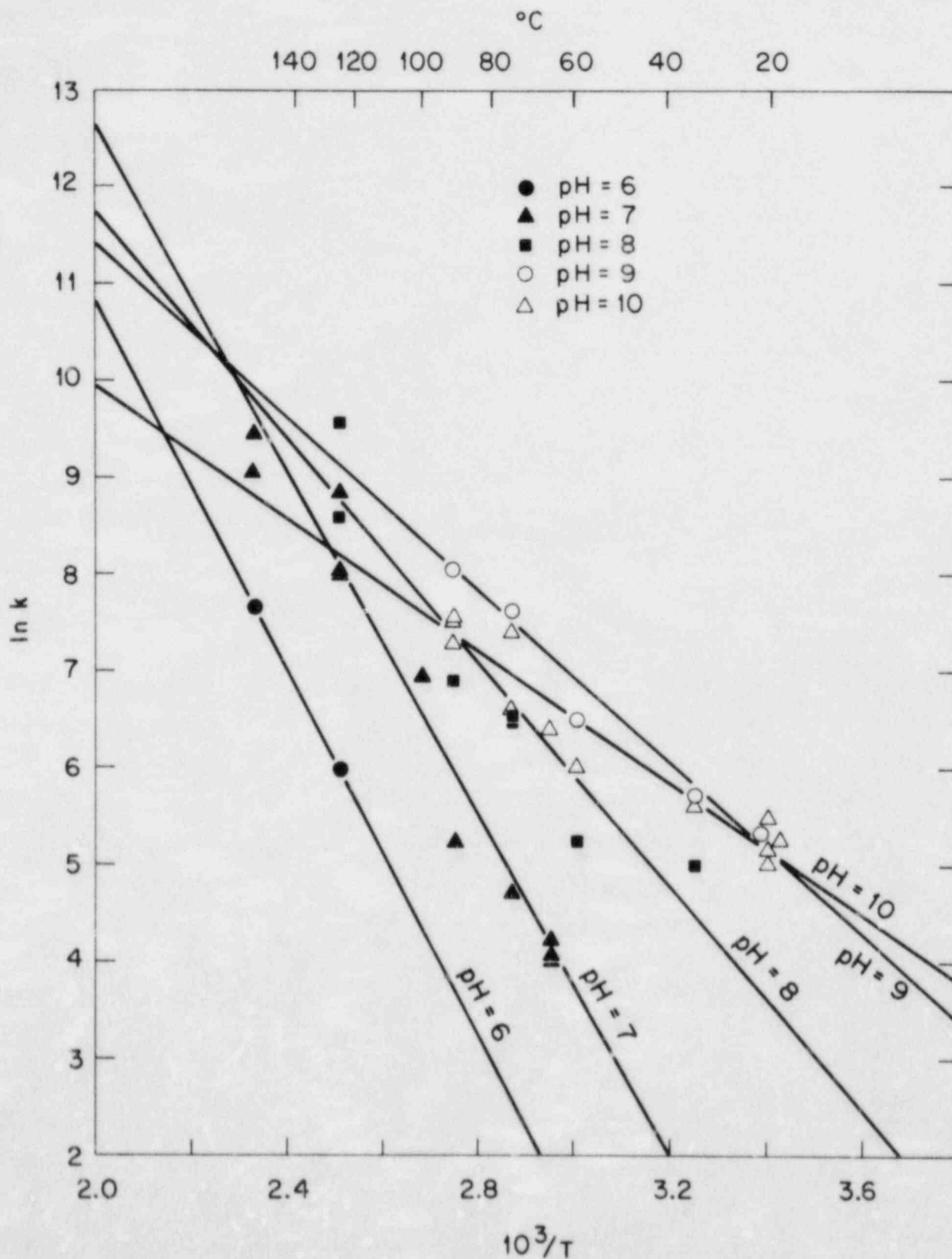
Fig. 5. Arrhenius plot of second-stage reaction ($3HOI \rightleftharpoons IO_3^- + 2I^- + 3H^+$) rate constants for 2×10^{-6} $\underline{M}$ I_2 release rate into 0.231 $\underline{M}$ boric acid solution adjusted to the indicated pH values.

Table 3. Parameters for the second-stage reaction rate
constant as determined by the least-squares lines
through the rate constant data shown in Fig. 5

pH	A^a	B^a	Activation energy, E^b (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

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

[b]Determined from the slopes of the lines (values of
A in column 2).

A classical expression can be derived for the relationship between the ionic strength and the kinetic rate constant, $\log_{10}(k/k_o) = Az_az_bI^{1/2}$, where k and k_o are the rate constants for the reaction in question at a particular ionic strength, I, relative to that at infinite dilution, k_o; z_a and z_b are the charges on the interacting ions; and A is a constant equal to 1.018 for H_2O. A plot of $\log(k/k_o)$ vs $I^{1/2}$ should yield a line with slope equivalent to z_az_b. The sign of the slope (+, -, or 0) tells whether the species are of like charge, unlike charge, or uncharged, respectively, while the magnitude gives an indication of the magnitude of the charges on the ions themselves.

To test the effect of ionic strength changes on the kinetics of the disproportionation reaction, a series of experiments was performed where the ionic strength was varied by adding $NaClO_4$ to the reaction mixture and measuring the rate constants in the fashion described above. The rate constants in Table 4 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 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 is expected if the charges on the interacting ions are greater. Therefore, we must conclude that at least one of the interacting species in the disproportionation reaction is uncharged; with no basis for suspecting such a distribution of species exists other than the OI^- ion (which does not occur until pH 10 is reached), both interacting species are assumed to be uncharged. The triatomic, HOI, is the most probable form of the intermediate in the rate-determining disproportionation reaction.

One other point that should be acknowledged before leaving the ionic strength subject is also evident in Table 4. 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 Table 4. It was, however, beyond the scope of this work, and consequently the subject was not pursued any further.

3.2 CHARACTERIZATION OF "HOI"

Much attention has been given to calculating the concentration of "HOI" in the vapor, its volatility, and many other pertinent properties. Nevertheless, "HOI" has never been characterized to the extent that the HOCl and HOBr analogs have. In the current research effort, several approaches were taken to produce a species which should be the intermediate "HOI" and then to characterize it with absorption spectrophotometry (or any other physicochemical technique that appeared to be practical). The liquid and vapor phases over typical solutions have been examined with iodine at the highest possible concentrations to ensure detection of the intermediates. In addition, some of the classical preparations for "HOI", followed by traditional wet-chemical

Table 4. Ionic strength tests on the second stage disproportionation reaction: $3 \text{ "HOI"} \rightleftarrows IO_3^- + 2I^- + 3H^+$ where the rate constant values have been determined by the simplistic model of Eq. (4)

[NaClO$_4$]	ln k	Medium
0.0 M	2.56	0.231 M H$_3$BO$_3$
0.05	1.23	pH = 7
0.50	1.70	25°C
0.0004	0.79	
0.001	0.71	0.01 M H$_3$BO$_3$
0.005	0.95	pH = 7
0.01	0.43	25°C
0.05	0.73	
0.10	0.48	
0.50	0.33	

analyses, were performed to demonstrate the occurrence of the intermediate; these were, followed, in turn, by absorption spectral measurements to characterize the intermediate thus produced. The results of these three approaches are described separately below and summarized by a general evaluation of the nature of the intermediate in typical reactor accident-related situations.

Although neither HOI nor the OI⁻ ion has been directly identified under conditions similar to those found in LWR and BWR aqueous systems, a brief examination of the recent chemical literature leads one to the conclusion that the presence of the hypoiodite ion, OI⁻, has been fairly well established. This conclusion arises mainly from a comparison of the results of Haimovich and Treinin[5] with those known for the OCl⁻ and OBr⁻ analogs.

Haimovich and Treinin first reported[5] the electronic spectrum of OI⁻, which was produced by dissolving iodine in 4 $\underline{M}$ NaOH to make solutions that are ~10^{-2} $\underline{M}$ in OI⁻. They also measured a second-order rate of disappearance for the absorption bands attributed to OI⁻ (at 365 and ~270 nm), which is given as 4×10^{-2} $\underline{M}^{-1}$ s⁻¹; that is, a solution of 0.04 $\underline{M}$ OI⁻ decomposed within 80 min. The reaction,

$$OI^- + OI^- \rightarrow IO_2^- + I^- , \qquad (5)$$

is claimed to be analogous to the OCl⁻ and OBr⁻ disproportionation reactions. Treinin and co-workers later gave more details on the disproportionation[6] and the photolysis[7] of OI⁻.

