For the other two sites A and C ( $\lambda_{det} = 717.2$  and 713.4 nm for the corresponding 479-cm<sup>-1</sup> satellite<sup>11</sup>), no resonances could be found in the investigated frequency range. This result is not surprising, since different sites usually exhibit different zero-field splittings representing different resonance frequencies.<sup>16,17,19</sup> Presumably, the resonances of the sites A and C lie outside the investigated frequency range.

An interesting correspondence can be seen comparing the signal found for the lowest excited state of  $[Os(bpy)_3]^{2+}$  to the ones found for the lowest excited state of neat  $[Ru(bpy)_3](ClO_4)_2$  which is also assigned to be doubly degenerate. In both compounds the

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signals are negative (the second excited state of  $[Ru(bpy)_3]^{2+}$  exhibits positive resonances).<sup>17</sup> This points to similarities in the behavior of the two different complex ions.

#### Conclusion

The assignment of the lowest excited state of the title compound to a nearly degenerate state is substantiated by the observation of a microwave resonance between the sublevels of this state detected as an ODMR signal. From the frequency of the signal the zero-field splitting can be evaluated to be in the order of tenths of a wavenumber. Hence, the lowest excited state of  $[Os(bpy)_3]^{2+}$ can be considered to be nearly degenerate in the scope of the resolution of usual optical absorption and emission spectroscopy.

# Oxidation of Hydroxylamine by Periodate in a Continuous-Flow Stirred Tank Reactor: A New pH Oscillator<sup>1</sup>

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The periodate oxidation of hydroxylamine exhibits a complex and variable stoichiometry at pH 5. There are two limiting cases. In excess periodate the products are nitrate and iodate, while in a large excess of hydroxylamine  $IO_4^-$  is reduced to  $I^-$ , and the nitrogen-containing product is N<sub>2</sub>O. The formation of nitrite ion and iodine is important when neither of the reactants is present in large excess. The reaction shows clock type kinetics in closed conditions if no buffer is present. In a flow reactor sustained oscillations in [H<sup>+</sup>], in color, and in redox potential are found experimentally in a narrow range of flow rate and input concentrations. A simple model is proposed to explain the oscillation.

#### Introduction

Chemical oscillations and related dynamical phenomena have been found almost exclusively in redox reactions. In such reactions in aqueous solution, hydrogen ion is usually involved, and the change in its concentration can be an indicator of, or even drive, the oscillation. The concentration of  $H^+$  can be measured selectively, simply, and reliably, which offers an advantageous experimental method for the study of oscillatory reactions. Many pH oscillators have been found in a continuous-flow stirred tank reactor (CSTR) as well as in closed (batch) systems,<sup>3</sup> and they supply much information concerning the mechanistic requirements for this phenomenon to occur. A complete picture, however, has yet to emerge. In an effort to understand the general nature of hydrogen ion driven oscillators, we have sought new oscillatory systems of this kind.

A peculiarity in the oxidation of hydroxylamine by periodate or iodate at a constant pH of 2.5 is that  $[I^-]$  shows several extrema as a function of time.<sup>4</sup> In an unbuffered reaction mixture of iodate and hydroxylamine,  $[H^+]$  shows an autocatalytic increase followed by a decrease and then a second increase.<sup>5</sup> An analysis of the known pH oscillators suggests that many of them display this kind of change in the concentration of hydrogen ion. Such considerations led to the construction of a new oscillatory reaction from the reactions of hydrogen peroxide with hydrogen sulfite, which produces hydrogen ions in an autocatalytic manner, and hydrogen peroxide-ferrocyanide, which consumes them.<sup>6</sup> Since the hydroxylamine-periodate (or iodate) reaction involves a similar pair of component processes, we anticipated that these systems might give rise to pH driven oscillation in a CSTR.

Our experimental investigations reveal several types of bistability and oscillation in pH, in the potential of a Pt electrode, and in the color of the solution, which is due to the appearance and disappearance of iodine, when hydroxylamine is oxidized by periodate in a CSTR. Despite concerted efforts, we were unable to find any indication of similar oscillatory behavior in the iodate oxidation of hydroxylamine.

#### **Experimental Section**

*Materials*. Hydroxylamine sulfate (Aldrich), sodium metaperiodate, sodium hydroxide, 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 made with doubly distilled water. The periodate stock solution was protected from light during storage.

