Mechanism of the Reaction between Iodate and Iodide Ions in Acid Solutions (Dushman Reaction)
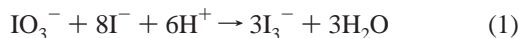
Yi Xie, Michael R. McDonald, and Dale W. Margerum*

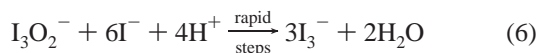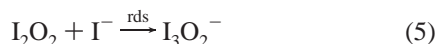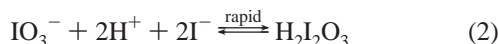Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Introduction

The interaction between iodate and iodide ions to form triiodide (eq 1) has long been used for iodometric methods of

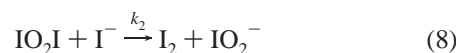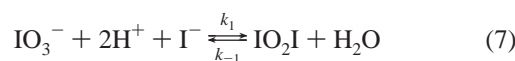$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O \qquad (1)$$

analysis. Burchard[1] studied the reaction rate as early as 1888 but was unable to obtain a rate expression. In his classic 1904 study of the kinetics of the reaction now named for him, Dushman[2] found evidence for a two-term rate expression with one term dependent on $[H^+]^2[I^-][IO_3^-]$ and the other on $[H^+]^2[I^-]^{1.9}[IO_3^-]$. Subsequent work[3] showed that the latter term could be expressed with a second-order dependence in $[I^-]$ to give a fifth-order overall rate expression. At low concentrations of iodide ion the fourth-order term was confirmed[4] with a first-order dependence in $[I^-]$. In 1930, Bray[5] proposed that I_2O_2 and its hydrate, $H_2I_2O_3$, were intermediates in rapid equilibrium with the reactants (eqs 2 and 3) and that their subsequent

$$IO_3^- + 2H^+ + 2I^- \underset{}{\overset{rapid}{\rightleftharpoons}} H_2I_2O_3 \qquad (2)$$

$$H_2I_2O_3 \overset{rapid}{\rightleftharpoons} I_2O_2 + H_2O \qquad (3)$$

$$H_2I_2O_3 \overset{rds}{\longrightarrow} HIO_2 + HOI \qquad (4)$$

$$I_2O_2 + I^- \overset{rds}{\longrightarrow} I_3O_2^- \qquad (5)$$

$$I_3O_2^- + 6I^- + 4H^+ \underset{steps}{\overset{rapid}{\rightleftharpoons}} 3I_3^- + 2H_2O \qquad (6)$$

reactions were the rate-determining steps (eqs 4 and 5) followed by a series of fast reactions summarized by eq 6. Reactions 2 and 4 accounted for the fourth-order rate term, and reactions 2, 3, and 5 accounted for the fifth-order rate term. Under most experimental conditions, the fifth-order term predominates, and the rest of our discussion concerns this pathway.

In 1968, Barton and Wright[6] showed base (B^-) catalysis of the IO_3^- reaction by carboxylate and phosphate ions, and they derived rate laws in which IO_2I and/or BIO_2I^- were considered to be steady-state intermediates. Their mechanism (without the base catalysis terms) is given in eqs 7 and 8, followed by fast reactions of IO_2^- to give additional I_2 and I_3^-. Under their conditions $k_2[I^-] \ll k_{-1}$, so this mechanism could not be distinguished from a preequilibrium mechanism.

$$IO_3^- + 2H^+ + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} IO_2I + H_2O \qquad (7)$$

$$IO_2I + I^- \overset{k_2}{\longrightarrow} I_2 + IO_2^- \qquad (8)$$

In 1979, Liebhafsky and Roe[7] reviewed many different rate expressions that have resulted from kinetic studies of the Dushman reaction. They attempted computer-generated fits to a general mechanism similar to that proposed originally by Bray[5] (who had mentioned Liebhafsky's input 49 years earlier). The rate constants that were generated for the formation and decay of $H_2I_2O_3$ indicated that this species, as well as I_2O_2, should be present in extremely low concentrations. They suggested that the second-order dependence in $[I^-]$ might decrease when the iodide ion concentration became very high. However, they did not test this experimentally.