Comparison of Treinin's spectrum at 365 nm with the spectra reported for OCl⁻ and OBr⁻ by Anbar and Dostrovsky[8] lead to some interesting correlations, as shown in Table 5. The only anomaly rests on the relatively low value for the OI⁻ molar absorptivity, for which there is no satisfactory explanation. From the corresponding values reported[8] for the hypohalous acids, also given in Table 5, we can estimate that HOI would absorb at 280 nm and would have a molar absorptivity in the range 10-100 $\underline{M}^{-1}$ cm⁻¹.

Since the equilibrium constant for the dissociation of HOI at 25°C is reported to be 2.3×10^{-11},[9] the OI⁻ ion should not be a significant species at pH <10. Therefore, attempts to characterize the "HOI" intermediate under simulated reactor accident conditions should be focused on the undissociated form. With so many known aqueous iodine species absorbing strongly in the uv region (e.g., I⁻, IO_3^-, and I_3^-), the greatest chances of isolating an HOI spectrum occur in the vapor region where only I_2 and, possibly, HI could be present.

3.2.1 Search for "HOI" Intermediate in the Vapor

We have examined the vapor phase over an aqueous solution contained in the ballast-pressured silica cell at temperatures up to 150°C with the intention of identifying any bands that could be attributed to an "HOI" species. It was anticipated that such a species might be volatile

Table 5. Molar absorptivities for hypohalous
acids and their related ions

Species	Band (nm)	Molar absorptivity ($\underline{M}^{-1}$ cm^{-1})
OCl^-[a]	290	360
OBr^-[a]	331	326
OI^-[b]	365	32
$HOCl$[a]	240	90
$HOBr$[a]	260	92
HOI	(280)[c]	(10-100)[c]

[a]Values taken from ref. 8.
[b]Value taken from ref. 7.
[c]Values are estimated.

enough at this temperature to be present in concentrations that could be detected by absorption spectrophotometry. However, no bands other than those assigned to I_2 have been observed in the vapor if it had an intensity as predicted above. Furthermore, by digitally subtracting sample and reference spectra, the region around the very weak 270-nm I_2 band (see Fig. B.2, Appendix B) has been shown to contain no unresolved bands that might be attributed to species other than I_2. In an alternative approach, we have studied the vapor equilibrium,

$$H_2O + I_2 = HI + HOI , \qquad (6)$$

by using such small amounts of I_2 and H_2O in a sealed silica cell that the condensed phases (I_2 and H_2O) evaporated completely at 150°C. In this procedure, then, there was no liquid phase into which the HI would dissolve. Examination of the vapor absorption spectrum revealed only I_2 — and no HI — as might be expected from the above equilibrium. Using the measured absorptivity for HI in the vapor, we have calculated an upper limit for the equilibrium quotient of the <u>vapor</u> reaction at 150°C, $Q = [HI]["HOI"]/[I_2] = 10^{-8}$.

3.2.2 Intermediate Species in Aqueous Solution

In another approach, we have sought to produce the "HOI" intermediate at high concentration by releasing I_2 into the boric acid buffer solution and following the change in the absorption spectrum by rapidly scanning the interval from 400 to 250 nm. If the molar absorptivity correlations given in the first part of this section are reasonably correct, a value of 10 to 100 $\underline{M}^{-1}$ cm^{-1} would be expected for the intermediate. If an absorbance of 0.1 is taken as the practical detection limit for the species, then by Beer's law it would have to be present at a concentration of at least 3.3×10^{-5} to 3.3×10^{-4} $\underline{M}$ in a 30-cm-pathlength absorption cell.

Considering the kinetics calculations,[2] the optimal conditions for identifying the intermediate would be at a pH of 9 to 10 with the release of 1×10^{-4} g-atoms/L iodine (i.e., 5.0×10^{-5} $\underline{M}$ I_2). Under these conditions, the intermediate would remain at measurable concentration levels in the system for a period of approximately 2 min. Unfortunately, the kinetics calculations predict that the range of conditions under which the "HOI" intermediate would be measurable is very narrow. Longer lifetimes of the intermediate could be obtained by going to lower concentrations of the reagent, I_2, but the concentration of the intermediate is reduced proportionately and the chances of its detection are compromised. Increases in the concentration of the reagent would cause similar increases in the intermediate concentration, but this would be accompanied by greater amounts of unreacted I_2 and the associated I_3^- formed by:

$$I_2 + I^- = I_3^- , \qquad (7)$$

which would obscure the 280-nm region being examined for the intermediate species.

Furthermore, it is not possible to vary the pH of the system significantly and still maintain optimal conditions for the detection of the intermediate. At higher pH values we would anticipate an increase in the OI^-/"HOI" ratio with the OI^- obscuring the spectral region in which "HOI" is expected, while at lower pH values we would expect an increase in the amount of unreacted reagent I_2. (The reader is encouraged to examine the figures in ref. 2 that illustrate our predictions.)

With these considerations in mind, several experiments were performed under the optimal set of conditions as predicted by calculations illustrated in ref. 2. In addition, I_2 was also released into solutions where the conditions were varied slightly from the optimum in order to gain a better understanding of the species giving rise to the spectra.

When 1×10^{-4} $\underline{M}$ I_2 is released into a 0.231 $\underline{M}$ boric acid solution of pH 10 and the absorption spectrum is scanned from 400 to 250 nm, the results shown in Fig. 6 are obtained. A shoulder appears at approximately 280 nm and decreases with time (according to second-order kinetics) at a rate similar to that observed for the +1 valence iodine at higher pH values.[5] In addition, a weak band at 365 nm is indicative of the presence of trace OI^- in the solution. If the species giving rise to the absorbance at 280 nm is another species of the +1 valence iodine in equilibrium with the OI^-, for example,

$$\text{"HOI"} = H^+ + OI^- , \tag{8}$$

the release of I_2 into a solution at a higher pH should shift the above equilibrium to the right and the band due to OI^- at 365 nm should increase while that of the other in equilibrium with it should decrease.

Figure 7 illustrates the changes that were observed when the above experiment was performed at a pH of 11. The intensity of both the 280-nm and the 365-nm band increased, thus demonstrating that these two bands are due to the same species. The single species is identified as OI^- since the 365-nm band has already been assigned to it.[5] If the experiment is performed at a pH of 9, the results shown in Fig. 8 are obtained. These spectra are merely due to I_3^- that was anticipated from the earlier kinetics calculations.[2]

