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Large Amplitude pH Oscillation in the Oxidation of Hydroxylamine by Iodate in a Continuous-Flow Stirred Tank Reactor[1]

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Large amplitude pH oscillation occurs in the iodate oxidation of hydroxylamine in a continuous-flow stirred tank reactor (CSTR) in a narrow range of flow rates and input concentrations. In addition to pH, the redox potential, the iodide ion concentration, the rate of gas (N_2O) formation, and the color of the solution (I_2) change periodically. The oscillatory period is extremely long, 2–6 h. The dynamical behavior of the reaction was modeled by a scheme that takes into account the following component processes: the protonation equilibrium of NH_2OH, the dissociation of water, the direct redox reaction between IO_3^- and NH_3OH^+, the Dushman reaction between IO_3^- and I^-, the autoinhibitory reaction between I_2 and NH_3OH^+, the fast dimerization of NOH to N_2O, the reaction of NOH with NH_2OH, and the volatility of iodine. Empirical rate laws of the component reactions were used successfully to calculate the kinetic behavior in a closed system, as well as in the CSTR.

Introduction

As part of our program to design new oscillatory reactions, we recently demonstrated that the periodate oxidation of hydroxylamine can show sustained pH oscillations in a continuous-flow stirred tank reactor (CSTR).[3] However, our earlier experimental efforts failed to find oscillation when iodate was used instead of periodate as the oxidant.

We did not accept this failure as the final result, because it was clear that the periodate is reduced to iodate rather quickly in the early stages of the oscillatory reaction and the iodate oxidation of the remaining hydroxylamine must dominate on the time scale of the flow experiments on that system. The iodate oxidation must thus be a subsystem of the periodate oscillator. Earlier studies reveal that there are other similarities between the periodate and iodate systems. Similar oligo-oscillatory kinetics were found in both the periodate and iodate oxidations of hydroxylamine in a closed reactor. In both cases, the concentration of iodide ion shows three extrema in acidic buffered solution.[4] Furthermore, the empirical rate law model we proposed[3] for the periodate–hydroxylamine oscillator predicts oscillation for the iodate–hydroxylamine reaction as well.

With these considerations in mind, we continued to search for oscillation in the iodate–hydroxylamine reaction in an extended region of the experimental constraint space. We report here that oscillation does take place in the iodate–hydroxylamine reaction in a CSTR in unbuffered aqueous solution. Oscillations can be observed in several experimentally measurable quantities: the pH, the potential of a Pt electrode, [I^-], the rate of gas evolution, and the color of the solution (i.e., [I_2]). The conditions of the present oscillations are somewhat different from those of the periodate–hydroxylamine oscillator. Perhaps the most striking feature of the iodate–hydroxylamine oscillator is that it has an unusually long period. In this paper, we present both our experimental observations and an empirical rate law model for the iodate–hydroxylamine reaction.

Experimental Section

Materials. Hydroxylamine sulfate (Aldrich), sodium iodate, and standardized solutions of sodium hydroxide were used in the CSTR experiments. Sodium acetate, acetic acid, sodium thiosulfate, sodium iodide, sulfanilic acid (all Fisher), iodine (Merck), and 1-naphthylamine (Fluka) were of the highest purity available and were used without further purification. Stock solutions were prepared with deionized water by dissolving accurately weighed amounts of chemicals or, in the case of sodium hydroxide, by diluting standard solutions. Working solutions were made by diluting stock solutions.

Analytical Procedures. As in our study of the hydroxylamine–periodate reaction,[3] the pH was determined with an Aldrich pH electrode and [I^-] was measured with a calibrated Orion iodide-selective electrode and a saturated calomel electrode as reference. The redox potential was measured with a bright platinum electrode. The sum of the free iodine and triiodide ions could be followed spectrophotometrically at their isosbestic point (468 nm, $\epsilon = 740$ dm^3 mol^{-1} cm^{-1}). The nitrite ion concentration was determined by using the Griess–Ilosvay reaction.[5]

Kinetic Experiments. The reaction was studied in both batch and CSTR configurations at room temperature (25 °C). Three input solutions were used for the CSTR experiments: hydroxylamine sulfate, sodium hydroxide, and sodium iodate. They were not prethermostated. The air temperature in the laboratory was kept constant (23–25 °C) and close to the temperature of the reactor during the experiments. The basic methods and the apparatus have been described in our earlier work.[3] A few modifications were introduced because of the very slow inflow required by the oscillatory reaction. We used inlet tubes with a smaller (1-mm) i.d., and the input solutions used for the CSTR experiments were pretreated under vacuum to remove dissolved gases. Without this treatment, gas bubbles formed in the inlet tubes, which disturbed the stability of the inflow during the unusually long duration of the experiments. Control experiments showed that atmospheric oxygen does not affect the reaction.

