Disproportionation Kinetics of Hypoiodous Acid As Catalyzed and Suppressed by Acetic Acid−Acetate Buffer

Edward T. Urbansky, Brian T. Cooper,[†] and Dale W. Margerum*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

Received June 21, 1996[⊗]

The kinetics of the disproportionation of hypoiodous acid to give iodine and iodate ion ($5HOI \rightleftharpoons 2I_2 + IO_3^- + H^+ + 2H_2O$) are investigated in aqueous acetic acid-sodium acetate buffer. The rate of iodine formation is followed photometrically at $-\log [H^+] = 3.50$, 4.00, 4.50, and 5.00, $\mu = 0.50$ M (NaClO$_4$), and 25.0 °C. Both catalytic and inhibitory buffer effects are observed. The first process is proposed to be a disproportionation of iodine(I) to give HOIO and I$^-$; the iodide then reacts with HOI to give I$_2$. The reactive species (acetato-*O*)iodine(I), CH_3CO_2I, is postulated to increase the rate by assisting in the formation of I$_2$O, a steady-state species that hydrolyzes to give HOIO and I$_2$. Inhibition is postulated to result from the formation of the stable ion bis(acetato-*O*)iodate-(I), $(CH_3CO_2)_2I^-$, as buffer concentration is increased. This species is observed spectrophotometrically with a UV absorption shoulder ($\lambda = 266$ nm; $\epsilon = 530$ M^{-1} cm^{-1}). The second process is proposed to be a disproportionation of HOIO to give IO$_3^-$ and I$_2$. Above 1 M total buffer, the reaction becomes reversible with less than 90% I$_2$ formation. Rate and equilibrium constants are resolved and reported for the proposed mechanism.

Introduction

This investigation into the rate and mechanism of the disproportionation of hypoiodous acid continues our work on the aqueous chemistry of the halogens, their oxyacids, and their oxyanions. A sizable portion of the research to date on the fundamental chemistry of iodine has been supported by nuclear power regulatory agencies; the driving force behind these studies has been the threat to public safety posed by radioactive iodine species in the event of a containment breach.[1−14] The importance is underscored by the incident that took place in 1979

when reactor 2 at Three Mile Island suffered core damage severe enough to release radioactive fission products within the containment building and several auxiliary buildings.[3] Knowledge of aqueous iodine chemistry is essential to prevent the loss of radioactive species in the event of an accident, particularly HOI and I$_2$ which are volatile.[15] Furthermore, iodine chemistry is important in studies of oscillatory chemical systems,[15−20] which routinely contain iodine in several oxidation states. The kinetic behavior of chemical oscillators is highly complex; therefore, kinetic information about specific reactions can be extremely valuable in constructing meaningful models of such systems.

Hypoiodous acid disproportionates in aqueous solution according to eq 1.[21] There is widespread agreement that the

$$5HOI \overset{K_D}{\rightleftharpoons} 2I_2(aq) + IO_3^- + H^+ + 2H_2O \qquad (1)$$
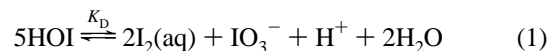
reaction rate is second-order in iodine(I) concentration;[1−13,20,22−26] however, there is considerable disparity among the values of the rate constants reported. Table 1 shows reported rate constants that vary from 5.6 to 250 M^{-1} s^{-1} for this reaction. Such discordance suggests a more complex behavior and offers a compelling reason to further study this system.

* Author to whom correspondence should be directed.

† Present address: Department of Chemistry, Iowa State University of Science and Technology, Ames, IA 50010.

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) Paquette, J.; Sunder, S.; Torgerson, D. F.; Wren, C. J.; Wren D. J. *Water Chemistry of Nuclear Reactor Systems 3*; British Nuclear Energy Society: London, 1983; Vol. 1, pp 71−79.

(2) Bawden, R. J. *Water Chemistry of Nuclear Reactor Systems 3*; British Nuclear Energy Society: London, 1983; Vol. 1, pp 81−88.

(3) Paquette, J.; Wren, D. J.; Ford, B. L. In *The Three Mile Island Accident: Diagnosis and Prognosis*; Toth, L. M., Malinauskas, A. P., Eidam, G. R., Burton, H. M., Eds.; ACS Symposium Series 293; American Chemical Society: Washington, DC, 1986; Chapter 10, pp 193−210.

(4) Paquette, J. *At. Energy Can. Ltd., [Rep.] AECL-9923, Proc. CSNI Workshop Iodine Chem. React. Saf., 2nd* **1988,** 216−234.

(5) Wren, J. C.; Paquette, J.; Sunder, S.; Ford, B. L. *At. Energy Res. Establ., [Rep.] AERE-R 11974, Proc. Spec. Workshop Iodine Chem. React. Saf.* **1986,** 29−46.

(6) Paquette, J.; Ford, B. L. *Can. J. Chem.* **1985,** *63,* 2444−2448.

(7) Wren, J. C.; Paquette, J.; Sunder, S.; Ford, B. L. *Can. J. Chem.* **1986,** *64,* 2284−2296.

(8) Buxton, G. V.; Kilner, C.; Sellers, R. M. *Proc. Tihany Symp. Radiat. Chem., 6th* **1987,** No. 1, 155−159.

(9) Buxton, G. V.; Sellers, R. M. *J. Chem. Soc., Faraday Trans. 1* **1985,** *81,* 449−471.

(10) Palmer, D. A.; Lietzke, M. H. *Radiochim. Acta* **1982,** *31,* 37−44.

(11) Rahn, R. O. *Anal. Chim. Acta* **1991,** *248,* 595−602.

(12) Toth, L. M.; Pannell, K. D.; Kirkland, O. L. *The Chemical Behavior of Iodine in Aqueous Solutions up to 150 °C: I. An Experimental Study of Nonredox Conditions*; NUREG/CR-3514, Vol. 1; Report ORNL/TM-8664/V1; Oak Ridge National Laboratory: Oak Ridge, TN, April 1984.

(13) Shiraishi, H.; Okuda, H.; Morinaga, Y.; Ishigure, K. *Nippon Genshiryoku Kenkyusho, [Rep.] JAERI-M 92-012, Proc. CSNI Workshop Iodine Chem. React. Saf., 3rd.* **1991−1992,** 152−161.

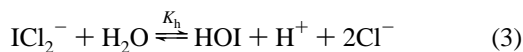(14) Harrell, J. R.; Lutz, J. B.; Kelly, J. L. *J. Radioanal. Nucl. Chem.* **1988,** *127,* 13−20.

