traction of halogens from Si(100).

Further support for the ER reaction mechanism comes from investigations using TPD mass spectroscopy. These studies help differentiate various desorption products as a result of different surface reactions, generally under equilibrium conditions. Figure 4 shows series of TPD spectra taken after the Br-terminated Si(100) was exposed to different atomic hydrogen exposures at a substrate temperature of 430 K. Figure 4a shows the results of the thermal desorption for Br/Si(100) without exposing the prepared surface to the atomic hydrogen. The only detectable desorption products are $SiBr_x$ and/or Br.[11] With a medium H exposure on the same prepared Br/Si(100) surface, the corresponding TPD spectra (Figure 4b) show the desorption of HBr,[30] in addition to the desorption of β_2-H_2, β_1-H_2,[9] $SiBr_x$, and/or Br. Notice that the temperature-programmed desorption of HBr is only observable in the temperature range of the β_1-H_2 desorption from the monohydride phase of Si(100), above 720 K. With a high atomic H exposure, the prepared Si(100) surface then becomes almost free of bromine as a result of the extraction process (see Figure 3), and the corresponding TPD spectra (Figure 4c) show mainly the β_2- and β_1-H_2 desorption.

Thermal desorption of HBr occurring in the same temperature range of the monohydride β_1-H_2 desorption provides important information relevant to the H-induced extraction reaction. First of all, no desorption of HBr under thermal equilibrium conditions is observed in the temperature range from 300 to 720 K. Similar results have also been observed for other halogen adsorbates.[10,11] *This indicates that this efficient removal of halogen adsorbates by atomic hydrogen at* $T \leq 720$ *K cannot be explained as a result of thermal desorption of the hydrogen halide under equilibrium conditions.* In the other words, during the extraction process, the incoming hydrogen atom is not thermally accommodated on the surface before reacting with the surface halogen adsorbate, and the extraction reaction therefore occurs at low temperatures where the Langmuir–Hinshelwood process $H(a) + X(a) \rightarrow HX(g)$ does not occur. Secondly, the temperature range of HBr thermal desorption is nearly coincident with that of β_1-H_2 desorption from the monohydride phase, suggesting that excitation of the monohydride Si–H bond is required for the desorption of HBr in this second surface reaction channel.

IV. Conclusions

A surface reaction driven by collisions with gas-phase atomic hydrogen has been demonstrated on the halogen-terminated Si(100) surfaces. The extraction of adsorbed halogens on the Si(100) surface by atomic hydrogen has been shown to proceed via an Eley–Rideal reaction mechanism. The extraction kinetics are found to be first order in both the surface coverage of halogen and in the atomic hydrogen flux. In addition, the reaction rate constants follow the trend $k_I > k_{Br} > k_{Cl}$. The extremely low activation energy (1.6 – 2.1 kcal mol^{-1}) for the extraction process indicates that the thermal excitation of the Si(100) solid surface is of minor importance in controlling the halogen extraction kinetics.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

Registry No. Si, 7440-21-3; H, 12385-13-6; I_2, 7553-56-2; Br_2, 7726-95-6; Cl_2, 7782-50-5; HI, 10034-85-2; HBr, 10035-10-6; HCl, 7647-01-0.

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[30] Desorption of HBr is confirmed by comparing the mass spectrometer fragmentation ratio, Br^+ ($m/e = 79$)/HBr^+ ($m/e = 80$). Our measurements from the results of TPD show the ratio of $Br^+/HBr^+ \simeq 0.50$, which is in good agreement with the value from the literature (0.45 is obtained from: *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Interscience: New York, 1969; Vol. I, p 104).

A New Type of Oxyhalogen Oscillator: The Bromite–Iodide Reaction in a Continuous Flow Reactor[1]

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Abstract: The reaction between bromite and iodide ions in a flow reactor shows two steady states and sustained oscillations in pH, redox potential, and [I^-]. The oscillatory behavior is extremely sensitive to the inflow ratio [BrO_2^-]/[I^-], the flow rate, the initial pH of the input solutions, and the stirring rate. Batch experiments suggest that the system behaves in several respects like the analogous chlorite–iodide oscillator. The bromite–iodide system, however, is also a pH oscillator and is the first oxyhalogen oscillator to oscillate in the neutral and basic pH range.

Introduction

Chemical reactions involving halogen species have played a dominant role in the study of homogeneous liquid-phase oscillating chemical reactions. The first discoveries of periodic behavior in chemical solutions of nonbiological origin, the Bray[2] and Belousov–Zhabotinskii[3] (BZ) reactions, occurred with reactions of iodate and bromate, respectively. With the exception of the highly unstable OX^- and $OX^\cdot$ species, halogen and oxyhalogen species with every existing oxidation state from −1 to +7 have been utilized as starting reagents in chemical oscillators.

