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Kinetic Evidence for Accumulation of Stoichiometrically Significant Amounts of $H_2I_2O_3$ during the Reaction of I^- with IO_3^-

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The kinetics of the Dushman reaction, $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$, is considerably more complex in aqueous, acidic media than is the behavior of the analogous reaction of Br^- with BrO_3^-. The latter reaction is first order in both $[Br^-]$ and $[BrO_3^-]$ and is believed to proceed via a series of simple oxygen-atom transfers, there being no evidence for the intermediacy of polybromine species such as $H_2Br_2O_3$. In contrast, the $[I^-]$ order in the Dushman reaction is reported variously to be one or two, depending upon experimental conditions, especially $[IO_3^-]_0/[I^-]_0$, and the kinetics of this reaction is generally very complex with the intermediacy of $H_2I_2O_3$ having been suggested by several authors. Stopped-flow kinetic measurements of the Dushman reaction are reported here with excess $[KIO_3]_0 \approx 40[KI]_0/5$ and $[HClO_4]_0 \geq 140 \times 6[KI]_0/5$ in which the observed $[I^-]$ order is cleanly two, but saturation kinetics is observed for the pseudo-second-order rate constant as $[KIO_3]_0$ and $[HClO_4]_0$ increase. This observation is rationalized by a mechanism assuming the intermediacy of $H_2I_2O_3$ at concentrations significant compared to those of I^-, requiring that the kinetic equations be constrained by the iodide-ion mass balance. It is suggested that $H_2I_2O_3$ is a kinetically and stoichiometrically significant species in the Dushman reaction, while $H_2Br_2O_3$ is not in the analogous bromine system, because of the greater atomic radius, polarizability, and ability to expand its valence shell of iodine as compared to bromine.

Introduction

The kinetics of the reaction of IO_3^- with I^- in aqueous, acidic media

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O \qquad (1)$$

was first investigated by Dushman[1] in 1904 and proceeds far to the right in strongly acid media. The most complete experimental investigation of reaction 1 seems to be that of Abel and Stadler[2] in 1926 followed by that of Abel and Hilferding[3] in 1928. Interest in the oscillatory Bray−Liebhafsky reaction[4−7] led to a resurgence of work[8−11] on this system in the 1970s, including a review and simulation of existing data by Liebhafsky and Roe[11] in 1979. Such activity continues within the context of oscillating chemical reactions.[12−14] Some recent work has been motivated by a need to understand the aqueous chemistry of radioactive iodine species in the event of a nuclear reactor containment breach.[15]

The equivalent reaction with bromine seems kinetically clean and simple.[16]

$$BrO_3^- + 5Br^- + 6H^+ \rightleftarrows Br_2 + 3H_2O \qquad (2)$$

Reaction 2 is first order in both $[Br^-]$ and $[BrO_3^-]$ and appears to occur via a series of rapid oxygen-atom transfers without the intermediacy of polybromine species such as $H_2Br_2O_3$. However, the kinetics of the Dushman reaction is complex. Liebhafsky and Roe[11] attempted to describe the kinetics with rate expressions containing up to three terms in unbuffered media. All three terms are supposed by these authors to be first order in $[IO_3^-]$ and second order in $[H^+]$. However, the kinetic dependence on $[I^-]$ is very complex, with two of these terms being first order and second order, respectively, in $[I^-]$, and the third term being first order in both $[I^-]$ and $[I_3^-]$. The $[I_3^-]$ dependence arises from reaction 3, which is not a significant

$$I_2 + I^- \rightleftarrows I_3^- \qquad (3)$$

perturbation at the very low $[I^-]$ present here, for which $[I_3^-]/[I_2]$ seldom exceeds 0.05 (assuming[17] $K_3 = 740\ M^{-1}$), and then only early in the reaction when $[I_2]$ is relatively low and $[I^-]$ is relatively high. The kinetics of reaction 1 is even more complex in buffered media, leading to yet a fourth term in the rate expression.[8,9,11]

The kinetic complexity of the Dushman reaction was ascribed by Bray[4] in 1930 and later by Liebhafsky and co-workers[18−20] to the intermediacy of $H_2I_2O_3$ or its anhydride, I_2O_2. This species has been invoked by later workers[10,14,20,21] in more complex reactions, as have the related intermediate species $IO_3H_2SO_3^-$ suggested by Rabai et al.[12] in the $IO_3^-{-}SO_3^{2-}{-}Fe(CN)_6^{4-}$ system, and I_2O suggested by Urbansky et al.[15] in regard to the disproportionation of HOI, as well as by Schmitz[14] and by Kolar-Anic[22−24] and co-workers in regard to the mechanism of the Bray−Liebhafsky reaction.[4−7] Schmitz[14c] very recently also carried out a systematic analysis of then existing kinetic results on reaction 1. We report here stopped-flow kinetic evidence for both the participation and the accumulation of stoichiomet-

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rically significant (compared to $[I^-]$) amounts of $H_2I_2O_3$ in the Dushman reaction when $[KIO_3]_0 \gg [KI]_0/5$.