(15) Simoyi, R. H.; Manyonda, M.; Masere, J.; Mtambo, M.; Ncube, I.; Patel, H.; Epstein, I. R.; Kustin, K. *J. Phys. Chem.* **1991,** *95,* 770−774.

(16) Citri, O.; Epstein, I. R. *J. Phys. Chem.* **1988,** *92,* 1865−1871.

(17) Faria, R. B.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1992,** *114,* 7164−7171.

(18) Luo, Y.; Epstein, I. R. *J. Phys. Chem.* **1989,** *93,* 1398−1401.

(19) Edblom, E. C.; Györgyi, L.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987,** *109,* 4876−4880.

(20) Furrow, S. *J. Phys. Chem.* **1987,** *91,* 2129−2135.

(21) The HOI disproportionation equilibrium constant, K_D, was calculated indirectly from reported equilibrium constants. Reference 27: I$_2$(aq) + H$_2$O $\rightleftharpoons$ HOI + I$^-$ + H$^+$ ($K = 4.3 \times 10^{-13}$, 20 °C). Reference 28: 3I$_2$(aq) + 3 H$_2$O $\rightleftharpoons$ 5 I$^-$ + IO$_3^-$ + 6 H$^+$ ($K = 1.25 \times 10^{-47}$, 25 °C). No temperature correction was made.

(22) Wang, Y. L.; Nagy, J. C.; Margerum, D. W. *J. Am. Chem. Soc.* **1989,** *111,* 7838−7844.

(23) Thomas, T. R.; Pence, D. T.; Hasty, R. A. *J. Inorg. Nucl. Chem.* **1980,** *42,* 183−186.

(24) Li, C. H.; White, C. F. *J. Am. Chem. Soc.* **1943,** *65,* 335−339.

(25) Haimovich, O.; Treinin, A. *J. Phys. Chem.* **1967,** *71,* 1941−1943.

(26) Josien, M. L. *Bull. Soc. Chim. Fr.* **1948,** *15,* 301−304.

Table 1. Rate Expressions and Rate Constants for Different Pathways of the Disproportionation of Aqueous Iodine(I) at 25 °C as Reported in the Literature

rate expression	rate constants	medium	ref
$k[HOI]^2$	5.6 ± 1.2 M^{-1} s^{-1}	unspecified	9
	7.2 ± 3.3	borate	9
	10		26
	43	borate, pH 8	11
	75		20
	250	borate, pH 10	11
	250 ± 160	borate/phosphate, pH 9	23
$k[HOI]_T^2$	30 M^{-1} s^{-1}	phosphate, pH 10[a]	5
$k[IO^-]^2$	2.9 M^{-1} s^{-1}	0.9 M NaOH; 0.02−0.06 M I$^-$	24
	0.07	0.3−2.0 M NaOH	5
	0.04	4 M NaOH	25
	<0.14	≥0.1 M OH$^-$	9
$k[HOI][IO^-]$	40 M^{-1} s^{-1}	0.3−2.0 M NaOH	5
	120 ± 10	carbonate, pH 10	34
$k[OH^-][HOI]^2$	10^4 M^{-2} s^{-1}	borate[c]	9[b]
$k[B(OH)_3]_T[HOI]^2$	2200 M^{-2} s^{-1}	borate[c]	9
$k[PO_4]_T[HOI]_T^2$	236 M^{-2} s^{-1}	phosphate, pH 10[a,d]	5
$(k - a[H_2PO_4^-])[HOI]_T^2$	$k = 80$ M^{-1} s^{-1} $a = 32$ M^{-2} s^{-1}	phosphate, pH 6−8[a,e]	5

[a] $[HOI]_T = [HOI] + [IO^-] + [I^I(PO_4)_T \text{ complexes}]$. [b] As Buxton and Sellers point out, the expression $k_{OH}[OH^-][HOI]^2$ is kinetically indistinguishable from the expression $k_{ab}[HOI][IO^-]$. If we convert their k_{OH} to k_{ab} using $K_w = 10^{-13.60}$ and $K_a^{HOI} = 10^{-10.64}$,[24] we obtain $k_{ab} = 11$ M^{-1} s^{-1} (which differs from that of Wren et al.[5] by a factor of only 4—not so large as to be outside the uncertainty introduced by K_a^{HOI}). However, if we use $K_a^{HOI} = 10^{-10.0}$,[6] we obtain $k_{ab} = 2.5$ M^{-1} s^{-1} instead. Regardless of the value we choose for K_a^{HOI}, the value of k_{ab} reported by Thomas, Pence, and Hasty[23] varies by a factor of at least 10. This discrepancy is best attributed to catalysis by the buffer that was not taken into account. [c] $[B(OH)_3]_T = [B(OH)_3] + [B(OH)_4^-]$. [d] $[PO_4]_T = [H_2PO_4^-] + [HPO_4^{2-}]$. [e] Note that $H_2PO_4^-$ acts as an inhibitor rather than as a catalyst in this pH range.

Because it is so unstable to disproportionation ($K_D = 8.5 \times 10^{14}$ M^{-1}),[27−29] HOI must be generated in situ from some other reaction. There are many ways to generate HOI in solution, each with its respective advantages and disadvantages.[6−8,10,20,29−34] We have chosen to work with dichloroiodate(I), ICl$_2^-$(aq), to prepare HOI. ICl$_2^-$(aq) reacts rapidly and stoichiometrically give HOI upon adequate dilution and adjustment of acidity:[22]

$$ICl_2^- \underset{}{\overset{K_d}{\rightleftharpoons}} ICl(aq) + Cl^- \qquad (2)$$

$$ICl_2^- + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} HOI + H^+ + 2Cl^- \qquad (3)$$

The dissociation constant K_d (eq 2) is 0.013 M, and the hydrolysis constant K_h (eq 3) is 1.06×10^{-6} M^3; the hydrolysis of ICl(aq) is extremely rapid with a rate constant of 2.6×10^6 s^{-1}.[22] An aliquot of dichloroiodate(I) is quantitatively diluted into acetic acid−acetate buffer, and the production of iodine is followed photometrically. This is similar to the method of Wren et al.;[7] however, it avoids potential oxidation byproducts that can result when ICl(g) contacts air.[35] In addition, it avoids potential contamination from Hg^{2+} or Ag$^+$ cations that could

remain behind from other methods.[20,30−32] Moreover, the reagent is stored and delivered in a very convenient fashion.