Variations in the I_2 concentration produce similarly predictable results. Greater concentrations of I_2 obscure the 280-nm region through the formation of I_3^-, while lower concentrations of the reagent I_2 produce only reduced intensities of the same bands observed in the 1×10^{-4} I_2 case illustrated in Fig. 6. Because the band at 180 nm grows with the 365-nm band in going from pH 10 to 11 and is therefore due to the hypoiodite ion, OI^-, it was concluded from these experiments that "HOI" does not exist as the uncharged triatomic species at <u>detectable</u> concentrations. Any or all of the following reasons could be responsible: (1) the "HOI" molecular absorptivity is too low for this species to be seen at the concentrations produced, (2) the concentration
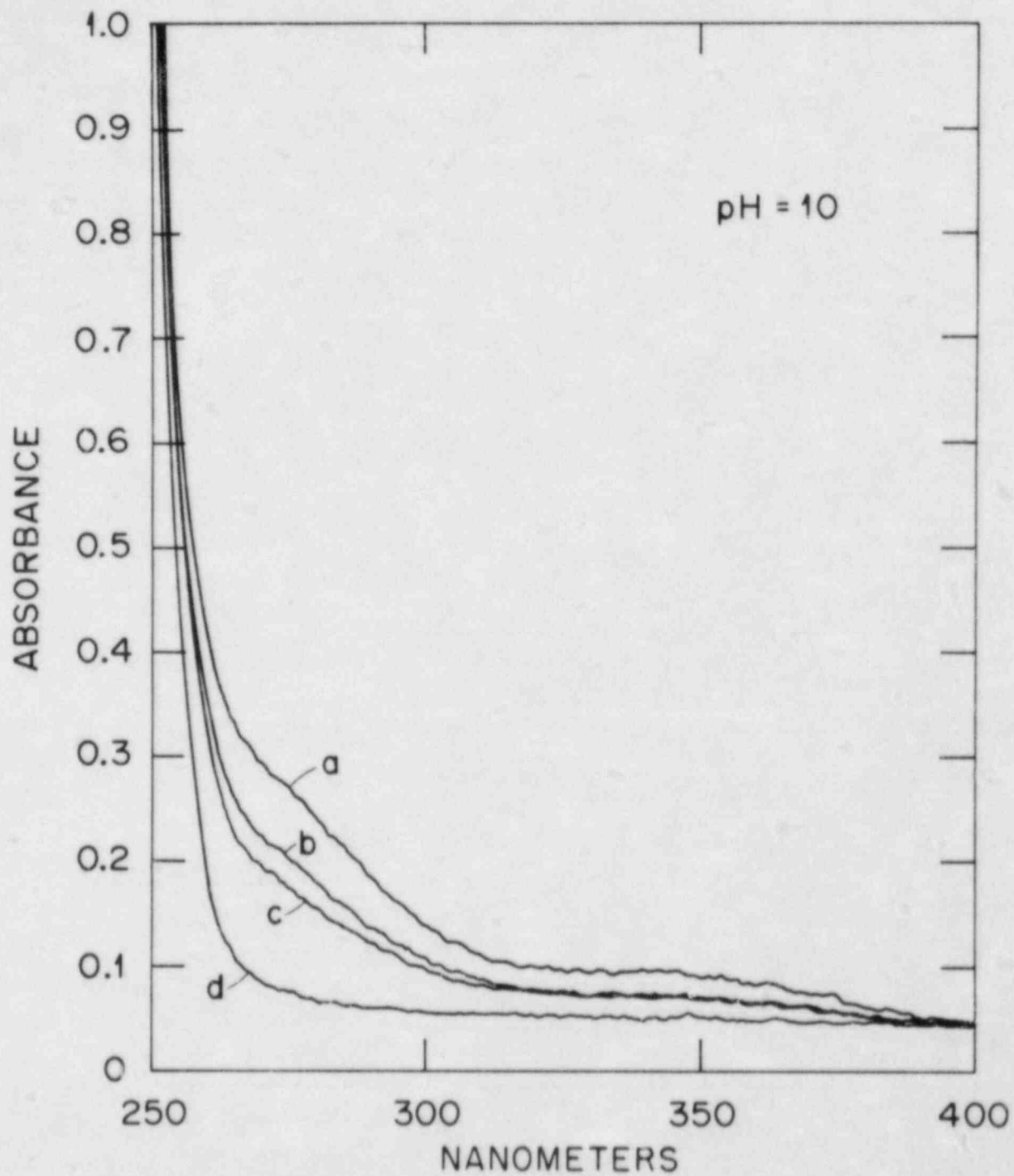
ORNL DWG 82-20639

Fig. 6. Intermediate species seen at pH 10 when 1×10^{-4} $\underline{M}$ I_2 was released into an aqueous 0.231 $\underline{M}$ boric acid solution and spectra were repetitively scanned.

ORNL DWG 82-20638
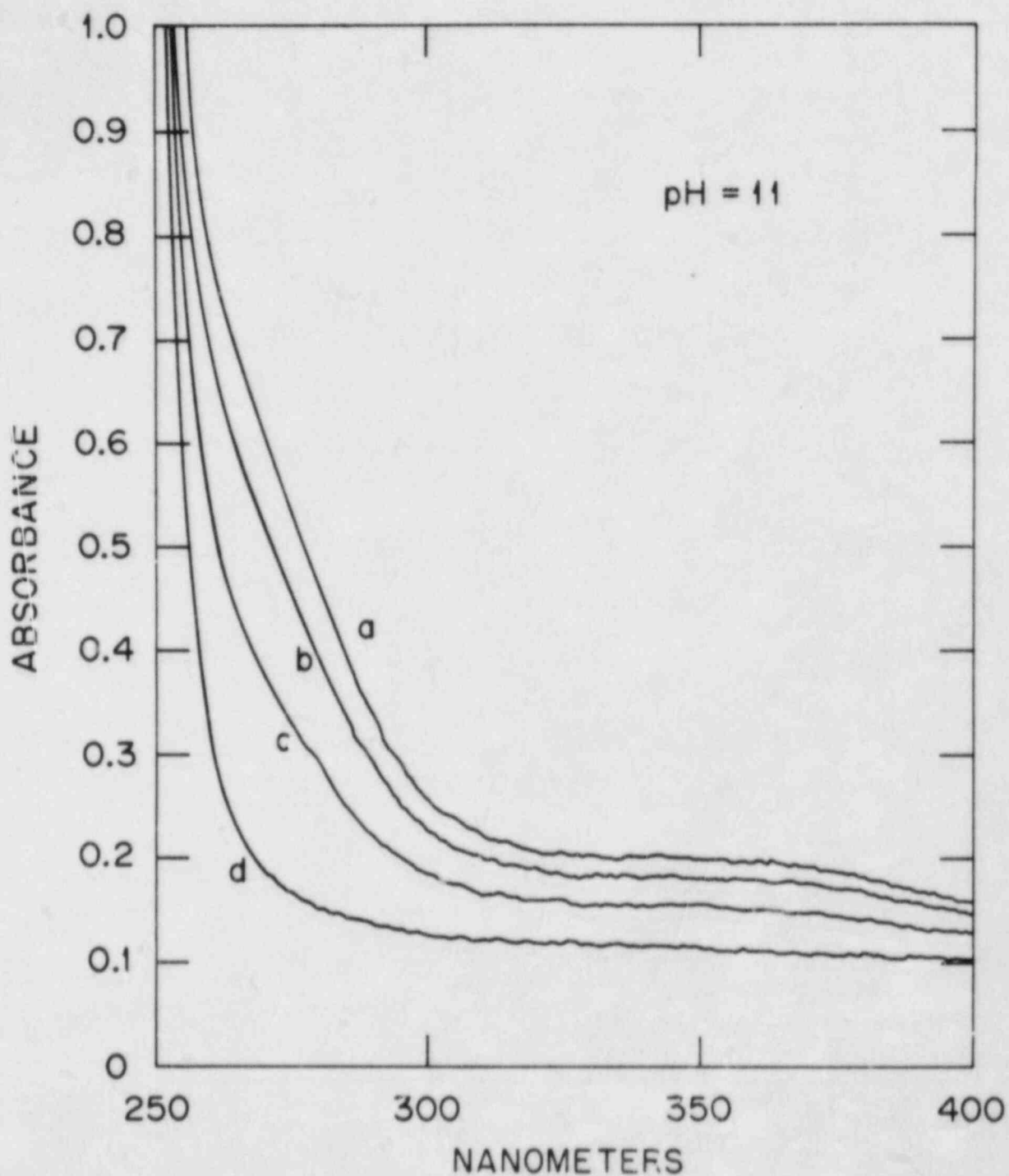
Fig. 7. Intermediate species seen at pH 11 when 1×10^{-4} $\underline{M}$ I_2 was released into an aqueous 0.231 $\underline{M}$ boric acid solution and spectra were repetitively scanned.