Results

Stoichiometry. The stoichiometry of the oxidation of hydroxylamine by iodate is complex and depends upon the ratio of the initial concentrations of the reactants.[4] The pH affects the stoichiometry as well. Hydroxylamine may be oxidized to N_2O, NO, and/or NO_2^-, and iodate is reduced to iodine or iodide depending on the initial conditions. In the concentration range and pH range of the oscillatory behavior (hydroxylamine in 5-fold excess and 3 < pH < 5), iodate is reduced completely to iodide, while an overwhelming majority of the hydroxylamine is oxidized to dinitrogen oxide, and no nitrite ion is detected as a reaction product or intermediate.

$$2IO_3^- + 6NH_3OH^+ \rightarrow 2I^- + 3N_2O + 9H_2O + 6H^+ \quad (1)$$

Since nitrite ion plays a critical role in the periodate oscillator, its absence here indicates an important difference between the two oscillators. We found the amount of iodate reacting to be

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[1] Part 63 in the series Systematic Design of Chemical Oscillators. Part 62: Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 1812.

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[3] Rábai, Gy.; Epstein, I. R. *J. Phys. Chem.* **1989**, *93*, 7556.

[4] Beck, M. T. Rábai, Gy. *J. Chem. Soc., Dalton Trans.* **1982**, 1687.

[5] Rábai, Gy.; Beck, M. T. *J. Chem. Soc., Dalton Trans.* **1982**, 573.

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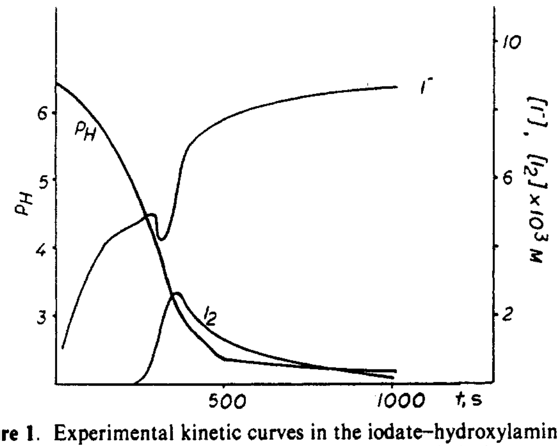

Figure 1. Experimental kinetic curves in the iodate-hydroxylamine reaction in a closed reactor. Initial concentrations: $[IO_3^-]_0$ = 0.010, $[NH_3OH^+]_0$ = 0.050, $[NaOH]_0$ = 0.030 M; T = 25 °C.

a little less than expected from reaction 1, which suggests that some hydroxylamine is oxidized to nitrogen:

$$IO_3^- + 6NH_3OH^+ \rightarrow I^- + 3N_2 + 9H_2O + 6H^+ \qquad (2)$$

The formation of nitrogen was not observed earlier[4] when the reaction was studied at pH 2.5 in the presence of relatively more oxidizing agent ($[NH_3OH^+]_0/[IO_3^-]_0 < 3$). The lack of nitrite ion makes the present system much simpler.

Kinetics Experiments in Batch. The initial pH of the unbuffered system was adjusted to 6.5 with NaOH. The closed reaction system of sodium iodate and hydroxylamine sulfate shows a kinetic behavior similar to that of the Landolt (iodate-sulfite) reaction,[6] exhibiting a pronounced increase in absorbance at a time that depends strongly upon the reactant concentrations and pH. The increase in absorbance in the visible range indicates the formation of iodine. Iodine formation in the iodate-hydroxylamine reaction is considerably slower than in the Landolt reaction. In the Landolt reaction, the appearance of iodine coincides with the complete consumption of sulfite. Here, however, some hydroxylamine remains after the first manifestation of the I_2 color. The reaction between iodine and hydroxylamine is relatively slow in the presence of iodide and at low pH. At the concentrations at which oscillation occurs, the accumulation of iodine is transient and I_2 disappears in a slow reaction with the remaining hydroxylamine. At higher initial iodate concentrations, iodine becomes the final product. Typical experimental curves are shown in Figure 1. The curve of $[I^-]$ vs time generally increases, except for a small minimum that occurs just before $[I_2]$ reaches its maximum. The decrease in pH shows a slight "S" shape. The first part of the reaction is accompanied by moderate gas evolution, which stops almost totally when the pH drops and iodine starts to form.