Experimental Section

All reagents were made up using deionized water. Experiments were carried out in 0.0968−0.489 M $HClO_4$ (Fisher 69−72% Metal Grade) aqueous media. Stock solutions were made up using EM Science GR grade KI without further purification. Baker Analyzed Reagent grade KIO_3 was slurried in methanol to remove I^- and then used to prepare stock solutions. Kinetic experiments were carried out spectrophotometrically, usually at 460 nm near the absorption maximum of I_2, at room temperature, 24 ± 0.5 °C, using an Aminco-Morrow stopped-flow apparatus upgraded by On-Line Instrument Systems, Route 2, Jefferson, GA 30549. Digital data-acquisition methods were used and results were manipulated using standard PC methods and software. The stoichiometric iodide remaining at time *t*, $[I^-]_s$, was calculated from the measured instantaneous $[I_2]_t$ absorbance using the relation $[I^-]_s = {}^5/_3([I_2]_\infty - [I_2]_t)$. In the mechanism described below, stoichiometric iodide, $[I^-]_s$ may be distributed between I^-, $[I^-]_t$, and $H_2I_2O_3$, $[H_2I_2O_3]_t$, i.e., $[I^-]_s = [I^-]_t + [H_2I_2O_3]_t$.

Results

All experiments were carried out with $[KIO_3]_0 \approx 40\,[KI]_0/5$, $[HClO_4]_0 \approx [H^+]_0 \geq 140 \times 6[KI]_0/5$, and $[HClO_4]_0 > 20[KIO_3]_0$, ensuring isolation kinetics in $[I^-]_s$ at constant $[HClO_4]_0$, and $[HIO_3]_0$, the last concentration being calculated from $[HIO_3]_0 = (K_a + [KIO_3]_0 + [HClO_4]_0 - ((K_a + [KIO_3]_0 + [HClO_4]_0)^2 - 4[HClO_4]_0[KIO_3]_0)^{1/2})/2$. The value $K_a^0 = [IO_3^-][H^+]/[HIO_3] = 0.157$ at 25 °C and infinite dilution ($\mu \to 0$) is given by Strong and Pethybridge.[25] It is expected[26] that the value of $\gamma_\pm$ will be nearly constant and about 0.7 for a one-to-one electrolyte such as HIO_3 in the range 0.1−0.5 M. Thus, we calculate $K_a = K_a^0/\gamma_\pm^2 = 0.32$. The kinetics under these conditions and in the concentration ranges $0.000\,058\ M \leq [KI]_0 \leq 0.000\,576\ M$, $0.000\,448\ M \leq [KIO_3]_0 \leq 0.004\,48\ M$, and $0.0968\ M \leq [HClO_4]_0 \leq 0.489\ M$ is found to be second order (after a very short induction period in some of the most rapid experiments; e.g., see Figure 6) in $[I^-]$, with no first-order component, i.e., eq 4. Figure 1 shows typical absorbance data

$$-\frac{1}{5}\frac{d[I^-]_s}{dt} = k_{exp}[I^-]_s^{\,2} \tag{4}$$

as well as the corresponding second-order plot of $1/[I^-]_s$, which is linear to nearly 99% completion. The values of k_{exp} reported here are the slopes of plots such as that displayed in Figure 1 divided by 5 in order to take into account the stoichiometric factor in eq 4.

Pseudo-second-order rate constants, k_{exp}, were determined with varying $[KIO_3]_0$ and $[HClO_4]_0$ and display saturation kinetics as these concentrations increase. Figure 2 shows five series of k_{exp} plotted vs ($[HIO_3]_0[HClO_4]_0$) with each series having constant $[HClO_4]_0$ but varying $[KIO_3]_0$. The series at lowest $[HClO_4]_0$ is nearly linear with no unequivocal evidence of an intercept, indicating a single-term form of k_{exp}. However, saturation (negative) curvature appears at higher ($[HClO_4]_0$ $[HIO_3]_0$) in the series at higher values of $[HClO_4]_0$. Figure 3 shows five series of k_{exp} plotted vs ($[HIO_3]_0[H^+]_0$) with each series having constant $[KIO_3]_0$ but varying $[HClO_4]_0$. The series at lowest $[HIO_3]_0$ again is nearly linear without unequivocal evidence of an intercept, but the series at higher $[HIO_3]_0$ show substantial saturation deviation as $[HClO_4]_0$ increases.