ORNL DWG 82-20640
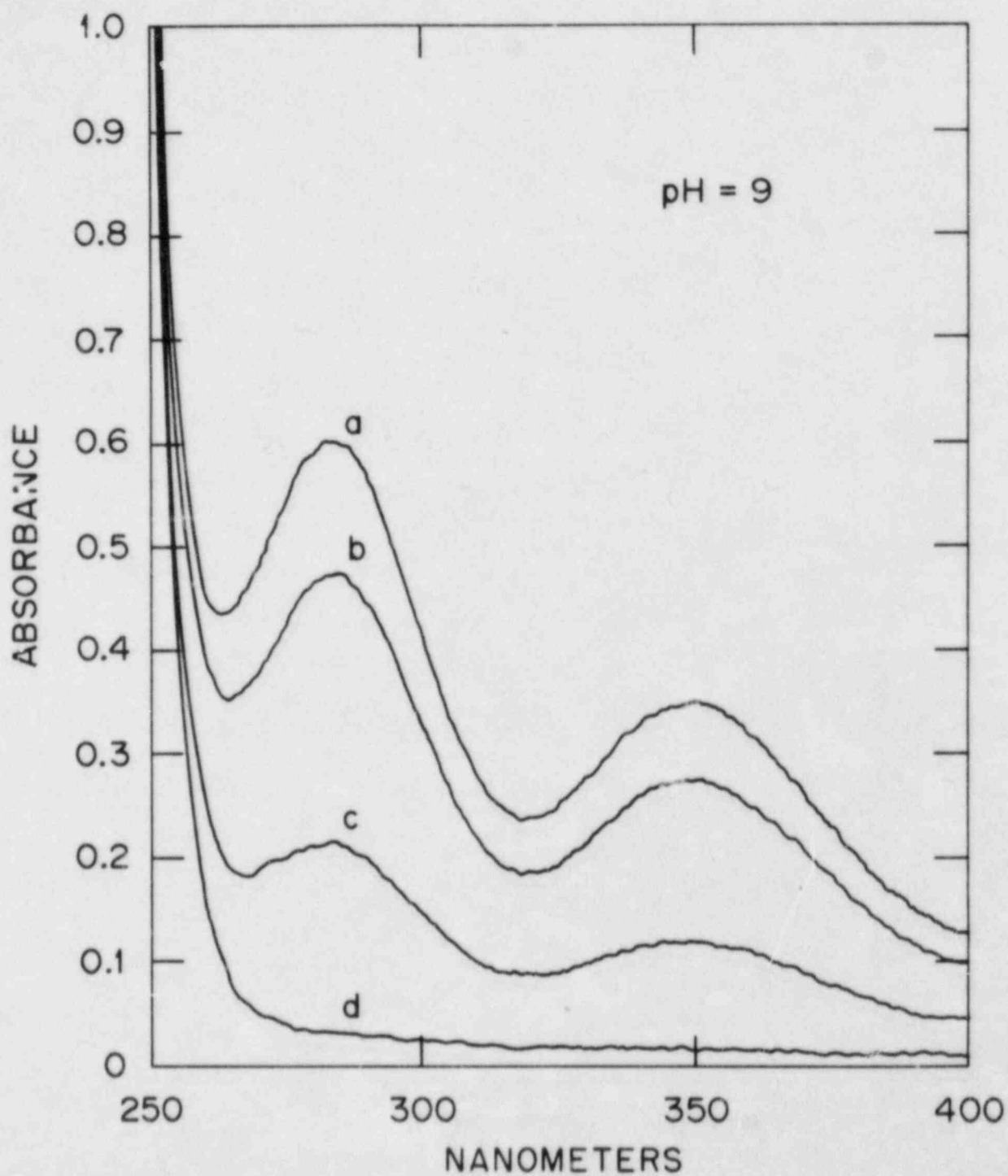
Fig. 8. Intermediate species seen at pH 9 when 1×10^{-4} $\underline{M}$ I_2 was released into an aqueous 0.231 $\underline{M}$ boric acid solution and spectra were repetitively scanned.

of "HOI" is much lower than predicted, or (3) another form of the intermediate species is present in solution and does not absorb in this region.

3.2.3 Classical Preparations of "HOI"

The +1 valence iodine species has been classically synthesized[10] by the combination of a metal ion, M^{n+}, such as Ag^+ or Hg^{2+}, with I_2 solutions to effect precipitation of the metal iodide and thereby drive the iodine hydrolysis reaction to the right:

$$M^+ + I_2 + H_2O = MI\downarrow + H^+ + \text{"HOI"} . \tag{9}$$
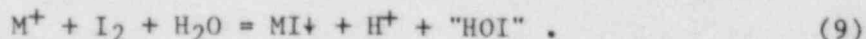
The "HOI" product is then titrated with sodium thiosulfate or complexed with phenol and then titrated to demonstrate the presence of the monovalent iodine. Concentrations of "HOI" equivalent to 1×10^{-3} M are possible by this method. By titrating at various times after generation of the "HOI," kinetic rates can be measured for this relatively unstable species; these rates are in reasonable agreement with those observed[6] 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 physicochemical methods have been used to characterize the structure of this species further. Customarily, the intermediate has been simply referred to as "HOI" even though there was no certainty that it existed in solution as the uncharged triatomic molecule.

Seal's method[10] has been used to prepare concentrations of the "HOI" intermediate as high as 3.7×10^{-3} M, which were then titrated by the thiosulfate method described in his article. By adding excess KI reagent to the solution containing the freshly generated "HOI", the first-stage equilibrium of Eq. (1) is reversed and the thiosulfate titration of the iodine thus produced is a direct measure of the "HOI" that was present. Next, acidification of the titrated solution with HCl reverses the second-stage reaction and also converts the IO_3^- end product [from the disproportionation of "HOI", Eq. (2)] to I_2; it, too, can be titrated with thiosulfate to establish the extent of "HOI" disproportionation prior to the excess KI addition. If the addition of the KI is not made immediately after the "HOI" generation step, the first titration will require significantly less titrant, while the second will take proportionately more.

By varying the time interval before the excess KI addition in a series of experiments, the kinetics of the "HOI" intermediate was studied. A rate constant of 6.39 M^{-1} s^{-1} has been determined in this laboratory for a solution where 1×10^{-2} M I_2 was converted to "HOI" using 2.6×10^{-3} M $AgNO_3$. Similarly, $HgCl_2$ was used in alternative experiments (instead of $AgNO_3$) with equal success. Lower temperatures increase the stability of the "HOI" intermediate somewhat because when the same kinetics study was performed at 5°C, a rate constant of 2.95 M^{-1} s^{-1} was found.

Having established an "HOI" intermediate concentration of $>1 \times 10^{-3}$ $\underline{M}$ in these solutions, as well as an understanding of its stability, the solutions were analyzed spectrophotometrically in order to determine whether "HOI" has an electronic absorption spectrum such as that predicted in Table 5. Simple as the procedure might seem, there were several limitations that could compromise the direct spectral measurements. First, the reaction that produces "HOI" by this procedure involves the formation of a precipitate which must be filtered or centrifuged from the solution. Second, any excess M^+ ion remaining in solution will combine with I^- produced during the disproportionation of the intermediate and precipitate after the filtration, thereby obscuring the subsequent spectral measurements. On the other hand, any deficiency of M^+ will leave a net excess of reagent I_2 which, with the I^- product, will form the intensely absorbing I_3^- species. Third, the solubility of the metal iodide itself may contribute to interference in the spectral measurement. (This is especially true in the case of HgI_2, which has a solubility of 1.3×10^{-4} $\underline{M}$ at 20°C and produces an intense uv band at 265 nm with a measured molar absorptivity of 4600 $\underline{M}^{-1}$ cm^{-1}.)

In spite of the above limitations, the intermediate was generated at concentrations as high as 3.7×10^{-3} $\underline{M}$ (as determined by thiosulfate titrations) at 0 and 20°C, and absorption spectra of the filtered solutions were measured immediately afterward. As anticipated, the spectral measurements were hampered by additional formation of precipitate and, at times, by excess iodine that caused interference from the resulting I_3^-. Nevertheless, no bands were observed that could be assigned to the "HOI" intermediate. Recalling the reasons cited previously for not observing the intermediate, it is now certain with these measurements that an unexpectedly low concentration of the intermediate was not responsible because the intermediate has been reproducibly titrated at values $>1 \times 10^{-3}$ $\underline{M}$ at the time which spectral measurements were being made. Therefore, this phase of the work demonstrates that the molar absorptivity of the uncharged HOI is much lower than predicted.

Chia has suggested[9] that the intermediate is, in fact, HOI_2^- in equilibrium with OI^-:

$$OI^- + I^- + H_2O = HOI_2^- + OH^- . \tag{10}$$
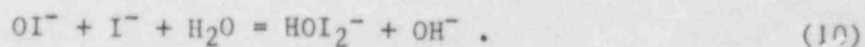
A molar absorptivity of 400 $\underline{M}^{-1}$ cm^{-1} has also been given for this species, which has a weakly pronounced band at $\sim$350 nm. In addition, an equilibrium constant of $K = [HOI_2^-][OH^-]/[OI^-][I^-] = 0.13$ estimated from his measurements suggests that it would be the dominant species at pH <10. We have not been able to identify such an intermediate and characterization of the "HOI" as an ionic species would not be consistent with the ionic strength effects noted in our kinetics experiments. Our study showed that HOI_2^- could not be generated in a typical kinetics experiment (illustrated in Fig. 3) because immediately after I_2 was released into the aqueous boric acid solutions of pH 6-10 and temperatures of 22-150°C, at least half of the iodine added to the system

was found to be present as iodide ion. If HOI_2^- were the dominant species disproportionating via Eq. (2), there would be no free I^- in the solution — which is not in agreement with the measurements over this region.