Dynamical Behavior in a CSTR. In an open CSTR, the reaction exhibits two different steady states and an oscillatory state depending on the input concentrations and flow rates. At a given ratio of input concentrations, a relatively high flow rate can keep the system in a state resembling the stage that precedes the sharp pH drop under closed conditions. In this steady state (SSI, flow branch), the reaction mixture is colorless (no iodine) and it is characterized by a relatively high pH (4.4-4.7). At lower flow rates, the reaction can approach its equilibrium state. The reaction mixture then has a yellow color, because of the presence of iodine in this second steady state (SSII, thermodynamic branch). The pH in SSII is between 2.8 and 3.2.

Sustained oscillation can arise at intermediate flow rates, as shown in Figure 2. This experiment was begun by filling the reactor at a flow rate of $k_0 = 0.01$ s^{-1}. The flow rate was then reduced to 2.5×10^{-4} s^{-1}. After the decrease in flow rate, the pH dropped sharply and then rose in an apparently autocatalytic fashion before decreasing to the final value of SSI. The oscillatory state is reached by a further decrease of the flow rate. At k_0 =

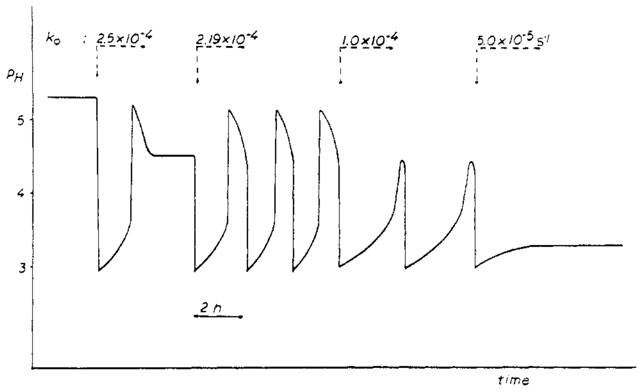

Figure 2. Observed dynamical behavior of the iodate-hydroxylamine reaction in a CSTR at different flow rates (reciprocal residence time, k_0, s^{-1}). Arrows indicate changes of the flow rate. Input concentrations in the combined feed: $[IO_3^-]_0$ = 0.010, $[NH_3OH^+]_0$ = 0.050, $[NaOH]_0$ = 0.030 M; T = 25 °C.

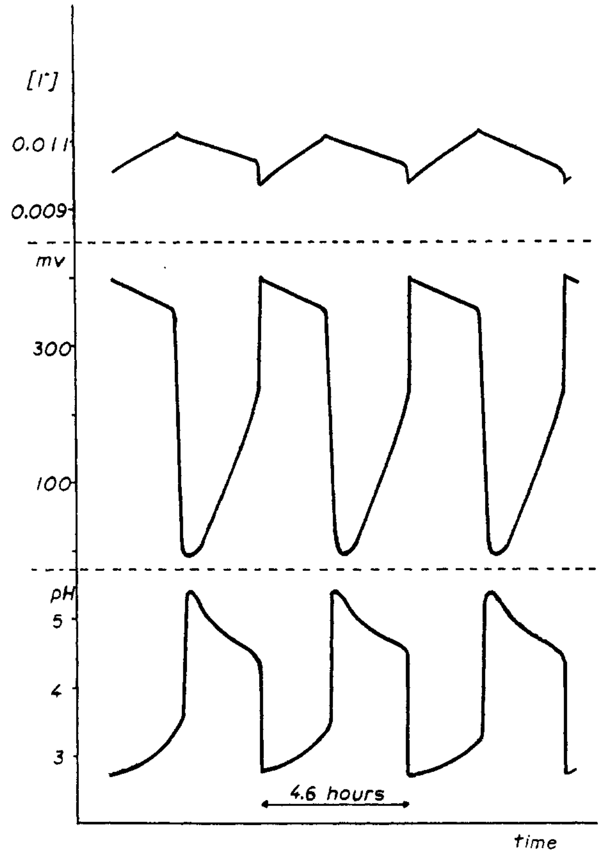

Figure 3. Typical oscillatory traces of iodide ion concentration, redox potential, and pH measured in the iodate-hydroxylamine reaction in a CSTR. Input concentrations: $[IO_3^-]_0$ = 0.0130, $[NH_3OH^+]_0$ = 0.050, $[NaOH]_0$ = 0.040 M; $k_0 = 1.51 \times 10^{-4}$ s^{-1}, T = 25 °C.

2.19×10^{-4} s^{-1}, sustained oscillations occur. The amplitude of the oscillations decreases and the period increases with decreasing flow rate. Finally, at very low flow rates, the oscillations cease and the system reaches SSII (Figure 2).