Among the oxyhalogen-based oscillators, bromate and chlorite ions have played particularly central roles. Bromate is the key species in the Belousov–Zhabotinskii reaction, undoubtedly the most familiar and most widely studied of the chemical oscillators. It also serves as the starting point for many other oscillating reactions, most of which may be thought of as derived from the "minimal bromate oscillator",[4] which consists of bromate, bromide, and a metal catalyst in a continuous flow reactor (CSTR). Chlorite ion was used in the first deliberately designed chemical

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[1] Paper 75 in the series: Systematic Design of Chemical Oscillators. Paper 74: Doona, C. J.; Kustin, K.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 7484.

[2] Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262.

[3] (a) Belousov, B. P. *Sb. Ref. Radiat. Med.* **1958**, 145. (b) Zhabotinskii, A. M. *Biofizika* **1964**, *9*, 306.

[4] Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 2657.

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oscillator, the chlorite–iodate–arsenite system,[5] and has proved to be a versatile reagent for the design of several families of new oscillating reactions.

One might expect that, given the versatility of BrO_3^- and ClO_2^- in generating chemical oscillators, bromite ion, BrO_2^-, should also prove a fruitful starting point for the design of new oscillating reactions. The key role of $HBrO_2$ in the BZ reaction[6] would seem to reinforce this expectation.

Surprisingly, no bromite-based oscillator has been reported previously, perhaps because of the difficulty of obtaining pure bromite compounds. Sodium bromite as $NaBrO_2\cdot 3H_2O$ is now commercially available in appreciable purity. We have therefore undertaken to construct bromite-based oscillating reactions. We report here the first example of a chemical oscillator containing BrO_2^- as a reactant, the reaction of bromite and iodide ions in a CSTR. This system is unique among halogen-based oscillators in that it oscillates at neutral and alkaline pH's. It is also strikingly sensitive to several experimental parameters, most notably the stirring rate in the reactor.

Experimental Section

Materials. Sodium bromite, $NaBrO_2\cdot 3H_2O$, was purchased from Aldrich and was used without further purification. The assay of the pale yellow solid was >95% for bromite, with BrO_3^-, Br^-, NaOH, and absorbed H_2O as the most significant impurities. Potassium iodide was Fisher analytical grade.

Aqueous solutions of $NaBrO_2$ and KI were made by dissolving the calculated amount of solid in distilled water. All solutions were freshly made and consumed within 2 h. Aqueous solutions of $NaBrO_2$ are stable only above pH 12. Massagli et al.[7] found that a 10^{-3} M bromite solution at pH $\approx$ 7 decreases in bromite content by less than 10% in 2 h. We thus take the usable lifetime of an aqueous bromite solution to be about 2 h. This time is shorter at lower pH and longer at higher pH. Aqueous bromite solutions are typically somewhat alkaline as a result of hydrolysis; thus, depending on the concentration, a solution may be usable for 6–8 h.

Apparatus and Methods. The glass CSTR had a volume of 20.5 cm^3 and was operated at a temperature of 25.00 ± 0.05 °C. The reactor was fed with a Sage 375A peristaltic pump through four inlet tubes inserted through the Teflon cap of the reactor. Two tubes contained bromite solution, one held iodide solution, and the fourth was used for either water or dilute (5×10^{-4} M) $HClO_4$. Some experiments were performed in a premixed configuration in which reagents could be united in a Y-tube with a 2.5-mm i.d. and a common segment of length 20 cm before reaching the reactor. The flow rate could be varied continuously between 0 and 1.8×10^{-2} s^{-1} (reciprocal residence time). All tubes and electrodes were fitted airtight through the reactor cap, and no air gap or bubbles were allowed to form.

The reactor was able to accommodate several different sensors, including a Pt redox electrode, iodide-selective electrode, combined glass electrode, and $Hg|HgSO_4|K_2SO_4$ reference electrode. Two signals were recorded simultaneously on a double channel recorder. The solutions in the CSTR were stirred magnetically with an adjustable speed stirrer (Heidolph 2002 or VWR 400 HPS) that allowed us to adjust and maintain the stirring rate to ±3% between 100 and 1200 rpm. In the batch experiments we were able to use both the potentiometric probes available in the CSTR and a diode array spectrophotometer (Hewlett-Packard 8452A) that allowed us to follow the spectrum of the solution nearly continuously in time.