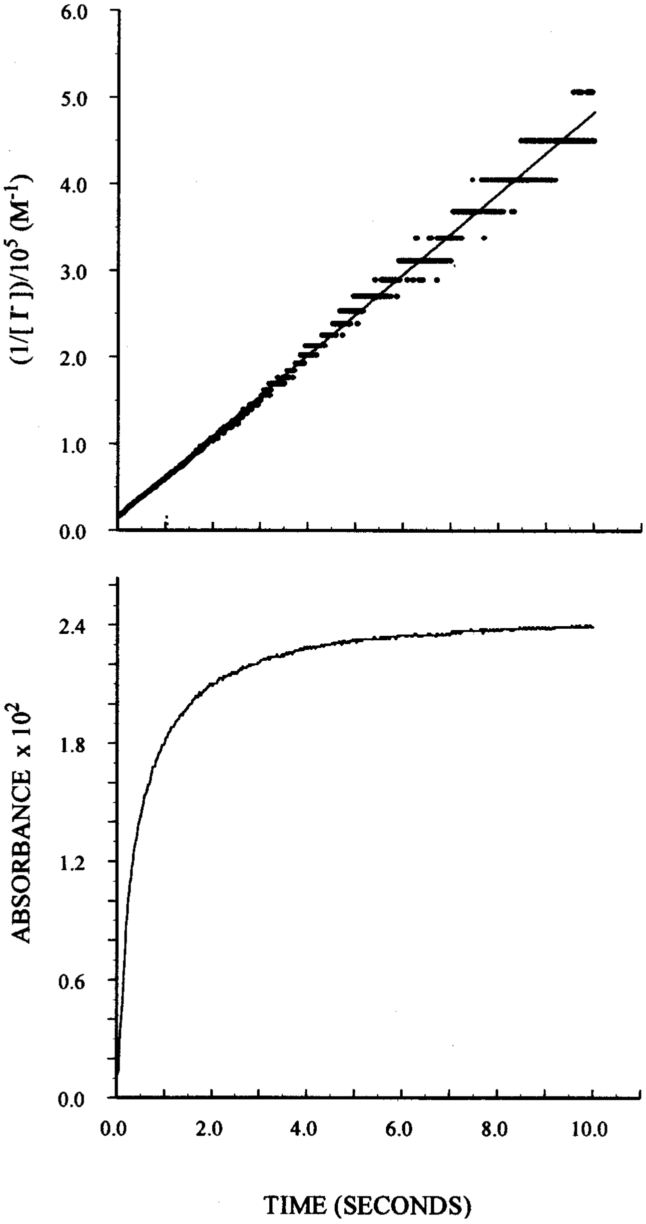


Figure 1. (Lower) typical stopped-flow kinetic data (500 points) showing the average absorbance × 10^2 due to I_2 at 460 nm in 10 duplicate experiments vs time (s). (Upper) second-order plot of $(1/[I^-]_s)/10^5$ (M^{-1}) vs time (s). The stoichiometric $[I^-]_s$ is calculated from the instantaneous $[I_2]_t$ according to $[I^-]_s = {}^5/_3([I_2]_\infty - [I_2]_t)$. Slope = $(4.6 \pm 0.5) \times 10^4\ M^{-1}\ s^{-1}$ and k_{exp} = slope/5 = $(9.2 \pm 1) \times 10^3\ M^{-1}\ s^{-1}$. $[HClO_4]_0 = 0.289$ M, $[KIO_3]_0 = 0.000\,448$ M, $[HIO_3]_0 = 0.000\,212$ M, $[KI]_0 = 0.000\,058$ M.

Figures 2 and 3 and the mechanism described below suggest eqs 5−7.

$$-\frac{1}{5}\frac{d[I^-]_s}{dt} = \frac{k[HIO_3]_0[HClO_4]_0}{(1 + k^*[HIO_3]_0[HClO_4]_0)^2}[I^-]_s^{\,2} = k_{exp}[I^-]_s^{\,2} \tag{5}$$

$$k_{exp} = \frac{k[HIO_3]_0[HClO_4]_0}{(1 + k^*[HIO_3]_0[HClO_4]_0)^2} \tag{6}$$

$$\left(\frac{[HIO_3]_0[HClO_4]_0}{k_{exp}}\right)^{1/2} = \frac{1}{k^{1/2}} + \left(\frac{k^*}{k^{1/2}}\right)[HIO_3]_0[HClO_4]_0 \tag{7}$$

Figure 4 shows the data in Figures 2 and 3 plotted according to

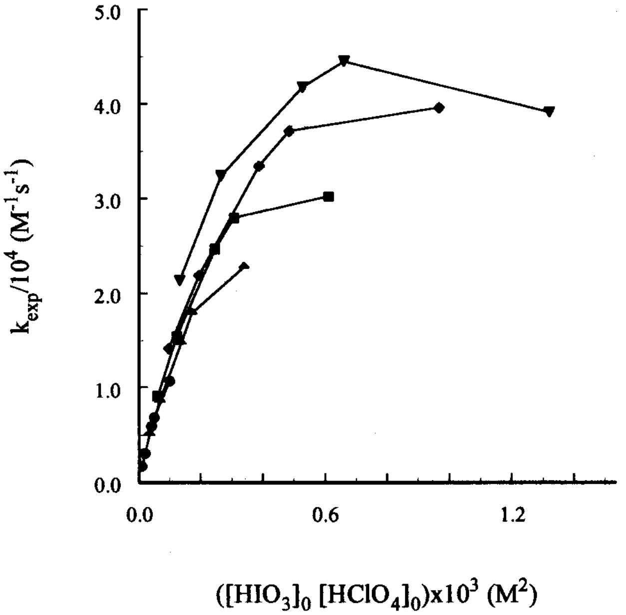


Figure 2. Saturation of $k_{exp}/10^4$ (M^{-1} s^{-1}) with increasing ($[HIO_3]_0$-$[HClO_4]_0$) × 10^3 (M^2) over the range 0.000 448 M ≤ $[KIO_3]_0$ ≤ 0.004 48 M) in five series of experiments at constant $[HClO_4]_0$ of (●) 0.0968 M, (▲) 0.199 M, (■) 0.289 M, (◆) 0.393 M, and (▼) 0.489 M.