Oscillations can be monitored not only in the pH but in the redox potential and in $[I^-]$ as well. Oscillatory traces are shown in Figure 3. The amplitude of the pH oscillation can be as large as 2.5 pH units. The change in redox potential may reach 400 mV in each period, corresponding to 7 orders of magnitude change in the concentration of the species responsible for the redox potential. Although a periodic change can be detected in the iodide ion concentration, $[I^-]$ always remains high at about $(1-1.1) \times 10^{-2}$ M, very close to $[IO_3^-]_0$, indicating nearly all of the iodate is reduced to iodide during the oscillatory reaction. Both the periodic appearance of elementary iodine (as I_3^-) in the low pH

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(6) Landolt, H. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 1317.

stage and the moderate evolution of gas during the high pH stage of the oscillation are easily visible. The period of the oscillation is unusually long, between 2 and 6 h depending on the experimental conditions (4.6 h in the experiment shown in Figure 3).

The ratio of input concentrations is critical for the oscillation. Oscillation takes place only if $2.9 < [NaOH]_0/[IO_3^-]_0 < 3.1$. If this ratio exceeds 3 by 5% or more, the system remains in SSI (high pH) at all flow rates. A similar deviation of the ratio toward the other direction forces the system into SSII. A ratio of 3 corresponds to the ratio of iodate ions consumed to hydrogen ions produced in the stoichiometric reaction (1), which suggests that the H^+ formed must just neutralize all the sodium hydroxide initially present in order for the system to oscillate.

In contrast to the periodate–hydroxylamine system, where two types of bistability are found, no bistability was seen here either between the two steady states or between one of the steady states and the oscillatory state. We note that the long-period oscillations found here in the iodate system can be generated in the periodate system by using an equivalent amount of IO_4^- (e.g., 7.5×10^{-3} M) in place of the IO_3^- (e.g., 1.0×10^{-2} M). However, we were unable to produce the short-period oscillations found in the periodate (0.0173 M)–hydroxylamine (4.9×10^{-2} M) reaction[3] by replacing periodate with an equivalent amount of iodate.

Empirical Rate Law Model

The iodate oxidation of hydroxylamine is a complex reaction, which consists of a number of component reactions. We discuss here a set of such reactions that appears to give an adequate description of the behavior reported above.

Fast Protonation Equilibrium of Hydroxylamine.

$$NH_2OH + H^+ \rightleftharpoons NH_3OH^+ \qquad (M1)$$

The dissociation constant of the hydroxylammonium ion (K_{M1}) is $\sim 1 \times 10^{-6}$ M, e.g., 1.09×10^{-6} M reported by Briegleb.[7] We are not aware of any kinetic investigation of the protonation reaction, (M1). In our earlier work,[3] we used estimated rate constants $k_{M1} = 1 \times 10^{-8}$ M^{-1} S^{-1} and $k_{-M1} = 1 \times 10^2$ s^{-1}, consistent with the value of the dissociation constant. The actual values of these rate constants may be higher, but control calculations show that only their ratio affects the simulated concentration–time curves.

Dissociation of Water. This reaction is an important component process in all pH oscillators, because it controls the $[OH^-]/[H^+]$ ratio in aqueous solution.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (M2)$$

The rate constants for (M2) are[8] $k_{M2}[H_2O] = 1 \times 10^{-3}$ M s^{-1} and $k_{-M2} = 1 \times 10^{11}$ M^{-1} s^{-1}.

Redox Reaction between Iodate and Hydroxylammonium Ion. The redox process starts with a direct interaction between iodate and hydroxylamine:

$$IO_3^- + 3NH_3OH^+ \rightarrow 3NOH + I^- + 3H_2O + 3H^+ \qquad (M3)$$

Earlier,[3] we assumed that hydroxylamine is oxidized to nitrite in a similar component process of the periodate–hydroxylamine oscillator. In that case, hydroxylamine was present in much smaller excess over periodate, and the formation of nitrite ion was detected experimentally. In the reaction with iodate, no nitrite ion was found, so we infer here the formation of the monomer of hyponitrous acid (NOH). We did not attempt to study reaction M3 separately, because (M3) is always accompanied by the reactions between iodate and iodide (reaction M4) and between iodine and hydroxylamine (reaction M5). In a study of oligo-oscillatory behavior in the iodate–hydroxylamine reaction, Beck and Rábai[4] proposed a second-order rate law for reaction M3 and used an estimated rate constant to simulate the observed behavior. We have adopted their rate equation with $k_{M3} = 0.15$ M^{-1} s^{-1}.