Most of the debate about rate expressions for the Dushman reaction has concerned the reaction order in $[I^-]$, buffer effects, and contributions from I_3^- at high concentrations. The second-order dependence in $[H^+]$ has not been challenged. However, the protonation constant, $K_H = [HIO_3]/[H^+][IO_3^-]$, to form iodic acid was determined in 1939 by Naidich and Ricci[8] over a wide range of ionic strengths. Their K_H values indicate that above 0.01 M $[H^+]$ the concentration of HIO_3 should be taken into account.

In the present work, we use a flow-mixing technique to test the kinetics and mechanism of the Dushman reaction in much higher concentrations of $[I^-]$ and $[H^+]$ than was possible in previous studies. The PAF-PRO instrument[9] (pulsed-accelerated flow with position-resolved observation) permits the measurement of pseudo first-order rate constants for this reaction over a range of 200−7000 s^{-1}.

Experimental Section

Reagents. Solutions for PAF-PRO studies were prepared with doubly distilled deionized water and were filtered through a 0.4 μm Millipore filter and degassed. Solutions of $HClO_4$ were prepared from the concentrated acid that was purged with Ar to remove volatile trace oxidants prior to dilution. Ionic strength was maintained with $NaClO_4$ that was recrystallized in water before use. Reagent grade $NaIO_3$ and NaI were used. Solutions of NaI were freshly prepared for each set of experiments because I^- is easily oxidized by O_2.

PAF-PRO Method. A detailed description of this instrument has been given previously.[9] A decelerated flow velocity of 20.8−2.0 m/s was used, and transmittance data (353 nm) were collected by use of a CCD detector at 128 different flow velocities for 128 positions along a 2.0 cm observation cell. The light path is 0.203 cm. Each kinetic trace was an average of five pushes. Pseudo-first-order conditions are used where $-d[IO_3]_T/dt = k_r[IO_3]_T$.

Results and Discussion

PAF-PRO Studies. In this method, the progress of a fast reaction is measured as the reactants flow down an observation cell. This instrument is not a stopped-flow device but rather uses continuous flow with a linearly decelerated velocity for a short time period. Turbulent flow exists for the full range of flow velocities (20.8−2.0 m/s) that occurs during each push. A

(1) Burchard, O. *Z. Phys. Chem.* **1888,** *2,* 796.
(2) Dushman, S. *J. Phys. Chem.* **1904,** *8,* 453−482.
(3) Abel, E.; Stadler, F. *Z. Phys. Chem.* **1926,** *22,* 49.
(4) Abel, E.; Hilferding, K. *Z. Phys. Chem.* **1928,** *136,* 186.
(5) Bray, W. C. *J. Am. Chem. Soc.* **1930,** *52,* 3580−3586.
(6) Barton, A. F. M.; Wright, G. A. *J. Chem Soc. A* **1928,** *136,* 186.

(7) Liebhafsky, H. A.; Roe, G. M. *Int. J. Chem. Kinet.* **1979,** *11,* 693−703.
(8) Naidich, S.; Ricci, J. E. *J. Am. Chem. Soc.* **1939,** *61,* 3268−3273.
(9) McDonald, M. R.; Wang, T. X.; Gazda, M.; Scheper, W. M.; Evetts, S. W.; Margerum, D. W. *Anal. Chem.* **1997,** *69,* 3513−3520.
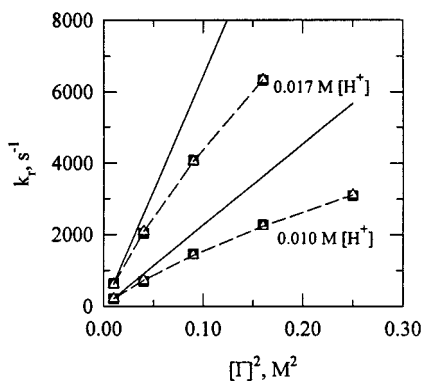
Figure 1. Dependence of the pseudo-first-order rate constant (k_r) on $[I^-]^2$ for the Dushman reaction at 0.017 and 0.010 M $[H^+]$. The solid lines correspond to values with no deviation from a squared dependence in $[I^-]$: ■, experimental data (25.0 °C, $\mu = 0.50$ M); △, global fit for the steady-state mechanism (dashed line) with $k_1 = (4.8 \pm 0.2) \times 10^7$ M^{-2} s^{-1}, $k_2/k_{-1} = 2.3 \pm 0.2$ M^{-1}, and $K_H = 2.53$ M^{-1}.