3.3 PARTITION COEFFICIENTS

Since I_2 was the only iodine species that could be found in both the liquid and the vapor phases (and here a pH <5 was required), it is the only species for which partition coefficients have been directly measured. Nevertheless, an indirect measurement of the volatility of the intermediate has been made, and the results will be discussed later in this section. In order to simplify the presentation of the data for future use, we have reported partition coefficients for each individual species, where D = (molar concentration in the liquid phase)/(molar concentration in the vapor phase). These data are far more practical to produce and analyze prior to their assembly into the recently discussed composite coefficients [see ref. 4, Eq. (5.7)].

3.3.1 I_2

The partition coefficients for molecular iodine as a function of temperature are shown in Table 6 as determined after equilibration in the ballast-pressured silica cell. Also shown in the table are those coefficients that would be predicted using available Henry's law constants. (These constants, k, can be derived for various temperatures from reported solubility and vapor pressure data. Thus, $k = P_B/X_B$, where P_B is the vapor pressure of the pure solute and X_B is its mole fraction at saturation for a given temperature.) In all the cases shown, the actual partition coefficients are slightly greater than the predicted values due to the lower concentration of I_2 in the vapor phase. The solvation of iodine by the water is believed to be responsible for the decreased vapor pressure of the iodine over iodine-containing solutions, and this association should decrease with temperature as indicated by the trend in the differences between the measured and the predicted partition coefficients.

3.3.2 HOCl and HOBr

Reliable partition coefficient data for "HOI" have been greatly desired because this intermediate is believed to be a significant species with a significant vapor pressure. However, the lack of evidence for its presence has precluded any direct measurement of a partition coefficient, D. As an alternative, the chlorine and bromine analogs have been examined, and a lower limit estimate for D has been made for "HOI" by correlation with the known hypohalites.

Hypochlorous acid, HOCl, can be generated by the simple acidification of hypochlorite solutions. Because the absorption spectra of both the hypochlorite ion, OCl^-, and the acid form, HOCl, are well

Table 6. Partition coefficients for molecular iodine
measured at 19 to 150°C in silica cells
containing only I_2 in water[a]

Temperature	Distribution coefficient	
(°C)	Measured	Predicted
19	108	97.1
52	29.7	27.2
86	11.6	11.4
92	10.9	10.3
151	5.1	5.2

[a]No buffers were added; no pH adjustments were made.

known,[8] the appearance of HOCl in solution was readily recognized when the pH of a 0.1 $\underline{M}$ sodium hypochlorite solution was reduced from 12.3 to 7.0; the OCl$^-$ band at 290 nm disappeared as the 240-nm band of HOCl increased. These solutions were simply transferred to the ballast-pressured silica cell (cf. Fig. 2), which was then sealed and inserted in the steel pressure cell. The system was equilibrated at various temperatures from 22 to 100°C, and partition coefficients were determined by measuring the HOCl absorption spectra in both the liquid and vapor phases. Partition coefficients of 3300^{+0}_{-1000} and 1000^{+0}_{-500} were determined for HOCl at 22 and 100°C, respectively.

Partition coefficients were sought for HOBr in a similar fashion, but when 0.1 $\underline{M}$ sodium hypobromite solutions were acidified, no HOBr spectrum at $\overline{2}60$ nm could be observed in the vapor over solutions containing as much as 0.1 $\underline{M}$ HOBr. All efforts to detect HOBr in the vapor were unsuccessful; and in contrast to the situation found for the iodine analog, the presence of HOBr as found in the liquid enabled the establishment of a lower limit for D of HOBr. If the practical detection limit in the vapor is 0.05 absorbance and the molar absorptivities for HOBr are the same for both liquid and vapor, then by Beer's law:

$$D = \frac{C_L}{C_V} = \frac{A_L/\epsilon \ell_L}{A_V/\epsilon \ell_V} ,$$

where

$A_L = 1.0$ (measured),
$A_V = <0.05$,
$\ell_V = 30$ cm,
$\ell_L = 0.01$ cm, and
$D = >1 \times 10^4$.

3.3.3 HOI

The partition coefficients for the elements Cl_2, Br_2, and I_2 at 20°C vary from 2.5 to 25 to 90 as calculated from their Henry's law coefficients (i.e., solubility of the gas divided by its vapor pressure at saturation for a given temperature, where both are expressed in the same units). Furthermore, if the partition coefficient for HOCl at 22°C is 3300, as measured, while that for HOBr is $>1 \times 10^4$, we can safely estimate that the coefficient for HOI will probably be $>1 \times 10^4$.

4. CONCLUSIONS

The kinetics of the iodine hydrolysis reaction has been shown to be very fast for the first stage (<1 s) and of varying rate for the second stage, depending on the temperature, pH, and concentrations of the reactants. Kinetic rate constants have been measured for the second-stage reaction, and the absence of any ionic strength dependency suggests that the intermediate is an uncharged species such as the tri-atomic HOI.

The failure to detect any absorption bands due to the "HOI" intermediate in the aqueous solution, even though the intermediate has been titrated at concentrations as high as 1×10^{-3} $\underline{M}$ during a textbook-type preparation, indicates that this species has an extremely low molar absorptivity. The very low molar absorptivity precludes the direct measure of the intermediate in the vapor; however, by correlation with the partition coefficients of the other hypohalous ions in solution, the partition coefficient for HOI is estimated to be $>1 \times 10^{4}$. On the other hand, partition coefficients have been measured for molecular iodine, I_2, and these are in accord with those predicted by Henry's law.

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6. APPENDIXES

Appendix A.

CHARACTERISTICS OF POTENTIAL CONTAINERS FOR
STUDYING AQUEOUS IODINE SOLUTIONS

Stainless steel. Stainless steel type 304L, like all iron alloys, is generally unsuitable for studies of iodine solutions due to the rapid corrosive loss of I_2 from such solutions, even at ambient temperatures. Steel cells are, however, useful as secondary containers for the ballast-pressured glass cells (see below).

Plastic-coated metals. Teflon or other halocarbons can be readily applied to metal surfaces by commercially established coating techniques. However, the halogens are significantly soluble in these materials and tend to diffuse through them. The slow loss of iodine by such a diffusion mechanism might be acceptable if it were not for the corrosion of the metal underneath and subsequent loosening of the coating from its attachment to the metal surface. High temperatures promote this diffusion to such an extent that 100°C appears to be the useful limit for coated cells in contact with iodine solutions; but simple glass cells are also useful up to this temperature, so no advantage is seen in using plastic coatings. Two final properties of these coatings should be noted. First, they are most successfully attached to metal surfaces by first applying a primer coat that contains metallic elements such as cobalt; and if the primer is not thoroughly covered by the final coat, it provides a very reactive surface for I_2 attack. Second, the plastic materials have very high thermal coefficients of expansion that can cause thick coatings to buckle and peel off the metal substrate.

Gold-plated metals. Even though corrosion reactions are eliminated by such coatings, direct halogenation of the gold appears to be responsible for the continuous and possible reversible loss of iodine from aqueous solution. Noble metal-coatings are therefore not considered practical for long-term usage in contact with aqueous solutions under the conditions of these experiments.

Titanium containers. At pH >5, corrosive loss of I_2 is either eliminated or too slow to be of consequence. Therefore, we believe that titanium is a suitable material for kinetic studies. The availability of a titanium optical cell in this laboratory has further encouraged its usage, and stoichiometric tests of the I_2 hydrolysis reaction have been used (see Sect. 3) to demonstrate that the homogeneous aqueous-phase reactions are the dominant chemical processes taking place.

Ballast-pressured glass cells. The low structural integrity of silica glass can be circumvented by balancing the vapor pressure of water on the inside of a silica cell with an equivalent pressure of gas on the outside. Toward this end, a custom-designed silica cell (Fig. 2) has been constructed at ORNL. It is normally filled with an aqueous solution containing iodine and other reagents, and the filling tubes are

then sealed off with a torch. The cell is next loaded into a heavy-walled steel cell which can be pressurized with dry helium so that the pressure drop across the glass cell is minimal. The pressure of helium that is applied to the exterior of the glass cell corresponds to the vapor pressure of the water within it. This system has been used successfully at 150°C, and it is believed that even higher temperatures could be readily achieved.

Appendix B.