$$v_{M3} = -d[IO_3^-]/dt = k_{M3}[IO_3^-][NH_3OH^+] \qquad (M3')$$

It is obvious that (M3) is not an elementary step but consists of stepwise reduction of iodate to iodide by hydroxylammonium ion.

$$IO_3^- + NH_3OH^+ \xrightarrow{\text{slow}} NOH + HIO_2 + H_2O \qquad (M3a)$$

$$HIO_2 + NH_3OH^+ \xrightarrow{\text{fast}} NOH + HIO + H_2O + H^+ \qquad (M3b)$$

$$HIO + NH_3OH^+ \xrightarrow{\text{fast}} NOH + I^- + H_2O + 2H^+ \qquad (M3c)$$

Dushman Reaction. The reaction between iodate and iodide ions[9] is a common component process in ioidate-based oligo-oscillatory and oscillatory reactions.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (M4)$$

The kinetics of this step have been the subject of many investigations, and a two-term rate law has been proposed.[10] A term first order in I^- is important only at low concentrations ($[I^-] < 10^{-3}$ M). The term second order in I^- becomes dominant at higher iodide concentrations as in the present oscillatory system where $[I^-] \sim 10^{-2}$ M. We used rate equation (M4′) in our calculations.

$$v_{M4} = -d[IO_3^-]/dt = k_{M4}[IO_3^-][I^-]^2[H^+]^2$$
$$k_{M4} = 5 \times 10^8 \text{ M}^{-4} \text{ s}^{-1} \qquad (M4')$$

Reaction M4 is responsible for the autocatalysis observed in many iodate oxidations. The more iodine formed, the faster the reaction goes, because iodine reacts faster with the reductant than does iodate.

Reaction between Iodine and Hydroxylamine. This process was studied earlier[5] at about pH 2.5. A variable stoichiometry was found. With excess I_2 or equal reactant concentrations, nitrite is formed. If hydroxylamine is in excess, the main product is N_2O. In the present oscillatory reaction, hydroxylamine is always in excess, and no nitrite is found. We therefore include the reaction

$$NH_3OH^+ + I_2 \rightarrow NOH + 2I^- + 3H^+ \qquad (M5)$$

An empirical rate equation (eq M5′) for reaction M5 was determined by measuring the initial rate of iodine consumption[5]. Both I^- and H^+ were found to exert significant inhibitory effects.

$$v_{M5} = -d[I_2]/dt = \frac{(k_{M5} + k_{M5'}/[H^+])[NH_3OH^+][I_2]}{1 + K[I^-] + Q[I^-]^2 + Q'[IO_3^-] + Q''[IO_3^-][I^-]} \qquad (M5')$$

Further study reveals that an additional inhibitory effect of iodate also must be considered.[4] We used the form of (M5′) and the reported values of the rate constants without any change: $k_{M5} = 2.3$ M^{-1} s^{-1}, $k_{M5'} = 6.7 \times 10^{-2}$ s^{-1}, $K = 785$ M^{-1}, $Q = 4.9 \times 10^4$ M^{-2}, $Q' = 5 \times 10^3$ M^{-1}, and $Q'' = 4 \times 10^6$ M^{-2}.

Dimerization of NOH. The species NOH formed in (M3) and (M5) is not stable. It can form N_2O or N_2 in a dimerization (reaction M6) and a reaction with hydroxylamine (reaction M7), respectively.

$$2NOH \rightarrow N_2O + H_2O \qquad (M6)$$

For the rate law of (M6), we took the simple form

$$v_{M6} = -\tfrac{1}{2}\, d[NOH]/dt = k_{M6}[NOH]^2 \qquad (M6')$$

Bazylinski and Hollocher[11] estimated the rate constant for the dimerization/dehydration of nitroxyl to lie in the range (1.8–7.2) $\times 10^9$ M^{-1} s^{-1}. We were unable to describe the dynamical behavior of the present system with such a high value for k_{M6}, even with a compensatory increase in the rate of the competing step (reaction M7). We used k_{M6} estimated as 1×10^6 M^{-1} s^{-1} in our calculations.

Reaction of NOH and Hydroxylamine. In the presence of hydroxylamine, there is a competition between the dimerization (reaction M6) and the reduction of NOH (reaction M7):[12]

$$NOH + NH_2OH \rightarrow N_2 + 2H_2O \qquad (M7)$$

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(7) Briegleb, G. *Z. Elektrochem.* **1949**, *53*, 350.