The uncatalyzed reaction is presumed to proceed through three possible pathways: HOI + HOI; HOI + IO$^-$; IO$^-$ + IO$^-$. Paquette et al.[5] found the reaction to be catalyzed by borate and phosphate buffer but not by carbonate or sulfate buffer. Buxton and Sellers[9] observed catalysis of the reaction by borate buffer, and they pointed out that others[23] failed to account for buffer catalyses. Buxton and Sellers[9] suggested that hydrogen carbonate accelerates the reaction. Buffer catalysis has also been reported for the Dushman reaction[36] (comproportionation of I$^-$ and IO$_3^-$ to give I$_2$) where carboxylates and phosphates increase the rate.[37−38] If we apply arguments of microscopic reversibility to Barton and Wright's[37] mechanism, similar catalysis should be expected here as well.

Paquette et al. confirmed by Raman spectroscopy that the disproportionation of IO$^-$ (in strong base) proceeds through IO$_2^-$, which then undergoes further reaction.[5,7] One of the points we must address is whether the overall reaction proceeds rapidly, with a stoichiometry of 5 HOI lost for every 2 I$_2$ formed, or whether iodine(III) may form as an intermediate in appreciable concentration. If iodine(III) does accumulate to appreciable levels, then we should expect to see a loss of 3 HOI for each I$_2$ formed.

Experimental Section

Acetic Acid pK_a Determination. Solutions of 0.01 M HOAc and 0.01 M NaOH were prepared and assayed by standard methods; precautions were taken to exclude CO$_2$. Potentiometric measurements were made on an Orion pH/pX meter (Model 720A) equipped with a Corning combination electrode (Model 476560) and standardized with NIST-traceable buffers. The electrode was calibrated to give $-\log [H^+]$ (rather than $-\log a_{H^+}$) on the basis of HClO$_4$/NaOH titrations at 25.0 $\pm$ 0.1 °C ($\mu = 0.10$ and 0.50 M (NaClO$_4$)). Three titrations were performed at each ionic strength with a microburet.

Acetic Acid−Acetate Buffers. Buffer solutions were prepared from standard NaOH and HOAc solutions. Buffers were prepared ($\mu = 0.50$ M (NaClO$_4$)) to give postmixing p[H$^+$] values of 3.50, 4.00, 4.50, and 5.00 over the range of total acetate 0.01 M $\leq$ [OAc]$_T$ $\leq$ 0.8 M, where total acetate is expressible as [OAc]$_T$ = [CH$_3$CO$_2^-$] + [CH$_3$CO$_2$H].

ICl$_2^-$(aq) Preparation. A stock solution of 0.1 M sodium dichloroiodate(I) was prepared from NaIO$_3$, HCl, and NaCl.[22] The net process is given by eq 4. The solution was standardized spectrophotometrically

$$IO_3^- + 2I^- + 6H^+ + 6Cl^- \rightarrow 3ICl_2^- + 3H_2O \qquad (4)$$
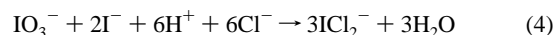
($\lambda = 343$ nm, $\epsilon = 275$ M^{-1} cm^{-1}).[22] It remains stable in 1.0 M Cl$^-$ and 0.20 M H$^+$. Postmixing concentrations of total iodine(I), [HOI]$_T^{init}$, were 0.10−0.20 mM after quantitative 25−1000-fold dilution into buffer.

I$_2$ Photometry and Kinetics. Iodine formation, (d[I$_2$]/dt)$_{init}$, was monitored on Perkin-Elmer Lambda 9 and 320 spectrophotometers ($\lambda = 460$ nm, $\epsilon = 746$ M^{-1} cm^{-1})[39] in 10.00 cm cells thermostated at 25.0 $\pm$ 0.1 °C with [HOI]$_T^{init} = 0.10−0.20$ mM . We verified that the spectral properties of I$_2$ are unaffected by the buffer. Because other species (e.g., HOI) have such small molar absorptivities, the only species that can be monitored is I$_2$. Concentrations required for other species to have measurable absorbances make the reaction too fast to follow.

Spectrophotometric Evidence for I(OAc)$_2^-$. Strong kinetic evidence for iodine(I)−acetate complexes (as described below) led us to seek spectrophotometric evidence. Aliquots of 0.100 mL of 0.0972 M ICl$_2^-$ were added to 100 mL of acetic acid−acetate solutions and the spectra were acquired. The concentration of total buffer was varied

(27) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355−1361.
(28) Sammet, V. *Z. Phys. Chem.* **1905**, *53*, 641−691.
(29) Chia, Y. Ph.D. Thesis, University of California at Berkeley, 1958.
(30) Palmer, D. A.; Van Eldik, R. *Inorg. Chem.* **1986**, *25*, 928−931.
(31) Nosticzius, Z.; Nosticzius, E.; Schelly, Z. A. *J. Am. Chem. Soc.* **1982**, *104*, 6194−6199.
(32) Seal, K. C. *J. Indian Chem. Soc.* **1961**, *36*, 811−816.
(33) Allen, T. L.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2957−2960.
(34) Bell, R. P.; Gelles, E. *J. Chem. Soc.* **1951**, 2734−2740.
(35) *Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 11th ed.; Budavari, S., Ed.; Merck: Rahway, NJ, 1989; see entry for iodine monochloride, p 794.

(36) Dushman, S. *J. Phys. Chem.* **1904**, *8*, 453−482.
(37) Barton, A. F. M.; Wright, G. A. *J. Chem. Soc. A* **1968**, 2096−2103.
(38) Schildcrout, S. M.; Fortunato, F. A. *J. Phys. Chem.* **1975**, *79*, 31−34.
(39) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842−1843.

from 0.20 to 4.0 M at [HOAc]:[AcO$^-$] ratios of 1:3 and 3:1. Ionic strength was adjusted to 0.50 M with NaClO$_4$.

Results and Discussion

Acetic Acid Dissociation Constants. Titrimetric data were analyzed by the Gran–Hofstee method.[40] Data from the domain 1.25 mL $\leq V_{NaOH} \leq$ 1.88 mL (before the equivalence point) were used in the linear regression. The pK_a is 4.26 ± 0.03 (μ = 0.10 M) and 4.41 ± 0.03 (μ = 0.50 M).