high degree of bulk mixing (macromixing) of the reactant solutions takes place in the 10-jet mixer before the reaction mixture enters the observation part of the cell. As this pseudohomogeneous solution travels down the cell, the turbulent flow permits relatively rapid micromixing to occur. The physical mixing rate constant (k_{mix}, s^{-1}) is a measure of the time dependence of micromixing. It is velocity dependent ($k_{mix} = k_m \nu$) because mixing increases with turbulence and the degree of turbulence of the reaction mixture increases with flow velocity. The reciprocal of the apparent rate constant for the reaction (k_{app}) has been shown to equal the sum of the reciprocals of the mixing rate constant and the rate constant (k_r) of the chemical reaction.[9-11] This leads to eq 9. Since k_{app} and ν are

$$\frac{1}{k_{app}} = \frac{1}{k_m}\frac{1}{\nu} + \frac{1}{k_r} \qquad (9)$$

measured, the k_r and k_m values are resolved for each run. PAF methods[9-11] permit rate constants for fast reactions to be determined because it is not necessary to wait for complete micromixing before measurements are taken.

PAF-PRO results for k_r are determined as $[I^-]$ increases from 0.10 to 0.50 M in 0.010 M $[H^+]$ and in 0.017 M $[H^+]$. Results also are obtained as $[H^+]$ varies from 0.03 to 0.21 M at a constant $[I^-]$ concentration of 0.030 M. Ionic strength is kept constant at 0.50 M with NaClO₄, HClO₄, and NaI. Low initial concentrations of IO_3^- are used (5.34×10^{-5} M) so that the I_3^- produced is at too low a level to contribute to the kinetics.[7] In these experiments we are able to measure pseudo-first-order rate constants for the Dushman reaction that are many orders of magnitude greater than previously determined values. Our results show deviation from the expected dependence in $[I^-]^2$ (Figure 1) and from the expected dependence in $[H^+]^2$ (Figure 2). The results also permit us to distinguish between a preequilibrium mechanism and a steady-state mechanism.

Mechanisms. We know from our results as well as the careful work of Naidich and Ricci[8] that appreciable HIO_3 exists in solutions at higher acidity. Their K_H value was 2.53 M^{-1} at 25.0 °C and $\mu = 0.50$ M, which agrees with our experimental value obtained from kinetic results. The formation of HIO_3 is a logical first step for a mechanism because proton-transfer
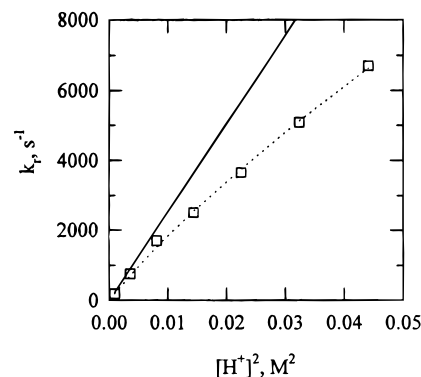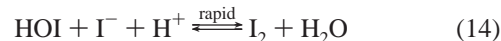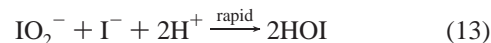
(10) Bowers, C. P.; Kimber, D. F.; Nagy, J. C.; Ridley, T. Y.; Wang, Y. L.; Evetts, S. W.; Margerum, D. W. *Anal. Chem.* **1997**, *69*, 431−438.