(8) Eigen, M. *Discuss. Faraday Soc.* **1954**, *17*, 194.

(9) Dushman, S. *J. Phys. Chem.* **1904**, *8*, 453.

(10) Liebhafsky, H. A.; Roe, G. M. *Int. J. Chem. Kinet.* **1979**, *11*, 693 and references therein.

(11) Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285.

TABLE I: Component Reactions for the Iodate-Hydroxylamine Oscillator

no.	reaction	rate
(M1)	$NH_2OH + H^+ \rightleftarrows NH_3OH^+$	$k_{M1}[NH_2OH][H^+] - k_{-M1}[NH_3OH^+]$
(M2)	$H_2O \rightleftarrows H^+ + OH^-$	$k_{M2}[H_2O] - k_{-M2}[H^+][OH^-]$
(M3)	$3NH_3OH^+ + IO_3^- \rightarrow 3NOH + I^- + 3H_2O + 3H^+$	$k_{M3}[IO_3^-][NH_3OH^+]$
(M4)	$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$	$k_{M4}[IO_3^-][I^-]^2[H^+]^2$
(M5)	$NH_3OH^+ + I_2 \rightarrow NOH + 2I^- + 3H^+$	$\dfrac{(k_{M5} + k_{M5'}/[H^+])[NH_3OH^+][I_2]}{1 + K[I^-] + Q[I^-]^2 + Q'[IO_3^-] + Q''[I^-][IO_3^-]}$
(M6)	$2NOH \rightarrow N_2O + H_2O$	$k_{M6}[NOH]^2$
(M7)	$NH_2OH + NOH \rightarrow N_2 + 2H_2O$	$k_{M7}[NOH][NH_2OH]$
(M8)	$I_2(aq) \rightarrow I_2(gas)$	$k_{M8}[I_2(aq)]$

To the best of our knowledge, the rate of reaction M7 has not been established. For this alternative fate of NOH, we assumed a simple second-order rate law

$$v_{M7} = -d[NOH]/dt = k_{M7}[NOH][NH_2OH] \quad (M7')$$

with an estimated rate constant $k_{M7} = 1 \times 10^3\ M^{-1}\ s^{-1}$.

Evaporation of I_2. In addition to the chemical reactions (M1)-(M7), an important physical process (reaction M8) also must be taken into consideration. Since the period of the oscillation is very long, the volatile iodine has enough time to leave the reactor not only in the liquid output flow but also by evaporation from the solution surface. In a study of the arsenite-iodate reaction, De Kepper et al.[13] determined the rate of evaporation of iodine from a CSTR by monitoring the exponential decay of optical density of an iodine solution in the reactor. The process was characterized by a first-order rate constant, $k_s = 3.4 \times 10^{-3}\ s^{-1}$.

$$I_2(aq) \rightarrow I_2(gas) \quad (M8)$$

The volatility of iodine depends upon such factors as the geometry of the reactor, the stirring and aspiration rates, and particularly the concentration of iodide ion, because of the possibility of formation of the nonvolatile triiodide complex. The $[I^-]$ level is higher by at least 1 order of magnitude in the present case than in the earlier work.[13] We determined the rate of iodine evaporation under the conditions of the present investigation to be $k_{M8} = 1.54 \times 10^{-4}\ s^{-1}$.

The physical process (reaction M8) is extremely important for the oscillation. Related iodate oscillators contain two reductants (sulfite + ferrocyanide,[14] sulfite + thiourea,[15] sulfite + thiosulfate[16]), one of which produces, while the other consumes H^+ during the oxidation. In the periodate-hydroxylamine oscillator, the nitrite generated by the reaction can consume hydrogen ion in a reaction with I^-. In the present case, neither an additional reductant nor any internally generated nitrite is available. However, the formation of iodine in the Dushman reaction (reaction M4) consumes hydrogen ion, and the loss of I_2 from solution by process M8 results in H^+ being depleted, thereby making oscillation possible.

The component reactions and their rate laws are summarized in Table I. Curves calculated for the closed system using this model are presented in Figure 4. They agree well with the measured curves in Figure 1, especially considering that the model has few free parameters. The calculated behavior in a CSTR at several flow rates is shown in Figure 5. Both the range of flow rate over which oscillation occurs and the shape of the curves show good agreement with experiment. The main differences are that the calculated oscillations appear at slightly lower flow rates and the calculated amplitudes are a bit smaller. The calculation reflects the experimental observation that small changes in the input concentrations produce dramatic effects upon the dynamical behavior. Our simulations do not result in oscillation at the input concentrations shown in Figure 3. However, at a slightly higher $[IO_3^-]$, we obtain oscillations very similar to those in the figure. With all other constraints as in Figure 3, oscillation is found in the simulations for $[IO_3^-]_0$ between 0.0135 and 0.0138 M, i.e., about 5% higher than in the experiment. The agreement between Figure 6, calculated with $[IO_3^-]_0 = 0.0136$ M instead of the experimental $[IO_3^-]_0 = 0.0130$ M, and Figure 3 is impressive. The resemblance between the calculated curve of log $[I_2]$ and the measured redox potential suggests that it is primarily the $[I_2]/[I^-]$