Results

CSTR Experiments. When aqueous solutions of bromite and iodide are introduced into the CSTR, the reaction mixture ultimately reaches either of two steady states or an oscillatory state. One steady state, designated SSI or the flow branch, occurs at high flow rates and is characterized by a low Pt potential (600–700 mV), high pH (8–9), and high $[I^-]$ (close to the input $[I^-]_0$). The extent of reaction in SSI is small. The steady-state stable at low flow rates, SSII or the thermodynamic branch, shows a high extent of reaction, a high Pt potential (800–900 mV), low pH (5–6), and low $[I^-]$ ($\approx 10^{-6}$ M). As the flow rate k_0 is increased past a critical value, the transition from SSII to SSI occurs at a moderate rate; the reverse SSI $\rightarrow$ SSII transition is much more rapid and shows pronounced autocatalytic character. No hysteresis between these states has been observed.

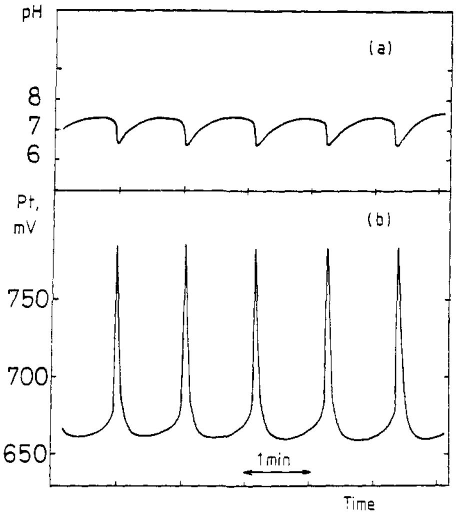

Figure 1. Oscillatory behavior of the bromite–iodide reaction in a CSTR. $[BrO_2^-]_0 = 2 \times 10^{-3}$ M, $[I^-]_0 = 1 \times 10^{-3}$ M, $k_0 = 3 \times 10^{-3}$ s^{-1}, stirring rate = 300 rpm. (a) pH, (b) potential of Pt electrode.

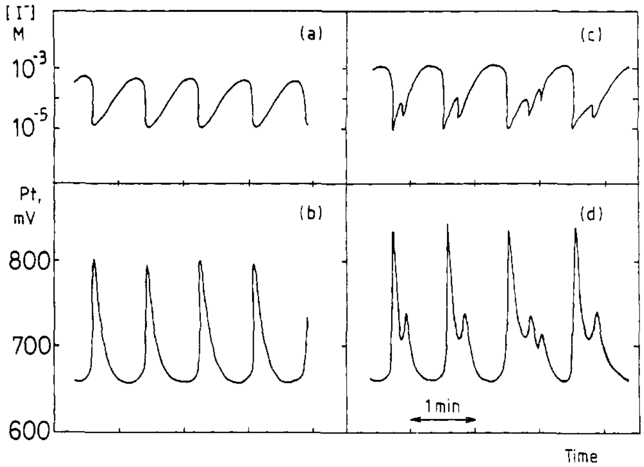

Figure 2. Oscillations in $[I^-]$ (a and c) and potential of Pt electrode (b and d) at different stirring rates. Concentrations and flow rate as in Figure 1. Stirring rates: (a and b) 250 rpm, (c and d) 600 rpm.

At appropriate values of the input concentrations, oscillatory behavior can appear at flow rates intermediate between those supporting SSI and SSII. Oscillatory responses with periods of 10–100 s, depending on concentrations and flow rate, were observed in: (a) the potential of the Pt electrode, with an amplitude of 10–250 mV; (b) the pH, with an amplitude of 0.1–1.0 unit about a mean of 6–7; (c) the potential of an iodide-selective electrode, with an amplitude of 50–100 mV, suggesting a change in $[I^-]$ of 1–2 orders of magnitude.

The potential of a bromide-selective electrode also oscillates, but this observation reflects changes in $[I^-]$ rather than in $[Br^-]$.[8] No color changes were visible during the oscillation, though our batch experiments described below suggest that I_3^- might form as an intermediate in the reaction. Introducing a buffer solution with a pH equal to that of the mean of the pH oscillations completely suppresses all oscillatory responses. Examples of the oscillatory behavior are shown in Figures 1 and 2.

The oscillations usually consist of single peaks, but at some flow rates and stirring speeds, complex oscillations, illustrated in Figure 2, c and d, may occur. Under some conditions, as a function of flow rate, very narrow ranges of hysteresis were observed between the oscillatory state and the steady states.

The oscillations are extremely sensitive to several factors, which renders the reproducibility of this system much less than in the chlorite–iodide[9] or bromate–iodide[10] reactions. Here we discuss the experimental

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(5) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 2133.