(11) Nemeth, M. T.; Kimber, D. F.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* **1987**, *59*, 283−291.
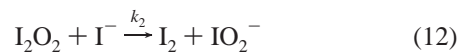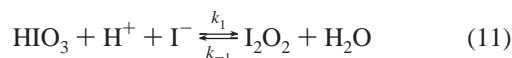
Figure 2. Dependence of k_r on $[H^+]^2$ at $[I^-] = 0.030$ M, $\mu = 0.50$ M. The solid line corresponds to the values with no reduction for HIO_3 formation: □, experimental; dotted line calculated for $K_H = 2.5 \pm 0.6$ M^{-1}, where the I^- effect causes only a 7% reduction of k_r.

reactions are known to be very rapid[12] even with bases as weak as IO_3^-. Two mechanisms can be written that would lead to the described saturation effects in $[H^+]$ and in $[I^-]$ concentrations.

Mechanism with I_2O_2 as a Steady-State Species.

$$H^+ + IO_3^- \overset{K_H}{\rightleftharpoons} HIO_3 \qquad (10)$$

$$HIO_3 + H^+ + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_2O_2 + H_2O \qquad (11)$$

$$I_2O_2 + I^- \overset{k_2}{\longrightarrow} I_2 + IO_2^- \qquad (12)$$

$$IO_2^- + I^- + 2H^+ \overset{rapid}{\longrightarrow} 2HOI \qquad (13)$$

$$HOI + I^- + H^+ \overset{rapid}{\rightleftharpoons} I_2 + H_2O \qquad (14)$$

$$I_2 + I^- \overset{rapid}{\rightleftharpoons} I_3^- \qquad (15)$$

For $[IO_3]_T = [HIO_3] + [IO_3^-]$

$$\frac{-d[IO_3]_T}{dt} = \frac{(k_1(k_2/k_{-1})K_H[H^+]^2[I^-]^2)[IO_3]_T}{(1 + K_H[H^+])(1 + (k_2/k_{-1})[I^-])} \qquad (16)$$

so that the pseudo-first-order rate constant for this mechanism, k_{ss}, is given by eq 17.

$$k_{ss} = \frac{k_1(k_2/k_{-1})K_H[H^+]^2[I^-]^2}{1 + K_H[H^+] + (k_2/k_{-1})[I^-] + K_H(k_2/k_{-1})[H^+][I^-]} \qquad (17)$$

Rate constants for eq 14 are known ($k_f = 4.4 \times 10^{12}$ M^{-2} s^{-1})[13] as are rate constants for eq 15 ($k_f = 5.6 \times 10^9$ M^{-1} s^{-1}).[14,15] Equation 13 represents a combination of rapid steps. At these high acidities, IO_2^- would be expected to immediately form HOIO. The rate constant for the reaction of HOIO with H^+ and I^- is not known, but reverse reactions suggest that it might proceed through I_2O before HOI is formed.[16] All these reactions are rapid and occur after the rate-determining steps.

(12) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1−72.

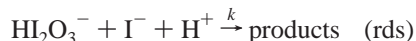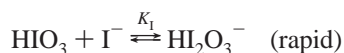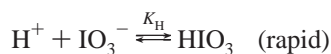(13) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355−1361.

(14) Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554−1559.

(15) Rausse, M.; Aubard, J.; Galland, B.; Adenier, A. *J. Phys. Chem.* **1986**, *90*, 4382−4388.

(16) Urbansky, E. T.; Cooper, B. T.; Margerum, D. W. *Inorg. Chem.* **1997**, *36*, 1338−1344.