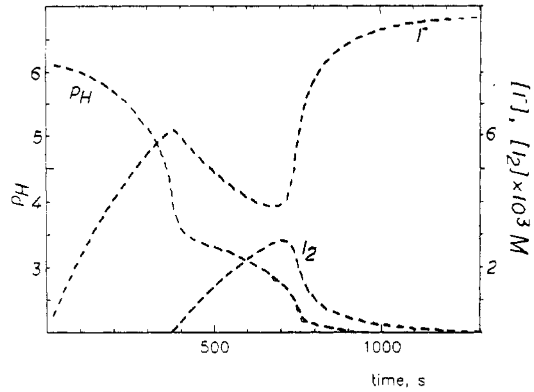

Figure 4. Calculated kinetic curves in the closed system with the initial conditions of Figure 1. The following rate constants were used: $k_{M1} = 1 \times 10^8\ M^{-1}\ s^{-1}$, $k_{-M1} = 1 \times 10^2\ s^{-1}$, $k_{M2}[H_2O] = 1 \times 10^{-3}\ M\ s^{-1}$, $k_{-M2} = 1 \times 10^{11}\ M^{-1}\ s^{-1}$, $k_{M3} = 0.15\ M^{-1}\ s^{-1}$, $k_{M4} = 5 \times 10^8\ M^{-4}\ s^{-1}$, $k_{M5} = 2.3\ M^{-1}\ s^{-1}$, $k_{M5'} = 6.7 \times 10^{-2}\ s^{-1}$, $K = 785\ M^{-1}$, $Q = 4.9 \times 10^4\ M^{-2}$, $Q' = 5 \times 10^3\ M^{-1}$, $Q'' = 4 \times 10^6\ M^{-2}$, $k_{M6} = 1 \times 10^6\ M^{-1}\ s^{-1}$, $k_{M7} = 1 \times 10^3\ M^{-1}\ s^{-1}$, $k_{M8} = 1.54 \times 10^{-4}\ s^{-1}$.

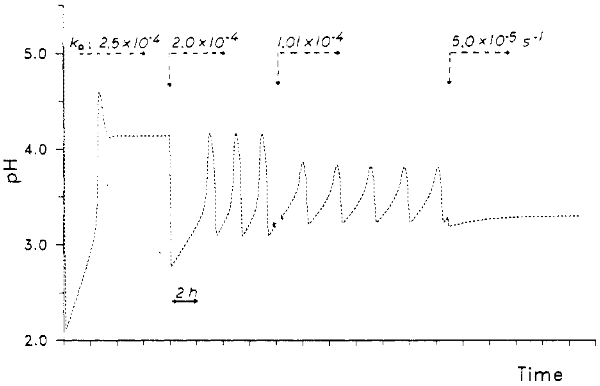

Figure 5. Calculated dynamical behavior in a CSTR. Input concentrations: $[IO_3^-]_0 = 0.01$, $[NH_3OH^+]_0 = 0.05$, $[NaOH]_0 = 0.03$ M. Flow rates are indicated in the figure. Values of the rate constants are given in Figure 4.

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(12) Bonner, F. T.; Dzelkalns, L. S.; Bonucci, J. A. *Inorg. Chem.* **1978**, *17*, 2487.

(13) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 6121.

(14) Edblom, E. C.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 2826.

(15) Rábai, Gy.; Nagy, Zs.; Beck, M. T. *React. Kinet. Catal. Lett.* **1987**, *33*, 23.

(16) Rábai, Gy.; Beck, M. T. *J. Phys. Chem.* **1988**, *92*, 2804.