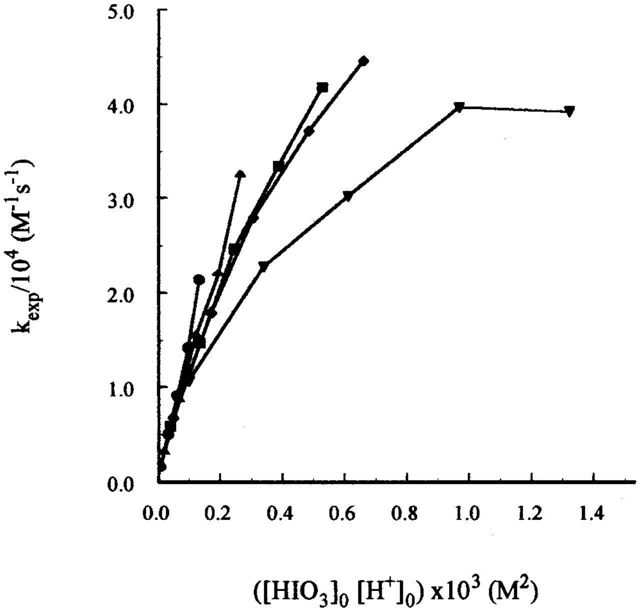


Figure 3. Saturation of $k_{exp}/10^4$ (M^{-1} s^{-1}) with increasing ($[HIO_3]_0$-$[HClO_4]_0$) × 10^3 (M^2) over the range 0.0968 M ≤ $[HClO_4]_0$ ≤ 0.489 M in five series of experiments at constant $[KIO_3]_0$ of (●) 0.000 448 M, (▲) 0.000 896 M, (■) 0.001 79 M, (◆) 0.002 24 M, and (▼) 0.004 48 M.

eq 7. The fit to eq 7 is excellent over the substantial concentration ranges cited above, and we assume eq 5 describes the kinetics of reaction 1 under the condition $[KIO_3]_0 \gg [KI]_0/5$. The slope and intercept of the plot in Figure 4 yield $k = (1.6 \pm 0.1) \times 10^8\ M^{-3}\ s^{-1}$ and $k^* = (9.9 \pm 0.8) \times 10^2\ M^{-2}$. The quoted precision of these quantities may be misleadingly high because of medium effects. The data in Figure 2 are for five series of experiments with varying $[KIO_3]_0$ (0.000 448−0.004 48 M) at constant and at least 20 times higher $[HClO_4]_0$ (0.0968−0.489 M). Thus, the ionic strength is nearly constant within each of these series of experiments, demonstrating that the basic saturation phenomenon observed is not a medium effect. However, the data in Figure 3 are for five series of experiments at constant $[IO_3^-]_0$ (0.000 448−0.004 48 M) with $[HClO_4]_0$ varying and about 20 times higher (0.0968−0.489 M) than $[IO_3^-]_0$. Thus, the ionic strength varies considerably within each of these series of experiments. Even though the data from Figures 2 and 3 fit together well in Figure 4, this varying ionic strength undoubtedly introduces some error into the inferred values of k and k^*.

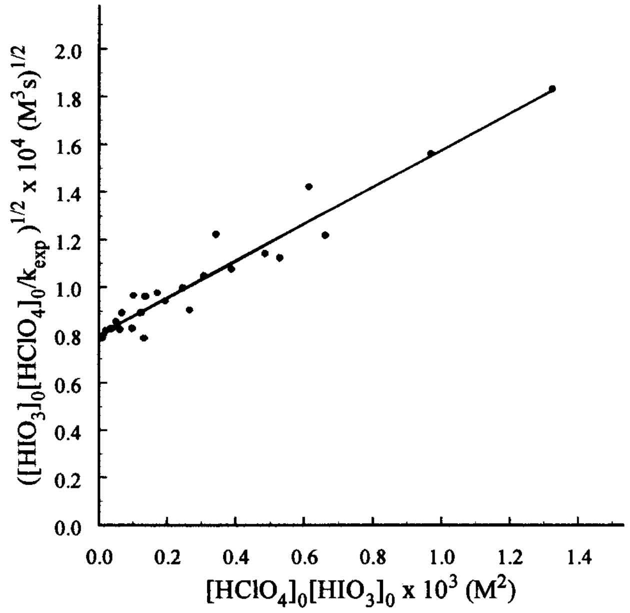
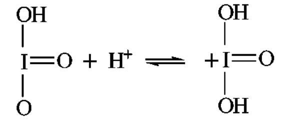
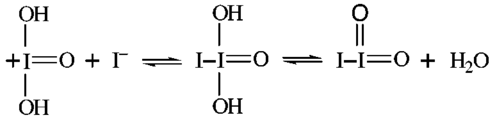
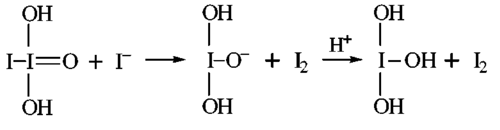


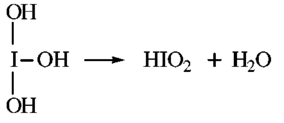
Figure 4. Plot of $([HIO_3]_0[HClO_4]_0/k_{exp})^{1/2} \times 10^4\ (M^3\ s)^{1/2}$ vs ($[HIO_3]_0$-$[HClO_4]_0$) × 10^3 (M^2) according to eq 7. Slope = $k^*/k^{1/2} = (7.8 \pm 0.4) \times 10^{-2}\ (s/M)^{1/2} = (K_9K_{10}/k_{11})^{1/2}$ and intercept = $1/k^{1/2} = (8.0 \pm 0.2) \times 10^{-5}\ (M^3\ s)^{1/2} = (1/K_9K_{10}k_{11})^{1/2}$.