Experimental Rate Expressions and Observed Rate Constants. Our data are consistent with other investigators' findings that the reaction is second-order in total iodine(I) concentration. Using the initial rates of iodine formation, (d[I$_2$]/dt)$_{init}$, obtained from the traces, we have obtained values for k_{obsd} from the slopes of the integrated rate plots as described below. Whenever possible, we used photometric trace data from the region where less than 15% of the reaction had taken place. Given the stoichiometry of eq 1 and [I$_2$]$_0$ = 0, hypoiodous acid concentration should be expressible as

$$[HOI] = [HOI]_T^{init} - {}^5/_2[I_2] \qquad (5)$$

and it follows that the rate of iodine formation is then given by

$$d[I_2]/dt = k_{obsd}([HOI]_T^{init} - {}^5/_2[I_2])^2 \qquad (6)$$

which leads to the following integrated rate expression:

$$\frac{1}{[HOI]_T^{init} - {}^5/_2[I_2]} - \frac{1}{[HOI]_T^{init}} = {}^5/_2 k_{obsd} t \qquad (7)$$

Since we expect the reaction to proceed through iodine(III), we might question whether the alternate stoichiometry of eq 8 is a

$$3HOI \rightarrow HOIO + I_2 + H_2O \qquad (8)$$
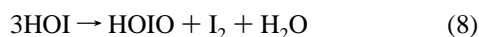
possibility. Kinetic behavior resulting from eq 8 leads to the integrated rate expression (9). Figure 1b shows a plot of eqs 7

$$\frac{1}{[HOI]_T^{init} - 3[I_2]} - \frac{1}{[HOI]_T^{init}} = 3k_{obsd} t \qquad (9)$$

and 9 for the trace in Figure 1a. The plot for the $-5\Delta[HOI]_T/2\Delta[I_2]$ stoichiometry is linear, while that for the $-3\Delta[HOI]_T/\Delta[I_2]$ stoichiometry shows marked upward concavity, thereby indicating that the stoichiometry of eq 1 is appropriate for the kinetics. However, Figure 2 shows the plots for a different [OAc]$_T$; the plot of eq 7 is concave down, while the plot of eq 9 is linear. This implies that the reaction is not following the $-5\Delta[HOI]_T/2\Delta[I_2]$ stoichiometry of eq 1 but rather the alternate stoichiometry of eq 8. A period is observed during which HOIO must accumulate to an appreciable level before further reaction can take place. To further complicate matters, the stoichiometry is not clear-cut for many values of [OAc]$_T$.

Figure 3 shows a case where the $-5\Delta[HOI]_T/2\Delta[I_2]$ stoichiometry applies while the $-3\Delta[HOI]_T/\Delta[I_2]$ stoichiometry fails at longer time just as expected. The inset shows that, even near time zero, a mixture of stoichiometries is observed; neither integrated rate plot is linear. The discontinuity in the integrated rate for the $-3\Delta[HOI]_T/\Delta[I_2]$ stoichiometry occurs because HOIO generates more I$_2$ than predicted for this stoichiometry. Consequently, the plot shows rapid increase with time followed
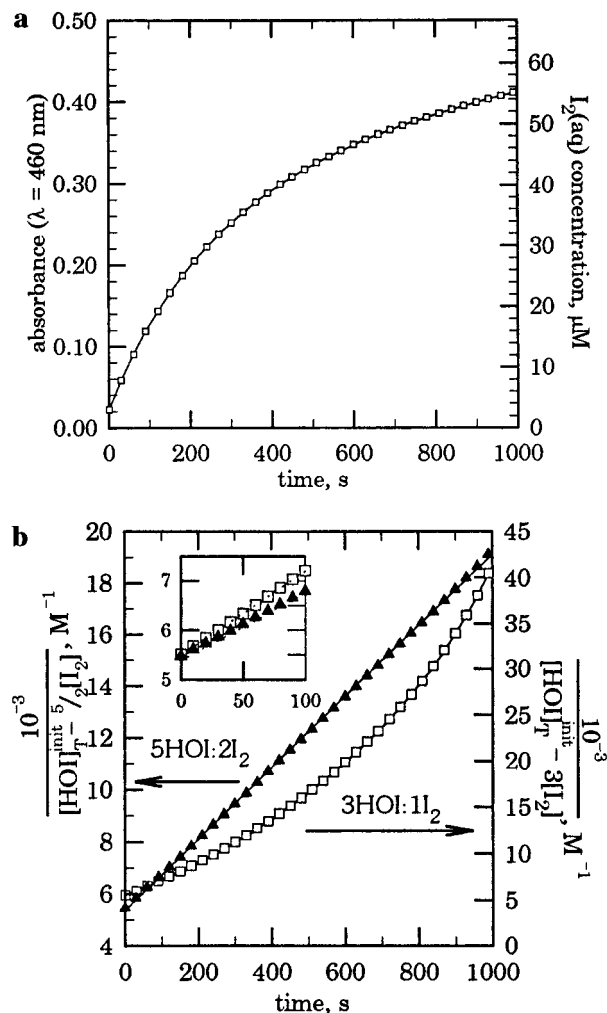
(40) (a) Gran, G. *Analyst* **1952**, *77*, 661–671. (b) Gran, G. *Anal. Chim. Acta* **1988**, *206*, 111–123. (c) Hofstee, B. H. J. *Science* **1960**, *131*, 39. (d) Harris, D. C. *Quantitative Chemical Analysis*, 3rd ed.; Freeman: New York, 1991; pp 250–251.


Figure 1. (a) Aqueous I$_2$ formation as followed by absorption photometry; λ_{max} = 460 nm, ϵ = 746 M^{-1} cm^{-1}, l = 10.00 cm. Conditions: [HOI]$_T^{init}$ = 0.19 mM, [OAc]$_T$ = 0.0112 M, p[H$^+$] = 5.00 ± 0.05; μ = 0.50 ± 0.02 M (NaClO$_4$); 25.0 ± 0.1 °C. (b) Integrated rate plots (eqs 7 and 9) for two possible stoichiometries shown for the photometric data in (a). In this case, the kinetics follow the stoichiometry of eq 1 and not eq 8.

by a plunge into negative values as 3[I$_2$] exceeds [HOI]$_T^{init}$. The $-5\Delta[HOI]_T/2\Delta[I_2]$ stoichiometry fits better, but this plot has noticeable curvature.

For some of the slower reactions, mixed stoichiometry is observed within 20 s. We should point out that the difference in k_{obsd} values resulting from the two alternative stoichiometries is no greater than 25% (in the worst case) and is generally less than 15%. We note that less than $^1/_{15}$th of the I$_2$ production can be carried by the disproportionation of HOIO since one-third of the initial iodine(I) must be converted to I$_2$ by eq 8; $\Delta[I_2]_{HOIO} = [I_2]_\infty - \Delta[I_2]_{3:1} = (^2/_5 - ^1/_3)[HOI]_T^{init} = ^1/_{15} [HOI]_T^{init}$.