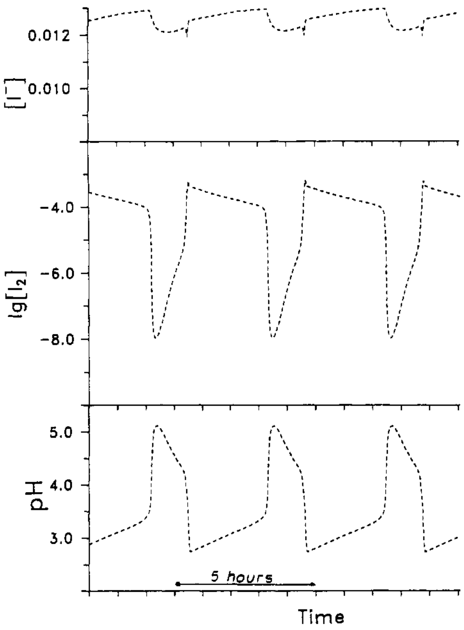

Figure 6. Calculated oscillations. Input concentrations: $[IO_3^-]_0 = 0.0136$, $[NH_3OH^+]_0 = 0.05$, $[NaOH]_0 = 0.04$ M; $k_0 = 1.51 \times 10^{-4}$ s^{-1}. Rate constants as in Figure 4.

ratio that determines the redox potential.

Discussion

The iodate–hydroxylamine oscillator has a number of fascinating features and raises several interesting questions. Its most striking feature, the very long period of oscillation, is to our knowledge rivaled only by the BZ reaction with methylmalonic acid as substrate[17] and by the Bray reaction.[18] There are clearly many biological oscillators with periods of 24 h or even longer. Is the existence of so few long-period chemical oscillators simply a matter of the experimental inconvenience of looking for them? While it seems clear that periodate is rapidly reduced to iodate in the periodate–hydroxylamine system, the increase by over an order of magnitude in the oscillation period and the absence of detectable nitrite suggest that the oscillation in the iodate–hydroxylamine reaction may have a fundamentally different origin. It will be of interest to clarify the relationship between these two systems and to see if each may be capable of supporting two different modes of oscillation.

The essential role of iodine evaporation is another special feature of this system. The removal of one species from the CSTR, not only by the common output flow but also selectively in another way, may be a useful approach to generating new oscillators. Evaporation of bromine plays a key role in several modified BZ-type oscillators[19,20] in a closed system. One may also envision systems in which the selective removal occurs not to the gas phase but to an immiscible liquid phase or by precipitation, as may occur with MnO_2 in the family of permanganate oscillators.[1] Perhaps the most important instances of this phenomenon may occur in biological oscillators where different products can be excreted through membranes at very different rates.

While our model built from component processes succeeds in reproducing the observed dynamics with only a handful of free parameters, it is by no means a complete mechanism for this complex system. The quest for mechanistic details should be aided considerably by the fact that, like the iodate–sulfite–ferrocyanide system,[14] the hydroxylamine–iodate system is one of the few oscillating reactions in which more than one or two periodic properties may be simultaneously monitored. Further detailed study of elementary steps in both the iodate and periodate oxidations of hydroxylamine and their connection to other iodate-based oscillators is an ongoing project in our laboratory.

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(17) Epstein, I. R.; Kustin, K. Unpublished results.

(18) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262.

(19) Beck, M. T.; Bazsa, G.; Hauck, K. *Ber. Bunsenges.* **1980**, *84*, 408.

(20) Noszticzius, Z.; Bodiss, J. *J. Am. Chem. Soc.* **1979**, *101*, 3177.

Isotope Effect on Weak Acid Dissociation

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Weak acid dissociation of the deuterium-substituted 1-naphthol-2-sulfonate potassium salt (1-ROD-2-S) was examined as a function of pD and temperature. The kinetics of k_{dis} and of the recombination rate k_{rec}, in agreement with our findings for 1-ROH-2-S, is dictated by the orientational motions of surrounding water molecules, specifically the Debye relaxation time τ_D. The dissociation rate k_{dis} declines by approximately 1/3 upon deuteration, while the activation barrier ΔE^* associated with k_{dis} remains essentially constant. As in our other studies, this isotope effect is attributed to a larger hydration entropy difference ΔS for the hydration of D^+ compared with H^+.

Introduction

Proton dissociation is one of the most fundamental processes in chemistry.[1] Steady-state measurements, such as those obtained by using the pH indicator, X-ray diffraction, and IR spectroscopy, provide information on equilibrium constants and averaged solution structure. However, the dynamic evolution from the initial-state neutral molecule to the final-state dissociated species cannot be investigated without a measuring technique having ultrafast time resolution.

Using picosecond laser spectroscopic methods and an acid that can be photon initiated on ultrafast time scales, molecular aspects of the proton dissociation process have been developed.[2] The

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(1) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Chapman and Hall: London, 1973.

(2) Robinson, G. W.; Thistlethwaite, P. J.; Lee, J. *J. Phys. Chem.* **1986**, *90*, 4224.

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