ABSORPTION SPECTRA OF THE MORE COMMON IODINE
SPECIES MONITORED DURING THIS STUDY
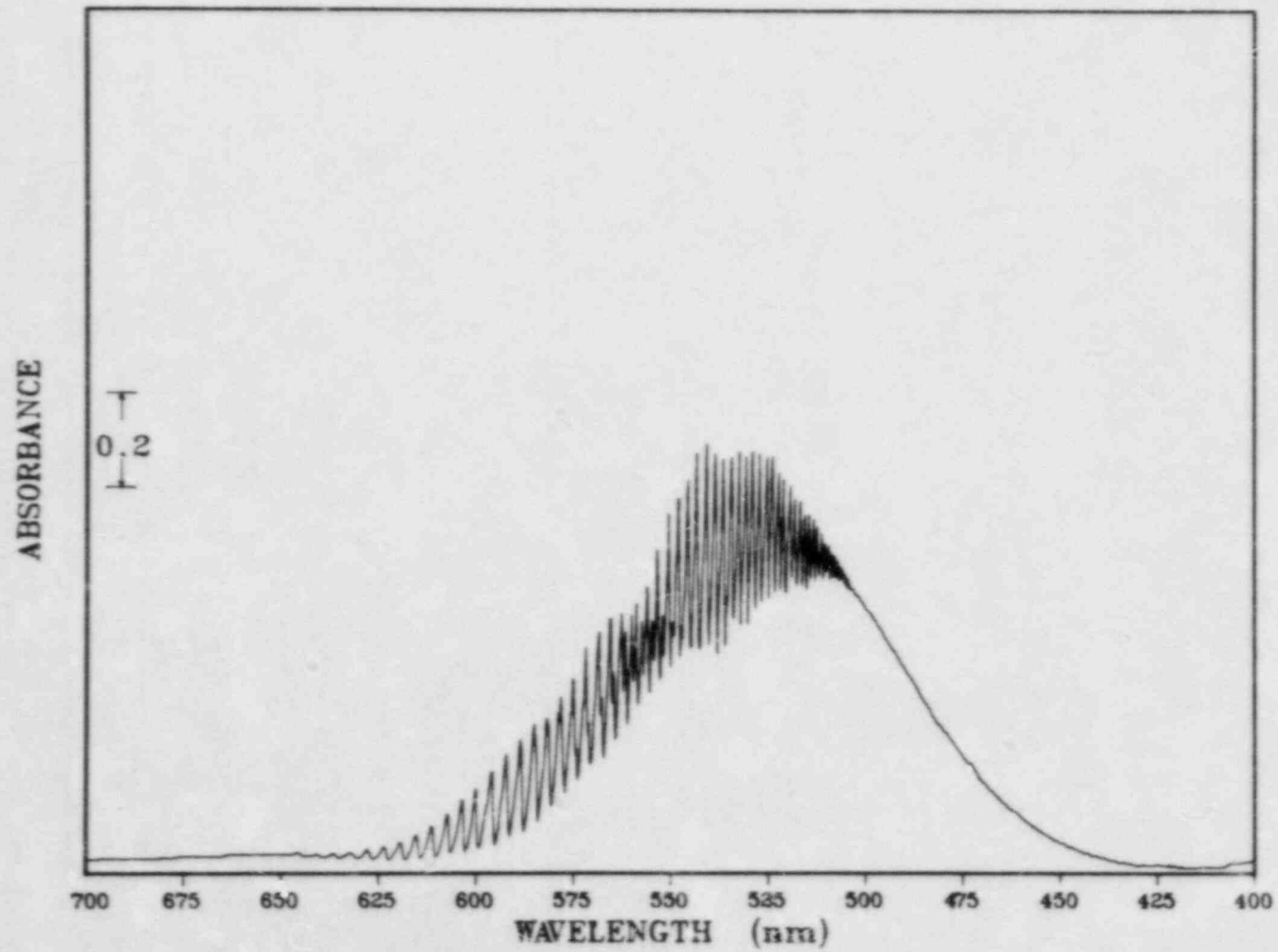
Fig. B.1. Visible absorption spectrum for I_2 vapor at room temperature.
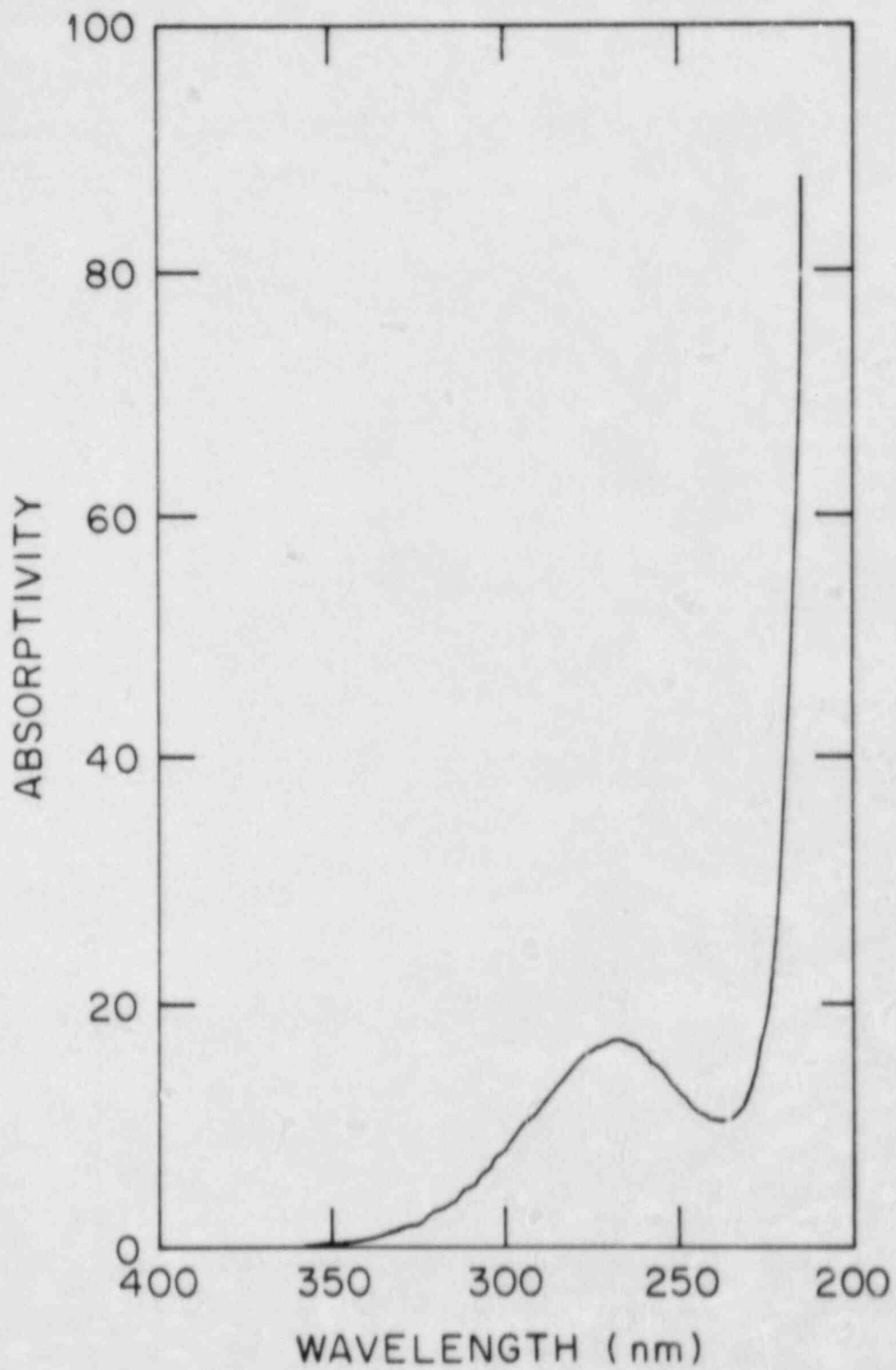
ORNL DWG 82-7917R