$$\mathrm{H^+ + IO_3^- \rightleftharpoons HIO_3} \tag{8}$$


$$\overset{\mathrm{OH}}{\underset{\mathrm{O}}{\mathrm{I}}}\mathrm{{=}O} + \mathrm{H^+} \rightleftharpoons +\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{=}O} \tag{9}$$

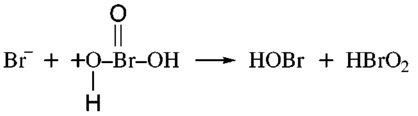

$$+\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{=}O} + \mathrm{I^-} \rightleftharpoons \mathrm{I{-}}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{=}O} \rightleftharpoons \mathrm{I{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{I}}}\mathrm{{=}O} + \mathrm{H_2O} \tag{10}$$


$$\mathrm{I{-}}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{=}O} + \mathrm{I^-} \longrightarrow \overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{-}O^-} + \mathrm{I_2} \xrightarrow{\mathrm{H^+}} \overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{-}OH} + \mathrm{I_2} \tag{11}$$


$$\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{I}}}\mathrm{{-}OH} \longrightarrow \mathrm{HIO_2} + \mathrm{H_2O} \tag{12}$$

$$\mathrm{2I^- + IO_3^- + 3H^+ \longrightarrow HIO_2 + I_2} \tag{13}$$

Mechanistic Interpretation. The mechanism below is in keeping with previous work, its recent analysis by Schmitz,[14c] and with eq 5. The species $H_2I_2O_3$ is suggested to be similar in structure but not isoelectronic with the thiosulfate ion, $S_2O_3^{2-}$; it is not possible for us to distinguish kinetically between the intermediacy of $H_2I_2O_3$ or its anhydride I_2O_2. Reaction 10 is to be contrasted with the simple oxygen-transfer process presumed to be rate determining in reaction 2, reaction 14. It is suggested



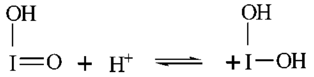
$$Br^- + {}^{+}O(H)\text{–}Br(=O)\text{–}OH \longrightarrow HOBr + HBrO_2 \quad (14)$$

that the difference between reactions 10 and 14 results from the greater size and tendency of iodine to expand its valence shell as compared to bromine, and the lower electronegativity of iodine as compared to bromine. We see no kinetic evidence that $H_2I_2O_3$ rearranges and decomposes directly to HOI and HIO_2, reaction 15, under the conditions employed here, and we

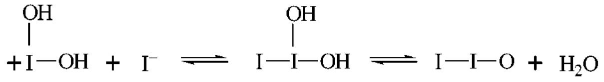
$$H_2I_2O_3 \rightarrow HOI + HIO_2 \qquad (15)$$

thus ignore this process, even though it is likely important at very low [I⁻].[14c]

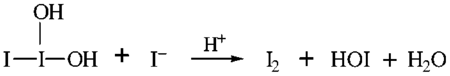
Reaction 13 is suggested to be followed rapidly by the reactions below, which are analogous to reactions 9−12.



$$I(OH)\text{=}O + H^+ \rightleftharpoons {}^{+}I(OH)\text{–}OH \qquad (16)$$



$${}^{+}I(OH)\text{–}OH + I^- \rightleftharpoons I\text{–}I(OH)\text{–}OH \rightleftharpoons I\text{–}I\text{–}O + H_2O \qquad (17)$$



$$I\text{–}I(OH)\text{–}OH + I^- \xrightarrow{H^+} I_2 + HOI + H_2O \qquad (18)$$

$$HIO_2 + 2I^- + 2H^+ \longrightarrow HOI + H_2O + I_2 \qquad (19)$$

Followed by

$$HOI + H^+ \rightleftharpoons H_2O\text{–}I^+ \qquad (20)$$

$$H_2O\text{–}I^+ + I^- \rightleftharpoons H_2O + I_2 \qquad (21)$$

$$H^+ + HOI + I^- \rightleftharpoons I_2 + H_2O \qquad (22)$$

We are not able here to distinguish kinetically any details of reactions 16−22.

Derivation of the rate expression predicted by this mechanism proceeds as follows under the assumption that concentrations of $H_2I_2O_3$ are significant compared to the concentration of I^- accumulated in the course of the reaction. The experiments reported here are based upon spectrophotometric measurement of the concentration of I_2 present at time t, i.e., $[I_2]_t$. The stoichiometric concentration of iodide ion, $[I^-]_s$, remaining at time t then is given by $[I^-]_s = {}^5/_3([I_2]_\infty - [I_2]_t)$. This iodide ion is distributed between free I^- and $H_2I_2O_3$ according to the mass balance, $[I^-]_s = [I^-]_t + [H_2I_2O_3]_t$. The assumption that reactions 9 and 10 are at equilibrium yields $[H_2I_2O_3]_t = K_9K_{10}[HIO_3]_0[HClO_4]_0[I^-]_t$, and substitution of this expression into the mass balance leads to eqs 23 and 24.