The time regions of the two stoichiometries are indistinct for much of the reaction; that is, mixed stoichiometry is observed in the integrated rate plots. We therefore choose to average the rate constants for the sake of uniformity, realizing that this introduces some uncertainty. We must point out that eq 1 is an accurate statement of the net reaction; nonetheless, it is not possible to kinetically isolate the consecutive reactions that take place. Accordingly, observing a mixed stoichiometry from an A → B → C system cannot be avoided.

Qualitative Buffer Effects. The effect of total acetate on k_{obsd} is shown in Figure 4; both catalysis and inhibition occur.
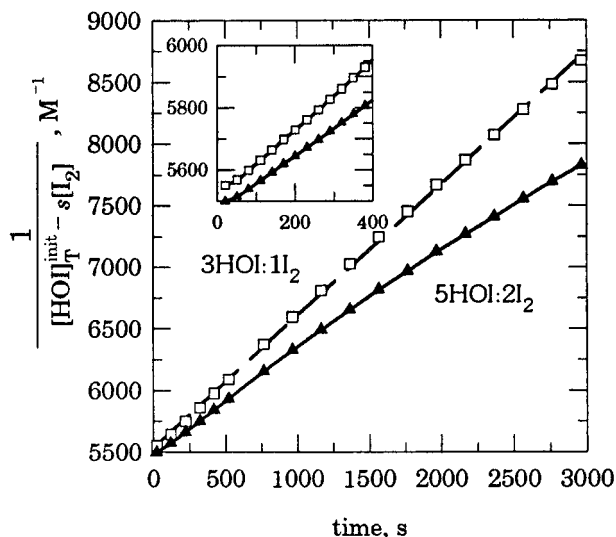
Figure 2. Integrated rate plots (eqs 7 and 9) for two possible stoichiometries shown for the formation of I_2(aq). Conditions: $[HOI]_T^{init} = 0.19$ mM, $[OAc]_T = 0.00745$ M, $p[H^+] = 4.00 \pm 0.05$; $\mu = 0.50 \pm 0.02$ M (NaClO$_4$); 25.0 ± 0.1 °C. In this case, the kinetics follow the stoichiometry of eq 8 and not eq 1, indicating a buildup of iodine(III). Inset: Early in the reaction, the slopes of the two plots vary by less than 4%.
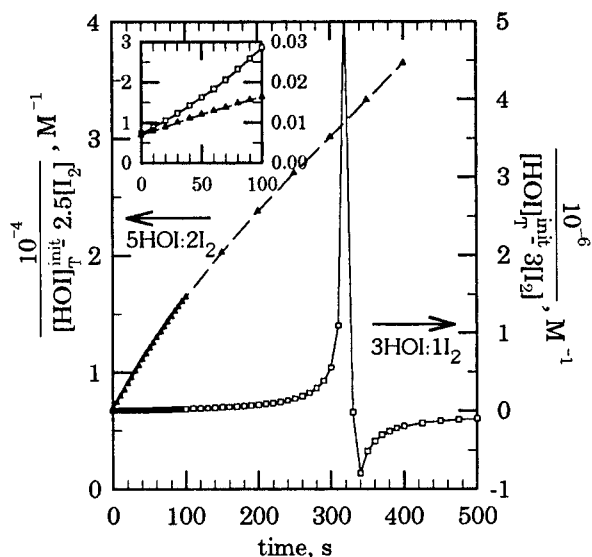

Figure 3. Integrated rate plots (eqs 7 and 9) for two possible stoichiometries shown for the formation of I_2(aq). Conditions: $[HOI]_T^{init} = 0.19$ mM, $[OAc]_T = 0.279$ M, $p[H^+] = 4.00 \pm 0.05$; $\mu = 0.50 \pm 0.02$ M (NaClO$_4$); 25.0 ± 0.1 °C. Reaction was followed until I_2 yield was 86% of the theoretical yield from eq 1. The discontinuity for the 3:1 plot occurred because the I_2 yield exceeded the 3:1 stoichiometry. Curvature in both plots, even early in the reaction (see inset), indicates a mixture of stoichiometries (eqs 1 and 8) influencing the kinetics.

Although such effects have never been reported for acetic acid−acetate, other buffers have been reported to catalyze HOI disproportionation (borate[9] and phosphate/borate[9,23]). However, the magnitude of the catalytic effect and the strong inhibition observed with increasing $[OAc]_T$ are unusual. Such an inhibition has not heretofore been reported. Wren[5] did report suppression by $H_2PO_4^-$, but it was not linked with acceleration.

Elucidation of the Mechanism. In solutions buffered with acetic acid−sodium acetate, we postulate that (acetato-*O*)iodine(I), also called acetyl hypoiodite or iodine(I) acetate, is responsible for this observed catalysis. CH_3CO_2I (IOAc) is considered to be an excellent agent for electrophilic iodination
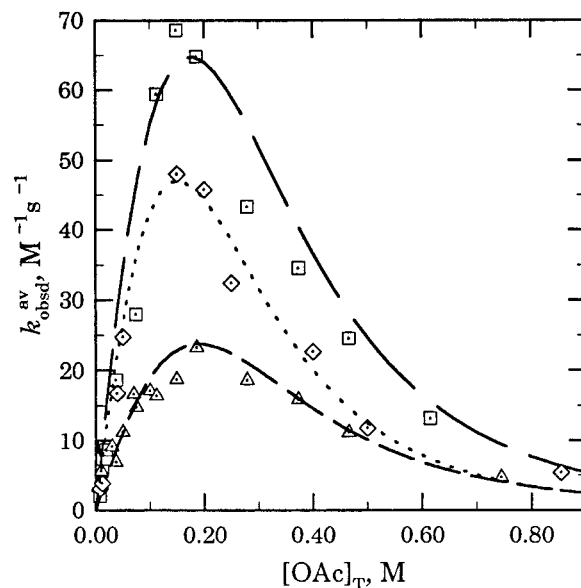

Figure 4. Fits of the average observed rate constant as a function of buffer concentration shown for each $p[H^+]$: 4.00 (short dashes), 4.50 (dots), 5.00 (long dashes). Calculated curves are based on the values of the constants reported in the text. Conditions: $[HOI]_T^{init} = 0.10-0.20$ mM; $\mu = 0.50 \pm 0.02$ M (NaClO$_4$); 25.0 ± 0.1 °C.
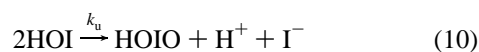
of organic substrates,[41] as well as an intermediate in other reactions,[42] even though it has not been isolated. IOAc has not been proposed previously in aqueous solution or in the reactions of oxyhalogen species. The mode of catalysis is likely provided by the ability of IOAc to transfer an iodine(I) cation to IO^- to form I_2O. The diiodine oxide thus formed (already known to be a highly reactive intermediate in aprotic media)[43] is expected to hydrolyze to HOIO, I^-, and H^+. In strong base, iodite has been confirmed as an intermediate in the overall reaction by Raman spectroscopy;[5,7] consequently, HOIO (along with H^+ and I^-) is the likely product of the initial catalytic steps. This further vindicates our acceptance of the important contribution made by the $-3\Delta[HOI]_T/\Delta[I_2]$ stoichiometry. Because of its speed, we have been unable to isolate and study the subsequent disproportionation reaction of HOIO.