Analytical Procedures. Hydroxylamine was determined iodometrically by using starch as indicator and solid magnesium oxide to adjust the pH according to Bartousek.<sup>7</sup> The iodide ion concentration was measured with an Orion iodide selective electrode and a saturated calomel electrode as reference. The concentration of iodine was followed spectrophotometrically at the isosbestic point of I<sub>2</sub> and I<sub>3</sub><sup>-</sup> (468 nm,  $\epsilon = 740$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). The nitrite ion concentration was determined as described earlier<sup>8</sup>

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TABLE I: Concentrations of Iodine and Nitrite Ion Formed in the Hydroxylamine-Periodate Reaction at Different Initial Periodate Concentrations<sup>4</sup>

10 <sup>3</sup> [IO <sub>4</sub> <sup>-</sup> ] <sub>0</sub> , M	10 <sup>3</sup> [I <sub>2</sub> ], M	10 <sup>3</sup> [NO <sub>2</sub> <sup>-</sup> ], M
2.00	0.0	0.0
4.00	0.0	0.0
6.00	0.415	3.6
8.00	2.29	4.6
10.00	2.57	5.3
12.00	2.65	5.8
14.00	2.45	6.2
16.00	2.01	6.9
18.00	1.50	6.8
20.00	1.01	6.5

<sup>a</sup> pH = 5.0 (0.2 M acetate buffer),  $[NH_2OH]_0 = 0.020 \text{ M}$ , T = 25.0 °C.

by using the Griess-Ilosvay reaction. In the stoichiometric experiments the pH was adjusted and kept constant with 0.2 M acetate buffer.

Kinetic Experiments in Batch. In contrast to the stoichiometric investigations, the kinetic runs were carried out without a buffer, and the initial pH was adjusted by adding sodium hydroxide to the acidic hydroxylamine sulfate solution. The reactions were started by adding periodate solution to the reaction mixture, which was stirred magnetically in a thermostated reaction vessel. The pH, [I<sup>-</sup>], and [I<sub>2</sub>] were monitored. The moderate gas evolution did not disturb the kinetic experiments significantly.

Flow Experiments. The flow experiments were performed in a thermostated glass CSTR of volume 50.0 mL equipped with a pH, Pt, or iodide selective electrode and a magnetic stirrer. To avoid the accumulation of gas, there was no cap on the reactor, and the effluent was removed by aspiration. The reactor was fed with solutions of hydroxylamine sulfate, sodium hydroxide, and sodium periodate through three 3.5-mm-i.d. Tygon inlet tubes by a Sage Model 375A peristaltic pump. Before starting the flow, 5 mL of water was poured into the CSTR to avoid local inhomogeneity and formation of iodine in the initial reaction mixture.

#### Results

Stoichiometry. Variable stoichiometry is a frequent observation in the oxidation of hydroxylamine. In reactions with one-electron oxidizing agents an important product is elementary nitrogen.9,10 Reagents capable of transferring two electrons in a single step usually oxidize hydroxylamine to higher oxidation states (N<sub>2</sub>O, NO,  $NO_2^{-}$ ),<sup>8,11</sup> and no formation of  $N_2$  is observed. Our experiments show that the stoichiometry of the periodate-hydroxylamine reaction is also complex, varying with the ratio of the reactants and with other conditions. Iodate ion, elementary iodine, and iodide ion can form as the reduction products of periodate. The relatively stable oxidation products of hydroxylamine are N<sub>2</sub>O, NO<sub>2</sub>, and NO<sub>3</sub>.

Two limiting stoichiometries must be considered. In a large excess of hydroxylamine eq 1 is chemically reasonable and thermodynamically favorable.

$$IO_4^- + 4NH_2OH \rightarrow 2N_2O + I^- + 6H_2O$$
(1)

Our studies show that if  $[NH_2OH]_0/[IO_4^-]_0 > 4$ , the only detectable iodine-containing product is iodide ion, and its measured concentration equals the initial concentration of periodate. Iodometric titration of the remaining hydroxylamine verifies the stoichiometry of eq 1. No nitrite ion is detected.

The other limiting case is eq 2, which is relevant in large excess

$$3IO_4^- + NH_2OH \rightarrow NO_3^- + 3IO_3^- + H_2O + H^+$$
 (2)

of periodate. If  $[IO_4^-]_0/[NH_2OH]_0 > 3$ , we find no I<sup>-</sup> or I<sub>2</sub>, and



Figure 1. Kinetic curves in the periodate-hydroxylamine reaction in a closed reactor. Iodine precipitated in the late stage of the reaction.  $[IO_4^-]_0 = 0.025$ ,  $[NH_3OH^+]_0 = 0.050$ ,  $[NaOH]_0 = 0.050$  M; T = 25.0٥Ċ.

only  $IO_3^-$  can be identified as a reduction product of periodate. We observe no significant gas evolution, but when  $[IO_4^-]_0/$  $[NH_2OH]_0 < 10$ , we do find transient formation of nitrite ion, some of which persists even after long reaction times. Thus, the stoichiometry of eq 2 is only a limiting case. When the initial concentration ratio lies between the two above values  $(1/_4 <$  $[IO_4^-]_0/[NH_2OH]_0 < 3$ ), the formation of NO<sub>2</sub><sup>-</sup> and I<sub>2</sub> has important consequences for the oscillatory system. Table I shows the concentrations of iodine and nitrite formed at different initial periodate concentrations at pH = 5. Both  $[I_2]$  and  $[NO_2^-]$  show maxima as functions of the initial periodate concentration. The formation of iodine is due to the Dushman reaction:<sup>12</sup>