$$[I^-]_t = \frac{[I^-]_s}{1 + K_9K_{10}[HIO_3]_0[HClO_4]_0} \qquad (23)$$

$$[H_2I_2O_3]_t = \frac{K_9K_{10}[I^-]_s[HIO_3]_0[HClO_4]_0}{1 + K_9K_{10}[HIO_3]_0[HClO_4]_0} \qquad (24)$$

Assuming reaction 11 to be rate-determining for the overall process leads to eq 25.

$$-\frac{1}{5}\frac{d[I^-]_s}{dt} = -\left(\frac{1}{5}\right)\left(\frac{d[I^-]_t}{dt} + \frac{d[H_2I_2O_3]_t}{dt}\right) = k_{11}[H_2I_2O_3]_t[I^-]_t \qquad (25)$$

Substitution of eqs 23 and 24 into eq 25 leads to eq 26 for the kinetics of reaction 1.

$$-\frac{1}{5}\frac{d[I^-]_s}{dt} = \frac{k_{11}K_9K_{10}[HIO_3]_0[HClO_4]_0}{(1 + K_9K_{10}[HIO_3]_0[HClO_4]_0)^2}[I^-]_s^{\,2} \qquad (26)$$

Equation 26 is identical in form to the experimental eq 5 and suggests the following identities: $k = k_{11}K_9K_{10} = (1.6 \pm 0.1) \times 10^8\ M^{-3}s^{-1}$, $k^* = K_9K_{10} = (9.9 \pm 0.8) \times 10^2\ M^{-2}$, and $k_{11} = (1.6 \pm 0.2) \times 10^5\ M^{-1}s^{-1}$. Substitution of these values of k_{11} and K_9K_{10} into eq 26 together with experimental values of $[HIO_3]_0$ and $[HClO_4]_0$ yields the observed values of k_{exp} to within experimental error.

A similar expression, eq 27, is recovered using the same methods for the circumstance $[I^-]_0 \gg [IO_3^-]_0$ where the appropriate mass balance is $[IO_3^-]_s = [IO_3^-]_t + [H_2I_2O_3]_t + [HIO_3]_t$.

$$-\frac{d[IO_3^-]_s}{dt} = \frac{k_{11}K_9K_{10}[HClO_4]_0[I^-]_0^{\,2}}{1 + K_a/[HClO_4]_0 + K_9K_{10}[HClO_4]_0 + K_9K_{10}[HClO_4]_0[I^-]_0} \times [IO_3^-]_s \qquad (27)$$

Equation 27 reduces to eq 28 at sufficiently high [I⁻]. Equation 28 is in keeping with the observation of a term first order in [I⁻] at high $[I^-]_0$.[8,14]

$$-\frac{d[IO_3^-]_s}{dt} = k_{11}[I^-]_0[IO_3^-]_s \qquad (28)$$

A transition between first- and second-order kinetics in [I⁻] as [I⁻] increases also can be rationalized via a rate expression derived from the same mechanism but without assuming accumulation of stoichiometrically significant amounts of $H_2I_2O_3$.[14c] One instead assumes that a very small, stoichiometrically insignificant (compared to [I⁻]) $[H_2I_2O_3]$ is controlled not solely by equilibrium 10, but instead by a steady-state involving reactions 10, −10, and 11.[14c] Perturbation of the iodine-atom mass balance may be neglected if only a very small concentration of $H_2I_2O_3$ is present. This approach leads to eq 29, which is first order in [I⁻] when k_{11} [I⁻] ≫ k_{-10} and second

$$-\frac{1}{5}\frac{d[I^-]}{dt} = \frac{k_{10}k_{11}K_9[HIO_3][HClO_4][I^-]^2}{k_{-10} + k_{11}[I^-]} \qquad (29)$$

order in [I⁻] when k_{11} [I⁻] ≪ k_{-10}. While it is very likely that complexity resulting from the competition of reactions −10 and 11 with each other, as well as with reaction 15, is sometimes important over the wide range of [I⁻] possible in this system,[14c] eq 29 is not able to rationalize the saturation of k_{exp} with $([H^+]_0[HIO_3]_0)$ that is a dominant feature of the data presented here. We thus emphasize the formation of binuclear iodine-containing species in this analysis.

A two-term rate expression of the form of eq 30, such as considered by Liebhafsky and Roe,[11] exhibits second-order