To account for the suppression that occurs at higher $[OAc]_T$, we conclude that a second acetate-containing species is responsible for reducing the rate of iodine(I) disproportionation. Iodine commonly expands its octet; IX_2^- (X = Cl, Br, I), I_2py, and
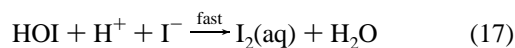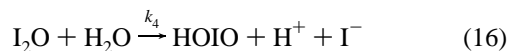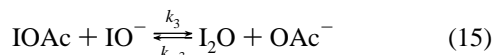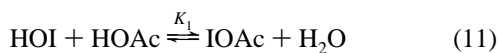
(41) (a) Ogata, Y.; Nakajima, K. *Tetrahedron* **1964**, *20*, 2751−2754. (b) Chen, E. M.; Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1967**, *89*, 428−430. (c) Ogata, Y.; Aoki, K. *J. Am. Chem. Soc.* **1968**, *90*, 6187−6191. (d) Aoki, K.; Ogata, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1476−1477. (e) Ogata, Y.; Urasaki, I. *J. Chem. Soc. C* **1970**, 1689−1691. (f) Ogata, Y.; Urasaki, I.; Ishibashi, T. *J. Chem. Soc., Perkin Trans. 1* **1972**, 180−184. (g) Beebe, T. R.; Barnes, B. A.; Bender, K. A.; Halbert, A. D.; Miller, R. D.; Ramsay, M. L.; Ridenour, M. W. *J. Org. Chem.* **1975**, *40*, 1992−1994. (h) Cambie, R. C.; Chambers, D.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1483−1485. (i) Cambie, R. C.; Rutledge, P. S.; Stewart, G. M.; Woodgate, P. D.; Woodgate, S. D. *Aust. J. Chem.* **1984**, *37*, 1689−1698. (j) Merkushev, E. V. *Russ. Chem. Rev. (Engl. Transl.)* **1984**, *53*, 343−350.

(42) (a) Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377−407. (b) de Armas, P.; Concepción, J.; Franscisco, C.; Hernández, R.; Salazar, J.; Suárez, E. *J. Chem. Soc., Perkin Trans. 1* **1989**, 405−411. (c) Doleschall, G.; Tóth, G. *Tetrahedron* **1980**, *36*, 1649−1665.

(43) (a) Forbes, C. P.; Goosen, A.; Laue, H. A. H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2346−2350. (b) Cambie, R. C.; Hayward, R. C.; Lindsay, B. G.; Phan, A. I. T.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1961−1966. (See also references therein.) (c) *Dictionary of Inorganic Compounds*; Macintyre, J. E., Ed.; Chapman & Hall: London, 1992; see entry for I_2O (IC-020223), Vol. 3, p 3492.

$I(py)_2^+$ are known.[44] Bis(acetato-O)iodate(I), $I(OAc)_2^-$, has been reported, and NR_4^+ salts have been isolated.[42] We suggest that $I(OAc)_2^-$ formation inhibits further reaction by tying up iodine(I) as an unreactive species, preventing I^+ transfer to IO^-. The following mechanism is proposed:

uncatalyzed path

$$2HOI \xrightarrow{k_u} HOIO + H^+ + I^- \qquad (10)$$

catalyzed path

$$HOI + HOAc \underset{}{\overset{K_1}{\rightleftharpoons}} IOAc + H_2O \qquad (11)$$

$$HOAc \overset{K_a{}^{HOAc}}{\rightleftharpoons} H^+ + OAc^- \qquad (12)$$

$$IOAc + OAc^- \overset{K_2}{\rightleftharpoons} I(OAc)_2^- \qquad (13)$$

$$HOI \overset{K_a{}^{HOI}}{\rightleftharpoons} H^+ + IO^- \qquad (14)$$

$$IOAc + IO^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I_2O + OAc^- \qquad (15)$$

$$I_2O + H_2O \xrightarrow{k_4} HOIO + H^+ + I^- \qquad (16)$$

$$HOI + H^+ + I^- \xrightarrow{fast} I_2(aq) + H_2O \qquad (17)$$

At this stage, the catalyzed pathway gives the net reaction as in eq 8. Once HOIO is formed from either the catalyzed or uncatalyzed pathway, iodine(III) reacts in a series of reactions that sum to the net disproportionation in eq 18. Equations 8

$$5HOIO \rightarrow I_2 + 3IO_3^- + 3H^+ + H_2O \qquad (18)$$
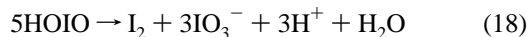
and 18 give the overall stoichiometry for iodine(I) shown in eq 1. Once H^+ and I^- are formed from either path (eq 10 or 16), they react with HOI (eq 17) to give I_2 and H_2O. Reaction 17 is sufficiently fast[27] to ensure rapid conversion of I^- to I_2(aq). For each molecule of HOIO formed, three HOI molecules are consumed; this stoichiometry leads back to eq 8.

We have treated the system as two disproportionations (eqs 8 and 18). While we do not include direct reactions of iodine-(I) with iodine(III) to give the net stoichiometry of eq 1, our treatment does not preclude elementary steps (in the process of eq 18) in which such reactions occur. However, eq 8 must be kinetically significant in order to explain the behavior of the integrated rate plots. The $-3\Delta[HOI]_T/\Delta[I_2]$ stoichiometry requires eq 8.

Under some conditions, the $-5\Delta[HOI]_T/2\Delta[I_2]$ stoichiometry fits well; nevertheless, our experimental data give little insight into the kinetics of the HOIO disproportionation (eq 18). Other investigators have suggested that iodine(I) reacts directly with iodine(III). Li and White[24] concluded that the reaction between IO^- and IO_2^- was fast in base. Wren et al.[5,7] have measured the rate constant as 0.50 M^{-1} s^{-1} for the reaction between IO^- and IO_2^- in 1 M NaOH, while the oxyacids react much faster; Paquette[4] reported a rate constant of 240 M^{-1} s^{-1} for the reaction between HOIO and HOI. The mixed-oxidation-state anhydride

I_2O_2 and its hydrate $H_2I_2O_3$ have been proposed[26,45] as intermediates in the Dushman reaction, and their decay is expected to be fast. Since the largest value for our second-order rate constant is less than Paquette's value, we conclude that any steps involving direct reaction of iodine(I) with iodine(III) must not be rate-limiting. Furrow[20] showed that the HOIO disproportionation is slow in the absence of HOI and concluded that HOI plays a catalytic role.[20,46] Since the buffer ties up iodine-(I) as $I(OAc)_2^-$, there may be insufficient HOI to effect rapid HOIO loss for initial rates with high $[OAc]_T$.