Mechanism with Preequilibrium of Reactants.

$$H^+ + IO_3^- \overset{K_H}{\rightleftharpoons} HIO_3 \quad (rapid)$$

$$HIO_3 + I^- \overset{K_I}{\rightleftharpoons} HI_2O_3^- \quad (rapid)$$

$$HI_2O_3^- + I^- + H^+ \overset{k}{\rightarrow} products \quad (rds)$$

For $[IO_3]_T = [HIO_3] + [IO_3^-] + [HI_2O_3^-]$

$$\frac{-d[IO_3]_T}{dt} = \frac{kK_HK_I[H^+]^2[I^-]^2[IO_3]_T}{1 + K_H[H^+](1 + K_I[I^-])} \quad (18)$$

so that the pseudo-first-order rate constant for this mechanism, k_{PE}, is given by eq 19.

$$k_{PE} = \frac{kK_HK_I[H^+]^2[I^-]^2}{1 + K_H[H^+] + K_HK_I[H^+][I^-]} \quad (19)$$

It can be seen that k_{ss} and k_{PE} values will have very similar $[H^+]$ and $[I^-]$ dependencies except that the k_{ss} values have an additional term, $(k_2/k_{-1})[I^-]$, in the denominator. This difference makes it possible to distinguish between these two mechanisms at high I^- concentrations.

Figure 2 shows the dependence of the experimental k_r values on the square of the hydrogen ion concentration at $[I^-] = 0.030$ M. Appreciable HIO_3 formation causes deviation from a linear dependence, and the best fit gives $K_H = 2.5 \pm 0.6$ M^{-1}. At this low I^- concentration, the $[I^-]$ terms in the denominator make only a 7% contribution, but this is taken into account with the fit shown.

Figure 1 shows the dependence of the experimental k_r values as a function of $[I^-]^2$ at $[H^+] = 0.010$ and 0.017 M. The data show an excellent fit (dashed line) for the steady-state mechanism (k_{ss}) for both acidities, where $k_2/k_{-1} = 2.3 \pm 0.2$ M^{-1} and $k_1 = (4.8 \pm 0.2) \times 10^7$ M^{-2} s^{-1}. On the other hand, attempts to fit the k_{PE} values gave K_I values that differ by a factor of 5 at the two acidities and attempts to combine the data sets to give global fits of k_{PE} were not satisfactory. We conclude that the steady-state mechanism is valid. As outlined previously,

Scheme 1. Proposed Mechanism for I^- and H^+ Reaction with HIO_3 To Give I_2O_2 as a Steady-State Intermediate That Reacts with I^- To Form I_2 and IO_2^- [a]
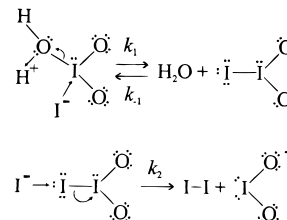
[a] Subsequent reactions of IO_2^- with H^+ and I^- to form I_2/I_3^- are rapid.

Barton and Wright[6] also suggested a steady-state mechanism but could not show that it existed. The steady-state species could be either I_2O_2 or its hydrate, $H_2I_2O_3$. Our results are consistent with Liebhafsky and Roe's suggested mechanism. Although in a steady-state situation only the ratio of k_2/k_{-1} can be determined, Liebhafsky and Roe assumed values of the individual rate constants in their computer-aided analysis. They were not able to measure rate constants with sufficiently high values of $[I^-]$ to test their estimates. Their predicted ratio of k_2/k_{-1} is eight times larger than our experimental value. Our value for the fifth-order rate constant ($k_c = k_1(k_2/k_{-1})K_H$) in the absence of saturation effects is 2.8×10^8 M^{-4} s^{-1} at 25.0 °C, $\mu = 0.50$ M.

In conclusion, we can now give a detailed stepwise mechanism for the reaction of iodate and iodide ion in acid some 94 years after Dushman first investigated the system. Scheme 1 shows the suggested pathway for eq 11, where nucleophilic I^- attack on the central I^{IV} atom accompanied by oxygen protonation leads to the elimination of H_2O and the formation of I_2O_2. In the subsequent step (eq 12), nucleophilic I^- attack on the I^I atom gives I_2 and IO_2^-. The ease with which iodine can expand its number of valence electrons is important in achieving the transition states for each reaction.

Supporting Information Available: A listing of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.