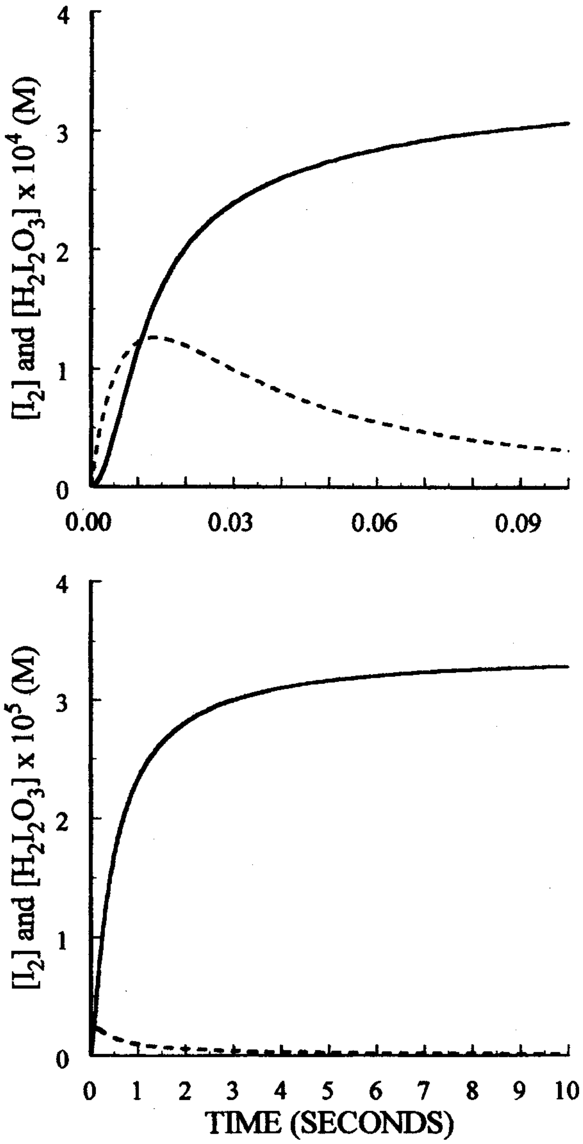


Figure 5. Simulation of the experiments in Figures 1 and 6 by numerical integration of the set of differential equations resulting from application of the law of mass action to reactions 8–12, 15–17, and 21. The assumed rate parameters are $k_8 = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_{-8} = 3.2 \times 10^9\ s^{-1}$, $k_9 = 6.0 \times 10^7\ M^{-1}\ s^{-1}$, $k_{-9} = 3.6 \times 10^8\ s^{-1}$, $k_{10} = 2.5 \times 10^5\ M^{-1}\ s^{-1}$, $k_{-10} = 42.2\ s^{-1}$, $k_{11} = 1.6 \times 10^5\ M^{-1}\ s^{-1}$, $k_{12} = 1.0 \times 10^8\ s^{-1}$, $k_{16} = 1.0 \times 10^8\ M^{-1}\ s^{-1}$, $k_{-16} = 1.0 \times 10^3\ s^{-1}$, $k_{17} = 1.0 \times 10^9\ M^{-1}\ s^{-1}$, $k_{-17} = 1.0 \times 10^5\ s^{-1}$, $k_{18} = 1.0 \times 10^6\ M^{-1}\ s^{-1}$, $k_{20} = 1.0 \times 10^9\ M^{-1}\ s^{-1}$, $k_{-20} = 1.0 \times 10^9\ s^{-1}$, $k_{21} = 1.0 \times 10^{10}\ M^{-2}\ s^{-1}$, $k_{-21} = 100\ s^{-1}$. (Lower) $[I_2] \times 10^5$ (M) (—) and $[H_2I_2O_3] \times 10^5$ (M) (---) vs time (s). $[HClO_4]_0 = 0.289$ M, $[KIO_3]_0 = 0.000\,448$ M, $[HIO_3]_0 = 0.000\,212$ M, and $[KI]_0 = 0.000\,058$ M. (Upper) $[I_2] \times 10^4$ (M) (—) and $[H_2I_2O_3] \times 10^4$ (M) (---) vs time (s). $[HClO_4]_0 = 0.489$ M, $[KIO_3]_0 = 0.004\,48$ M, $[HIO_3]_0 = 0.002\,70$ M, and $[KI]_0 = 0.000\,057\,6$ M.

kinetics at high $[I^-]$, and first-order kinetics at low $[I^-]$, the

$$-\frac{1}{5}\frac{d[I^-]}{dt} = k_a[HIO_3][H^+][I^-] + k_b[HIO_3][H^+][I^-]^2 \quad (30)$$

opposite of eqs 27 and 29 and to what is observed both here and in previous work. Thus, we do not consider here mechanistic paths involving two independent paths from reactants to products, such as is implied by eq 30.

Figure 5 shows simulated values of $[I_2]$ and $[H_2I_2O_3]$ for the experiments displayed in Figures 1 and 6 calculated by numerical integration of the mass-action rate equations resulting from reactions 8–12, 15–17, and 21 using the rate constants given in the legend of Figure 5. The values of k_{11} and $(k_9/k_{-9})(k_{10}/k_{-10}) = K_9K_{10}$ are set to the experimental values inferred from Figure 4 and eq 26, with all other rate parameters set to sufficiently large values that reactions 9–11 are rate-determining. Agreement between simulation and experiment is good, within the experimental error of the rate parameters, in both cases. The simulation in Figure 5 at relatively low values of $[HIO_3]_0$ and $[HClO_4]_0$ (lower) shows only a small fraction of I^- tied up as $H_2I_2O_3$, while the simulation at the highest values of $[HIO_3]_0$ and $[HClO_4]_0$ used experimentally (upper) shows a significant fraction of I^- tied up as $[H_2I_2O_3]$. Of note is that the small induction period appearing experimentally in Figure 6 is reproduced in the simulation (Figure 5 upper). This induction period appears in the simulation because of the time required for the formation of the intermediate $H_2I_2O_3$. Its appearance in both experiment and simulation is further evidence in support of the assumption of accumulation of stoichiometrically significant quantities of it in the Dushman reaction. Assuming that the proton transfer in reaction 10 is very rapid suggests that the value of $(k_{10} + k_{-10}) \approx 2.5 \times 10^5\ M^{-1}\ s^{-1}$ assumed in the simulation accurately reflects the time scale of formation of $H_2I_2O_3$ in reactions 9 and 10.