The proposed mechanism satisfactorily accounts for the observed behavior with I_2O as a steady-state species. The experimental rate dependence requires the existence of such a steady-state species. The decay of I_2O gives HOIO, a species with an intermediate oxidation state that is sufficiently stable to reach a significant concentration. Our results indicate that the HOIO concentration steadily increases until the second-phase reaction (eq 18) is sufficiently fast to be indistinct from the first-phase reaction (eq 8) and gives the $-5\Delta[HOI]_T/2[I_2]$ stoichiometry.

Derivation of the Rate Expression. The reaction rate is expressible as

$$rate = d[I_2]/dt = k_{obsd}[HOI]_T^2 \qquad (19)$$

where total hypoiodous acid is given by eq 20 (all aqueous

$$[HOI]_T = [ICl_2^-] + [ICl] + [IO^-] + [HOI] + [IOAc] + [I(OAc)_2^-] \qquad (20)$$

concentrations). Because the acid dissociation constant of HOI is so small,[47] $[IO^-]$ is not a significant contributor to $[HOI]_T$. Since the hydrolysis of ICl_2^- is nearly complete, $[ICl]$ and $[ICl_2^-]$ are very small. We treat diiodine oxide as a steady-state species, so that the rate of the catalyzed reaction is given by

$$rate\ (catalyzed) = k_4[I_2O]_{ss} = \frac{k_4 k_3[IOAc][IO^-]}{k_{-3}f_A[OAc]_T + k_4} \qquad (21)$$

I_2O must be a steady-state species rather than a species slow to build up since we observe I_2 formation immediately. If the I_2O concentration built up, no iodine formation would be observed during an initial induction period. The resulting observed rate constant, k_{obsd}, which includes the rate constant, k_u, for the uncatalyzed process, is given in equation 22. D represents the quantity $[HOI]_T/[HOI]$ (eq 23) where f_{HA} is the fraction of acetic acid and f_A is the fraction of acetate.

$$k_{obsd} = \frac{K_a{}^{HOI}K_1 k_3 k_4[HOAc] + k_u}{[H^+](k_{-3}[OAc^-] + k_4)D^2} \qquad (22)$$

$$D = \frac{[H^+][Cl^-]^2}{K_h} + \frac{K_d[H^+][Cl^-]}{K_h} + 1 + K_1 f_{HA}[OAc]_T + K_1 K_2 f_{HA} f_A[OAc]_T^2 \qquad (23)$$

Resolution of Rate and Equilibrium Constants. Using the observed rate constants and $[OAc]_T$ values (Table 2), the constants k_u, K_1, K_2, k_3, and k_{-3}/k_4 were determined by goodness

(44) (a) Cotton F. A.; Wilkinson G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 577, 579. (b) Maki, A. G.; Forneris, R. *Spectrochim. Acta* **1967**, *23A*, 867−880. (c) Ginn, S. G. W.; Wood, J. L. *Trans. Faraday Soc.* **1966**, *62*, 777−787. (d) Carter, S.; Gray, N. A. B.; Wood, J. L. *J. Mol. Struct.* **1971**, 7, 481−485. (e) Sasaki, K.; Kuwano, I.; Aida, K. *J. Inorg. Nucl. Chem.* **1981**, *43*, 485−489.

(45) Liebhafsky, H. A.; Roe, G. M. *Int. J. Chem. Kinet.* **1979**, *11*, 693−703.

(46) Noszticzius, Z.; Noszticzius, E.; Schelly, Z. A. *J. Phys. Chem.* **1983**, *87*, 510−524.

Table 2. Observed Rate Constants for the Disproportionation of Iodine(I) as a Function of Buffer Concentration[a−c] and p[H+][d]

[OAc]$_T$, M[c]	k^{av}_{obsd}, M^{-1} s^{-1}			
	p[H+] 3.50	p[H+] 4.00	p[H+] 4.50	p[H+] 5.00
0.0020	2.5*			
0.0050	4.4*	3.3*		
0.0074				2.0
0.0080			3.1	
0.010	4.8*	5.6*		
0.011				5.6
0.012			3.8	
0.015				9.1
0.019				8.7
0.020	4.8*			
0.030		9.1*		
0.037		6.9		18.6
0.040			16.8	
0.050	10.1*	11.2*	24.8	
0.070		16.6*		
0.074		14.8		28.0
0.10	16.2*	17.1		
0.11		16.4		59.4
0.15		18.8	48.0	68.6
0.19		23.2		64.8
0.20			45.8	
0.25			32.4	
0.28		18.6		43.3
0.30	13.7*			
0.37		15.9		34.5
0.40			22.7	
0.47		11.2		24.5
0.50			11.8	
0.62				13.1
0.74		4.7		
0.85			5.4	

[a] Conditions: [Cl$^-$] = 0.033 M or (*) 0.0010 M; μ = 0.50 ± 0.02 M (NaClO$_4$); 25.0 ± 0.1 °C. [b] Values for k^{av}_{obsd} are the average values. [c] [OAc]$_T$ = [HOAc] + [OAc$^-$]. [d] p[H+] = −log [H+] ± 0.05.

of fit to the data for the four p[H+] values concurrently. We are able to fit the data to the proposed mechanism for a wide range of [OAc]$_T$ at p[H+] 3.50, 4.00, 4.50, and 5.00. In this mechanism, the concentration of the intermediate IOAc is always small, but it is a highly reactive species that transfers an iodine(I) cation to hypoiodite to form I$_2$O, a steady-state intermediate. The criterion used for goodness of fit was a trial and error iterative process to minimize the residual: $\chi^2 = \sum_{all\ [OAc]_T} (k^{av}_{obsd} - k^{calc}_{obsd})^2$, where k^{av}_{obsd} is an experimentally determined constant and k^{calc}_{obsd} is the value calculated from eq 22. The function χ^2 was minimized for each parameter, one at a time, using the data for all acidities at once. This process was repeated until no improvement was found. The values for the constants in the proposed mechanism are as follows: K_1 = 0.24 ± 0.05 M^{-1}, K_2 = 160 ± 10 M^{-1}, k_3 = (1.90 ± 0.04) × 10^9 M^{-1} s^{-1}, k_{-3}/k_4 = 4.30 ± 0.06, and k_u < 2 M^{-1} s^{-1}. Because I$_2$O is a steady-state species, it is impossible to explicitly resolve k_{-3} from k_4; only the quotient k_{-3}/k_4 may be determined. Since the acetate ion is a product in the formation of I$_2$O (eq 15), there is a suppression that results as the term [OAc]$_T k_{-3}/k_4$ approaches and exceeds unity (i.e., [OAc]$_T \gtrsim 0.23$