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

The oxidation of hydroxylamine by iodate or iodine is the most likely source of nitrite. Iodate and iodine can oxidize hydroxylamine to nitrite in acidic medium:4,8

$$3NH_2OH + 2IO_3^- \rightarrow 3NO_2^- + 2I^- + 3H_2O + 3H^+$$
 (4)

$$NH_2OH + 2I_2 + H_2O \rightarrow NO_2^- + 4I^- + 5H^+$$
 (5)

Nitrite formed in reactions 4 and 5 reacts with both iodide and excess hydroxylamine.

$$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O$$
 (6)

$$NH_2OH + NO_2^- + H^+ \rightarrow N_2O + 2H_2O$$
 (7)

All the above reactions affect the stoichiometry of the hydroxylamine-periodate reaction. There are further, less significant reactions, which have not been taken into account in present study.

Kinetic Experiments in Batch. If the initial pH of the reaction mixture of hydroxylamine and periodate is adjusted near neutral, and the ratio of the initial concentrations is in the range that gives oscillation in the CSTR, we observe a small decrease in pH followed by a much larger pH drop, indicating that large amounts of H<sup>+</sup> are liberated as the protonated hydroxylamine is consumed during the reaction. The concentration of iodide ion increases, but no detectable iodine forms in this stage of the reaction (Figure 1). In the second stage of the reaction the pH increases, [I<sup>-</sup>] drops, and [I2] forms rapidly. Similar kinetic behavior is observed in the halogen-based clock reactions. This similarity is important. because from those reactions overshoot-undershoot<sup>13</sup> and oscillatory14,15 systems were constructed by adding appropriate reagents.

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Figure 2. pH vs time in the closed system at different  $[IO_4^-]_0$ . [NH<sub>3</sub>OH<sup>+</sup>]<sub>0</sub> = 0.050, [NaOH]<sub>0</sub> = 0.050, [IO<sub>4</sub><sup>-</sup>]<sub>0</sub> = 0.030 (a), 0.020 (b), 0.015 (c), 0.012 (d), 0.010 (e) M; T = 25.0 °C.



Figure 3. Measured (--) and calculated (---) pH oscillations in a CSTR.  $[IO_4^-]_0 = 0.0173$ ,  $[NH_3OH^+]_0 = 0.049$ ,  $[NaOH]_0 = 0.0457$  M; flow rate  $k_0 = 1.4 \times 10^{-3} \text{ s}^{-1}$  at 25 °C and 2.1 × 10<sup>-3</sup> s<sup>-1</sup> at 30 °C. The following set of rate constants were used for the calculations:  $k_8 = 1 \times 10^8 \text{ M}^{-1}$   $\text{s}^{-1}$ ,  $k_{-8} = 1 \times 10^2 \text{ s}^{-1}$ ,  $k_9 = 10 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{10} = 0.05 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{3} = 5 \times 10^8$  $\text{M}^{-1} \text{ s}^{-1}$ ,  $k_{11} = 400 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_6 = 1 \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$ . No [NaOH] input, but inputs of unprotonated hydroxylamine [NH<sub>2</sub>OH]<sub>0</sub> = 0.049 and [H<sup>+</sup>]<sub>0</sub> = 1 × 10<sup>-7</sup> M were included in the calculations.

The effect of the initial concentration of periodate on the rate of the pH drop is shown in Figure 2. The rate increases with increasing  $[IO_4^{-}]_0$ . In excess periodate the pH change is very fast, indicating that reaction 2 is a rapid one, and it cannot be followed by pH measurement. The reaction is accompanied with moderate gas evolution.

CSTR Experiments. When the reaction is run in the CSTR, we observe two different steady states and an oscillatory state, depending on the input concentrations, flow rate, and temperature. One of the steady states (SSI) is characterized by a relatively high pH (>5.5) and a colorless reaction mixture. In SSI the conversion of the reaction is lower (flow branch) than in the other steady state (SSII, thermodynamic branch), which has a pH of  $\sim 3.5$ . In SSII a yellow color due to elementary iodine is easily visible. In the oscillatory state, the flow system shows periodic changes in pH, in redox potential, and in color. Typical oscillatory traces are shown in Figure 3. Sustained oscillations are found only in a narrow range of flow rates, within  $\pm 5\%$  of the optimum value. The ratio of the input concentrations of hydroxylamine and sodium hydroxide is critical for the oscillation; [NH<sub>2</sub>OH]<sub>0</sub>/[NaOH]<sub>0</sub> must be between 1.0 and 1.1 for oscillation. The periodate:hydroxylamine ratio is less crucial: oscillations are found with 2.5 < $[NH_2OH]_0/[IO_4^-]_0 < 3.5$ . The absolute values of the initial concentrations are not as important as their ratios, but they must