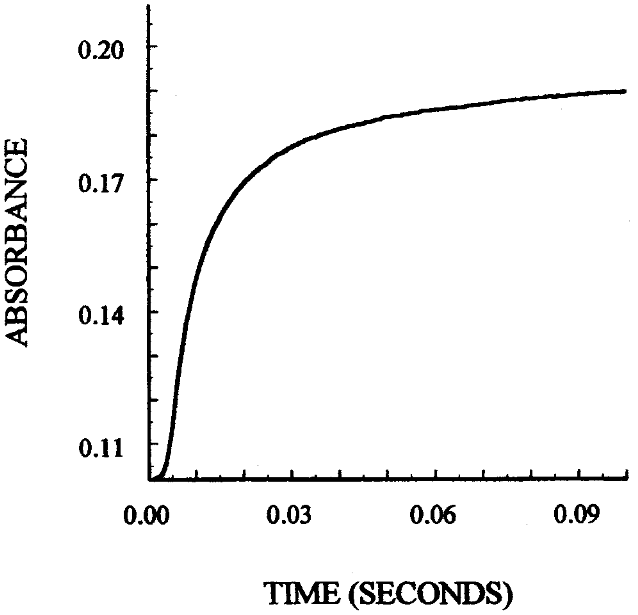


Figure 6. Stopped-flow kinetic data, absorbance vs time, for an experiment with $[HClO_4]_0 = 0.489$ M; $[KIO_3]_0 = 0.004\,48$ M; and $[KI]_0 = 0.000\,576$ M.

Discussion

Assuming the intermediacy of $H_2I_2O_3$ or its anhydride I_2O_2 in the reaction of I^- with IO_3^-, and that this species may accumulate to stoichiometrically significant levels in which the reactant present in excess complexes a substantial fraction of the other reactant, rationalizes both our data at $[IO_3^-]_0 \gg [I^-]_0/5$ and much of the complexity of previous experimental results under other conditions. The major experimental support for this assumption is the appearance of saturation kinetics in $[HClO_4]_0$ and particularly $[HIO_3]_0$. The importance of $H_2I_2O_3$ in the I^-/IO_3^- reaction, while the equivalent species $H_2Br_2O_3$ does not appear to be important in the Br^-/BrO_3^- reaction, likely results from the greater size and ability of iodine to expand its valence shell as compared to bromine, and the greater electronegativity of bromine as compared to iodine. Analogous reasoning suggests that $H_2I_2O_2$ or its anhydride I_2O likely is important in the reaction of HIO_2 with I^-.

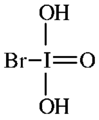
The $[HClO_4]_0$ and $[HIO_3]_0$ dependence of the I^-/IO_3^- reaction may be more complex than is indicated here and deserves further investigation. The complexity of iodic acid solutions has been considered by Furuichi and Liebhafsky,[27] who also found a form of saturation kinetics in the I^-/IO_3^- reaction and discussed the existence of $H_2I_2O_3$. Indeed, while the data presented here are best fitted by eq 5, the severe saturation of k_{exp} seen at the highest values of $([HIO_3]_0[H^+]_0)$ in Figure 2 may contain a contribution from

$$HIO_3 + IO_3^- + H^+ \rightleftarrows I_2O_5 + H_2O \tag{31}$$

We assume that I_2O_5 is less reactive with I^- than is HIO_3. This suggestion is in keeping with the major implication of the data reported here that stoichiometrically significant quantities of binuclear, iodine-containing species accumulate in this system.

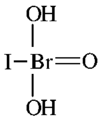
An induction period is observed in some of our experiments, apparently related to the time required for formation of $H_2I_2O_3$. Furthermore, at some wavelengths a transient absorbance is observed, perhaps related to $H_2I_2O_3$. Considerably more work is required to clarify these observations. The I^-/IO_3^- reaction also should be investigated by the stopped-flow kinetic methods for $[IO_3^-]_0 \ll [I^-]_0/5$.

The mixed halogen reactions, I^-/BrO_3^- and Br^-/IO_3^-, are a significant test of the suggestion that $H_2I_2O_3$ forms readily and is quite stable, while $H_2Br_2O_3$ does not. It is expected that



$\mathrm{Br{-}I({=}O)(OH)_2}$

will occur in the Br^-/IO_3^- reaction, leading under some conditions to kinetics second order in $[Br^-]$, while



$\mathrm{I{-}Br({=}O)(OH)_2}$

will not appear in the I^-/BrO_3^- reaction, which will occur instead via an oxygen-transfer mechanism as in the Br^-/BrO_3^- reaction, leading to kinetics first order in $[I^-]$. The kinetics of the I^-/BrO_3^- reaction has been investigated[21,28] and is indeed first order in $[I^-]$, but we know of no definitive kinetic investigation of the Br^-/IO_3^- reaction. This suggestion is supported by the observation[29] of a second-order term in the kinetics of the oxidation of Cl^- by BrO_3^-, presumably resulting from the stability of the species H_2ClBrO_3. Some work has been done on catalysis of the I^-/IO_3^- reaction by Br^- and Cl^-,[14c,30−32] but it is difficult to interpret this work within the context of the ideas presented here.

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