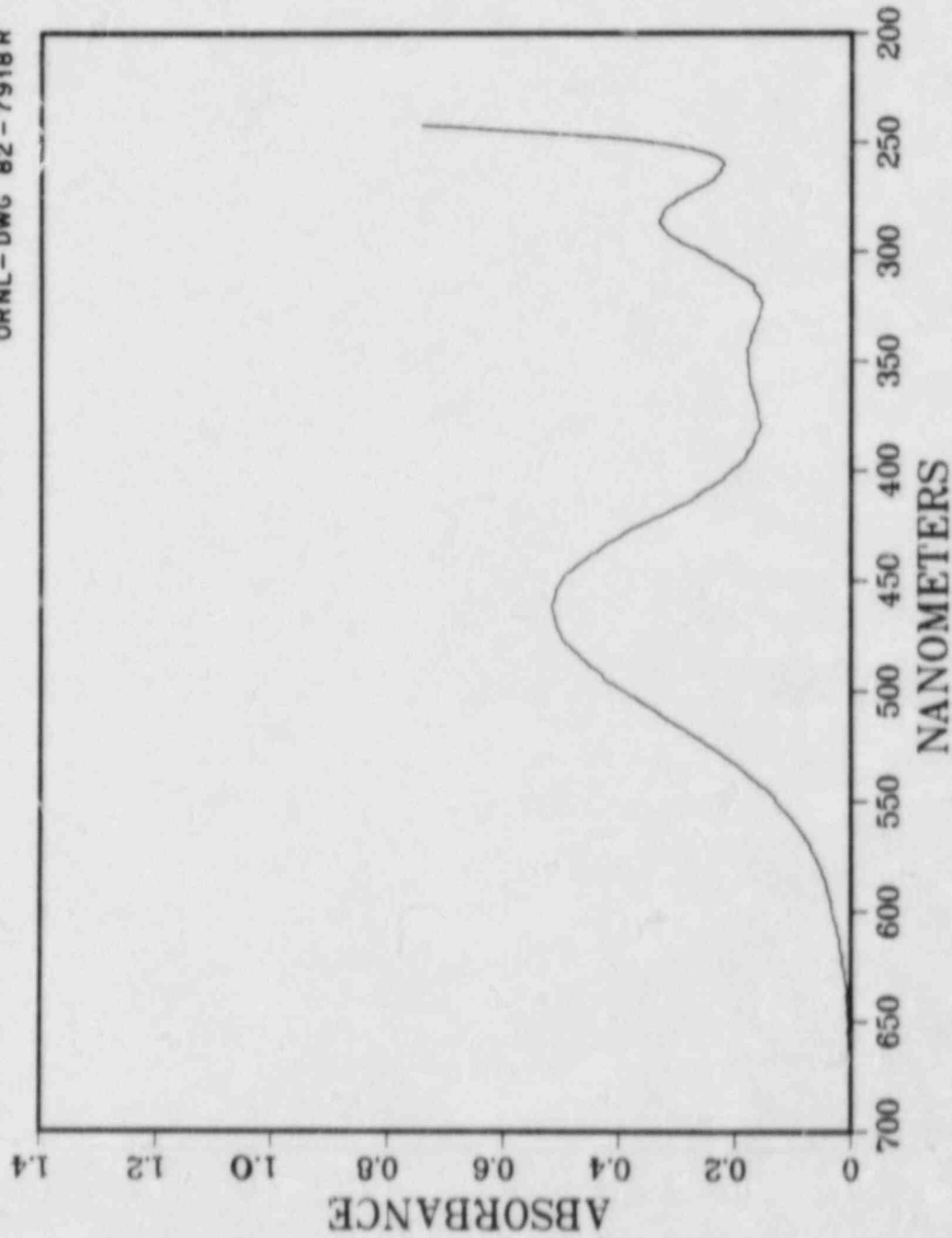Fig. B.2. Ultraviolet absorption spectrum of weak iodine band at 270 nm.

Fig. B.3. Absorption spectrum of I_2 in water at ~20°C. The band at 460 nm is due to I_2, while the other two bands are due to I_3^- that is formed by association of the I^- hydrolysis product with the parent I_2.
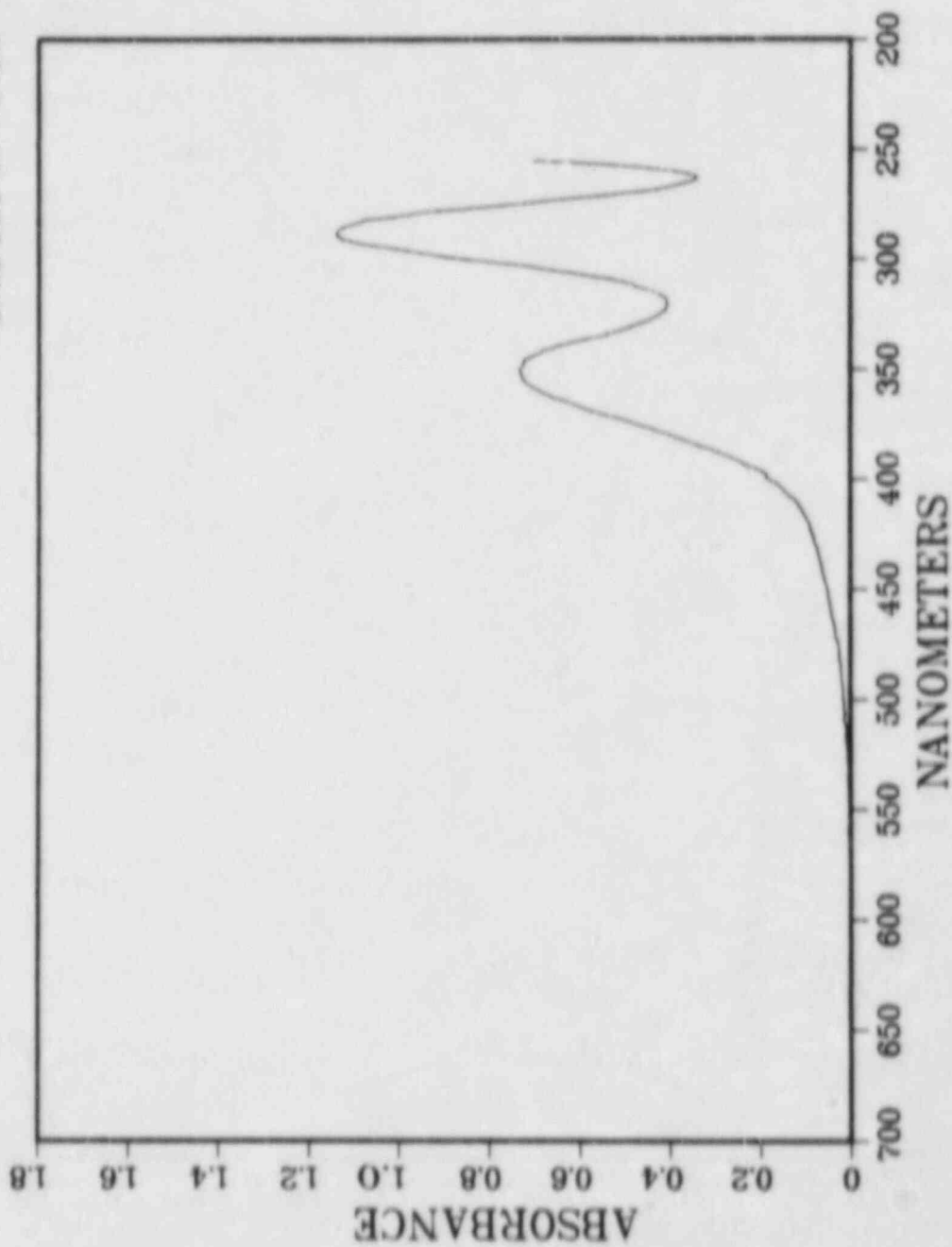
Fig. B.4. I_3^- absorption spectrum in aqueous solution at 20°C. The sharp ultraviolet cutoff is due to I^-, which was added in excess to convert all the I_2 reagent to I_3^-.
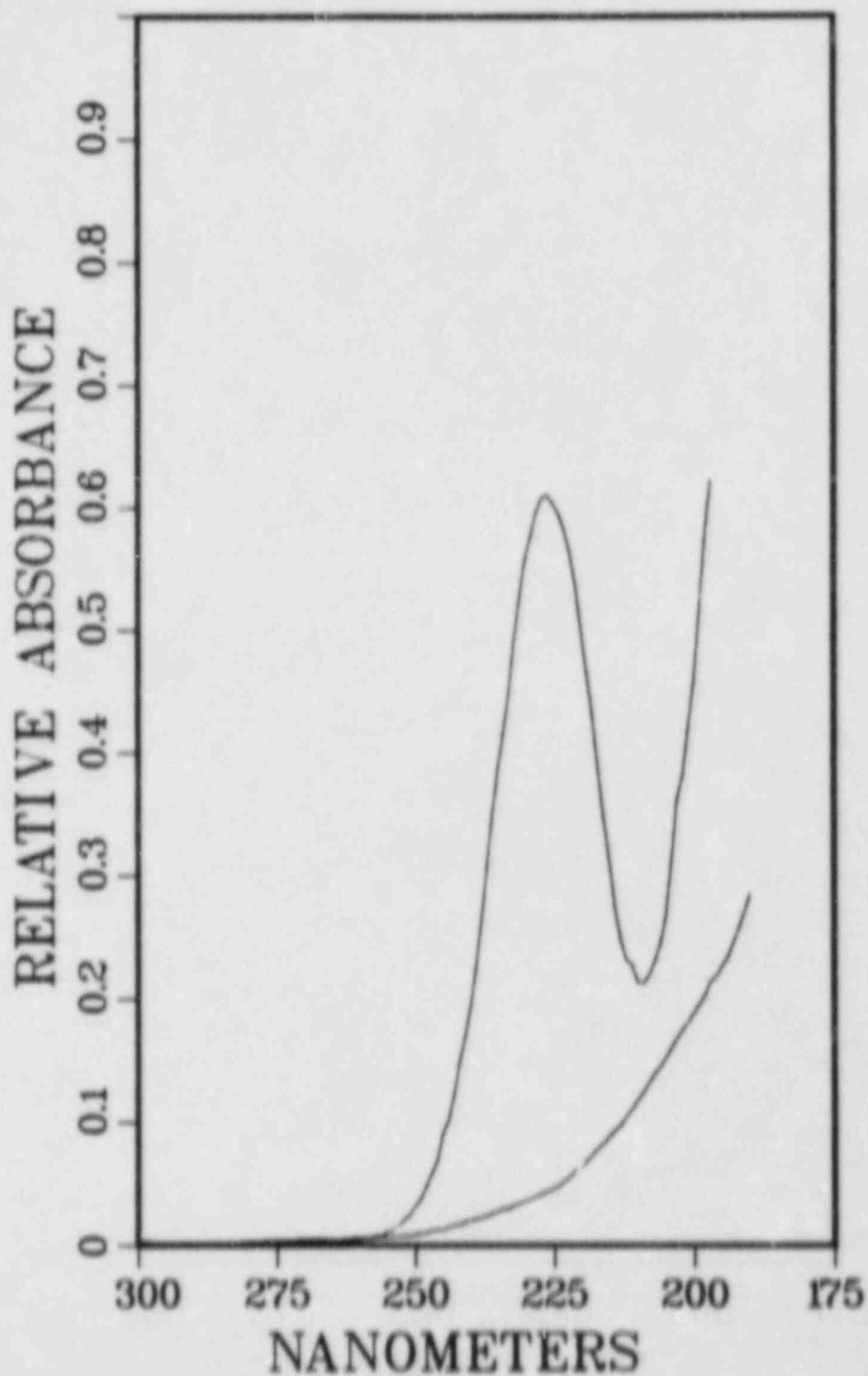
ORNL DWG 82-792OR