(47) Chia[29] reported K^{HOI}_a = 2.3 × 10^{-11}, calculated indirectly from four equilibria: IO$^-$ + 2I$^-$ + 2H$_2$O ⇌ I$_3^-$ + 2OH$^-$ (K_{com} = 5.65 × 10^{-3}); H$_2$O ⇌ H$^+$ + OH$^-$ (K_w = 1.0 × 10^{-14}); I$_2$(aq) + I$^-$ ⇌ I$_3^-$ (K_{tri} = 714); I$_2$(aq) + H$_2$O ⇌ HOI + I$^-$ + H$^+$ (K_{hy} = 5.4 × 10^{-13}). Chia determined K_{com} (pp 79−82) but used K_{hy} from ref 30 and K_{tri} from: Latimer, W. M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed.; Prentice-Hall: New York, 1952. However, Paquette and Ford[6] obtained K^{HOI}_a = 1.0 × 10^{-10} under conditions closer to ours; therefore, we use their value.
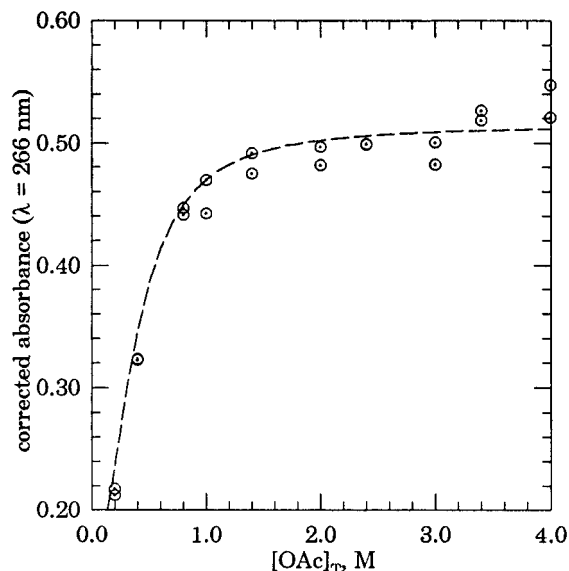

Figure 5. Effect of acetic acid−acetate buffer on the initial absorbance of iodine(I) at 266 nm. Experimental values were corrected for absorbance of the buffer; ϵ_{HOI} was estimated as 160 M^{-1} cm^{-1}. Smooth curve represents predicted absorbance (eq 24). Conditions: [HOAc]: [AcO$^-$] = 3:1, pH ≈ 5.2; [HOI]$^{init}_T$ = 9.72 × 10^{-5} M; [Cl$^-$] = 0.0010 M; μ = 0.50 ± 0.02 M (NaClO$_4$); l = 10.00 cm; 25.0 ± 0.1 °C.

M). Note that this suppression is in addition to that which occurs because of the formation of the bis(acetato-*O*)iodate(I) ion.

Spectrophotometric Evidence for I(OAc)$_2^-$. Spectra of iodine(I) in the presence of acetic acid−acetate buffer show a significant shoulder at 266 nm that increases with total buffer concentration and levels off for [OAc]$_T \gtrsim 1$ M. After correcting for the contributions of the buffer to the absorbance, we obtain a molar absorptivity of 530 ± 20 M^{-1} cm^{-1} for I(OAc)$_2^-$. By analogy to chloro and bromo complexes of iodine(I), we predict that IOAc has a molar absorptivity of ~64% of that of the bis-(acetato) complex. Using the stability constants K_1 and K_2 from the kinetic data, we are able to predict the absorbance as a function of total acetate. Thus, we have an independent spectrophotometric confirmation of the equilibrium constants. Figure 5 shows there is an excellent fit of the predicted model (eq 24) to the experimental data (for l = 10.00 cm).

$$\frac{A}{l[HOI]_T} = \frac{\epsilon_{IOAc}K_1[HOAc] + \epsilon_{I(OAc)_2^-}K_1K_2[HOAc][OAc^-] + \epsilon_{HOI}}{K_1[HOAc] + K_1K_2[HOAc][OAc^-] + 1}$$

(24)

Conclusions. The novelty of this system is that acetic acid−acetate buffer both catalyzes and suppresses the reaction. Strong association of iodine(I) with an oxygen-site Lewis base (and a weak Brønsted−Lowry base) is equally unusual. CH$_3$CO$_2$I is determined to be an excellent and readily-formed I$^+$ donor in *aqueous* solution. The I$^+$ transfer to IO$^-$ is followed by I$^-$ elimination to give iodine(III). The stability of the complex ion I(OAc)$_2^-$ is established kinetically by the fact that the reaction rate falls off at moderate concentrations [OAc]$_T$ > 0.2 M and spectrophotometrically by a strong UV absorption at 266 nm. The stability of this species in water suggests that other oxyanions, such as phosphate, may also form aqueous complexes with iodine(I). Since such species, especially acetate and phosphate, are often used as buffers in kinetics studies of

these systems, the possibility for the formation of coordinate complexes as opposed to general acid—base effects must not be overlooked. Furthermore, our results prove that acetic acid—acetate buffer—depending on its concentration—may be used either to activate iodine(I) as an electrophile or to stabilize it to disproportionation. Our equilibrium constants indicate that, for $[OAc]_T = 2$ M, the reaction gives ~70% I_2 formation at equilibrium and, for $[OAc]_T = 4$ M, ~30% I_2 formation at equilibrium; this is confirmed spectrophotometrically.

Buffer catalyses are extremely important in the disproportionation reactions of iodine(I). We were unable to measure a rate constant for the uncatalyzed pathway, but our data suggest that k_u is less than 2 M^{-1} s^{-1}, considerably smaller than many reported values. We conclude that all reported disproportionation rate constants are affected by buffers (carbonate, borate, phosphate, etc.) or by base. Accordingly, a rate constant of 40 M^{-1} s^{-1} for HOI + IO^- may be valid in NaOH solution, but buffer catalysis appears to completely dominate the kinetics in other cases.