Figure 4. Bistability between stationary and oscillatory states. Arrows indicate points of transition.  $[IO_4^-]_0 = 0.0173$ ,  $[NH_3OH^+]_0 = 0.049$ ,  $[NaOH]_0 = 0.0457$  M; T = 25.0 °C.

be between 0.01 and 0.1 M to get measurable oscillations. As Figure 4 shows, hysteresis is found in the transitions among the three states. The oscillatory state can be reached directly from only one (SSI) of the two steady states. The system can be forced from SSII to SSI by increasing the flow rate to high values.

The temperature affects the position and the shape of the oscillation. The narrow range of flow rates within which the system oscillates shifts to higher  $k_0$  by about a factor of 2 as T is increased from 20 to 30 °C. There is a slight broadening of the oscillatory region and a decrease in oscillation period (Figure 3) with increasing temperature.

### Discussion

The dynamical behavior of the periodate-hydroxylamine reaction has many similarities to that of the mixed Landolt systems consisting of iodate, sulfite, and an additional reductant (ferrocyanide,<sup>14</sup> thiourea,<sup>15</sup> thiosulfate<sup>16</sup>). To explain the oscillatory behavior, it is helpful to take into consideration a number of results for these earlier systems.

The first similarity is that the fast protonation equilibrium of hydroxylamine can play the same role as the protonation of sulfite:

$$NH_2OH + H^+ \rightleftharpoons NH_3OH^+$$
 (8)

The pK of step 8, 6.0, is close to the first pK of sulfite, 7.1, and reaction 8 can control the pH. Our experiments on the early phase of the reaction show that periodate is rapidly reduced to iodate by the protonated form of hydroxylamine.

$$2IO_4^- + NH_3OH^+ \rightarrow 2IO_3^- + NO_2^- + H_2O + 2H^+ \quad (9)$$

We assume a simple second-order rate equation for reaction 9

$$-d[NH_{3}OH^{+}]/dt = k_{9}[IO_{4}^{-}][NH_{3}OH^{+}]$$
(9')

A second similarity with the mixed Landolt systems is that iodate can oxidize hydroxylamine via an indirect autocatalytic pathway:

$$2IO_3^- + 3NH_3OH^+ \rightarrow 3NO_2^- + 2I^- + 3H_2O + 6H^+$$
(10)

Reaction 10 is much slower than reaction 9, and its assumed rate law is

$$-1/2d[IO_3^-]/dt = k_{10}[IO_3^-][NH_3OH^+]$$
 (10')

The Dushman reaction (3) has the well-established rate law

$$-d[IO_3^{-}]/dt = k_3[IO_3^{-}][I^{-}]^2[H^{+}]^2$$
(3')

Increasing  $[H^+]$  or  $[I^-]$  accelerates the rate-determining step (3)

Letters

$$2NH_2OH + 2I_2 \rightarrow N_2O + 4I^- + H_2O + 4H^+$$
 (11)

hydroxylamine is inhibited by hydrogen ion.<sup>8</sup> Note that the rate of reaction 11 is not as high as that of the corresponding reaction between iodine and sulfite in the mixed Landolt systems, and reaction 11 is inhibited not only by H<sup>+</sup> but by I<sup>-</sup> as well. In our experiments, [I<sup>-</sup>] remains high and constant ( $\sim 10^{-2}$  M) during the oscillation, and we did not include it in the rate law

$$-d[I_2]/dt = k_{11}[NH_2OH][I_2]$$
(11')

Owing to the autoinhibitory character of the component reaction 11, the autocatalytic pathway (10) + (3) + (11) is shut down at a critical pH.

A third similarity is that the nitrite ion formed in the present system can play the role of the perturbing reactant (ferrocyanide, thiourea) in the mixed Landolt systems, here consuming hydrogen ion in reaction 6. The rate of reaction 6 has been studied in acidic medium,<sup>17</sup> yielding a two-term rate law. We neglected the second term, which is important only in more acidic solution, and adopted (6') with a higher rate constant:

$$d[I_2]/dt = k_6[NO_2^{-}][I^{-}]^2[H^{+}]^2$$
(6')

Preliminary calculations demonstrate that these component reactions can produce oscillations similar to those seen experimentally. A typical calculated oscillatory curve is shown in Figure 3. Further detailed study of this system and its component reactions will be required for a complete description of the oscillation and a full mechanism of the reaction.

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