Fig. B.5. Relative absorption spectra of I⁻ and IO₃⁻ in aqueous solution at 20°C. Molar absorptivity of I⁻ peak at 225 nm is 13,500 $\underline{M}^{-1}$ cm^{-1}.
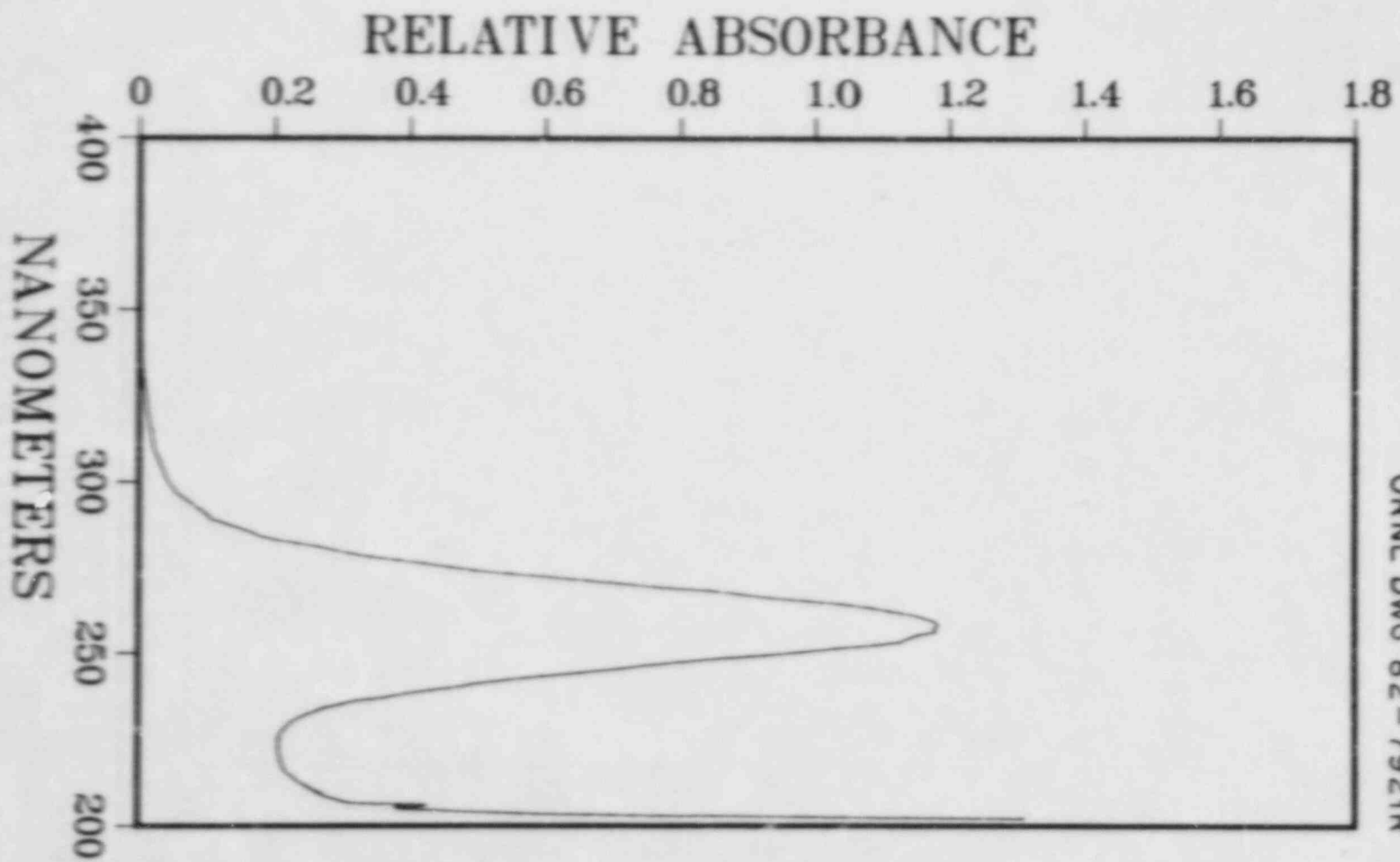
ORNL DWG 82-7921R

Fig. B.6. Absorption spectra of CH_3I vapor at $20°C$.

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16. ABSTRACT (200 words or less)

The chemical behavior of iodine, I_2, in (pH = 6 to 10) aqueous solutions containing 2500 ppm boron as H_3BO_3 (0.231 $\underline{M}$) was studied at temperatures up to 150°C. Absorption spectrophotometry was used to identify and monitor the iodine species present. Three objectives were considered: (1) species identification, with special attention given to "HOI"; (2) the kinetics of reaction between iodine and water to produce iodide and iodate ions; and (3) partition coefficients between liquid and vapor phases for individual iodine species.

Kinetic rate constants for the disproportionation of the "HOI" intermediate were measured. A typical activation energy for this reaction was found to be 28.4 kJ/mol (6.8 kcal/mol). No absorption bands can be assigned to the "HOI" intermediate even though it has been shown, in some cases, to be present at concentrations of $>1 \times 10^{-3}$ $\underline{M}$. A very low molar absorptivity (<10 $\underline{M}^{-1}$ cm^{-1}) is probably responsible for its undetectability. A partition coefficient of $>1 \times 10^4$ has been estimated for "HOI".

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