(6) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

(7) Massagli, A.; Indelli, A.; Pergola, F. *Inorg. Chim. Acta* **1970**, *4*, 593.

(8) Fifeld, F. W.; Kealey, D. *Principles and Practice of Analytical Chemistry*, 2nd ed.; International Textbook Co.: London, 1983; p 197.

Table I. Effect of Stirring Rate on the Non-Premixed Bromite–Iodide Reaction in a CSTR[a]

stirring rate, rpm	state[b]	remarks
100 and below	SSII	noisy
200	SSII	noisy
300	OS	single peak oscillation, low amplitude, high frequency
400	OS	single peak oscillation, higher amplitude, lower frequency
600	OS	complex oscillation
700 and above	SSI	noisy

[a] $[BrO_2^-]_0 = 2 \times 10^{-3}$ M, $[I^-]_0 = 1 \times 10^{-3}$ M, $k_0 = 5 \times 10^{-3}$ s^{-1}. [b] SS = steady state, OS = oscillatory state.

constraints that exert the greatest influence on the oscillatory behavior:

(i) Concentration Ratio of the Reactants. The bromite–iodide reaction exhibits oscillations in a CSTR only if the ratio of input concentrations $[BrO_2^-]_0/[I^-]_0 = 2.0 \pm 0.2$. The actual concentrations can vary from 5×10^{-4} to 4×10^{-3} M for bromite and from 2.5×10^{-4} to 2×10^{-3} M for iodide so long as the 2:1 ratio is maintained. At ratios much above 2, a rapid reaction brings the system to SSII, while for ratios significantly below 2 the reaction is quite slow and the system remains on the flow branch SSI.

(ii) Initial pH of the Input Solutions. The input sodium bromite solution tends to be somewhat alkaline as a result of hydrolysis and possible NaOH impurities. Although the distilled water is sometimes sufficiently acidic to bring the system to the appropriate pH for oscillation, in other cases a small amount of (5×10^{-4} M) $HClO_4$ must be introduced in one of the input flows. One can assess whether the initial pH is suitable by mixing the input solutions of bromite and iodide at zero flow rate. If a sharp transition in redox potential, pH, and $[I^-]$ occurs within 10–15 min, then the pH is appropriate for generating oscillations at some flow rate. If the transition is instantaneous or requires much longer than 15 min, then regardless of the flow rate, only SSII or SSI, respectively, can be attained. Suitable initial pH's are in the range 5.5 to 6.5 for the KI solution and about 4.4 for the dilute $HClO_4$. The freshly made $NaBrO_2$ solution has a pH of about 9, though the exact value depends upon the concentration.

(iii) Flow Rate. The most effective procedure for studying the dependence of the dynamics on k_0 is to start by filling the reactor with the input solutions at the highest available flow rate and then to switch off the flow, thereby inducing a rapid transition from SSI to SSII. If the flow rate is then slowly increased, one can observe a transition to low-amplitude, high-frequency oscillations. As k_0 is increased still further, the amplitude increases and the frequency decreases until, finally, another transition brings the system to the nonoscillatory state SSI. If this procedure is repeated several times, the oscillatory range of k_0 is found to shift and broaden slightly, perhaps as a result of slow decomposition of the input bromite solution. The oscillatory flow rates are usually in the range $k_0 = (3\text{–}15) \times 10^{-3}$ s^{-1}.

(iv) Stirring Rate. One of the most striking features of the bromite–iodide reaction in a CSTR is its extreme sensitivity to stirring rate. Table I provides a qualitative picture of the effect of stirring rate at fixed input concentrations and flow rates without premixing. In the premixed configuration, the behavior is qualitatively the same, but the stirring effects are less dramatic, and it is easier to obtain reproducible results. The range of the simple, single-peak oscillations is significantly broader with premixing. Menzinger et al.[11] observe that premixing produces a similar decrease in the sensitivity of the chlorite–iodide reaction to stirring effects.

A second indication of the system's extreme sensitivity to stirring is that the amplitude and frequency of the oscillations vary with the position of the electrodes in the reactor. Thus the extent of mixing cannot be characterized solely by the stirring rate in rpm, but also depends upon the configuration of the reactor. Menzinger and Dutt[12] have made quantitative measurements in the chlorite–iodide reaction at different positions in a CSTR and have found that concentrations can vary by an order of magnitude even at stirring rates around 1000 rpm. These observations imply that in a different CSTR the oscillatory ranges of flow rate and stirring rate for the bromite–iodide reaction may be significantly different from those found here.

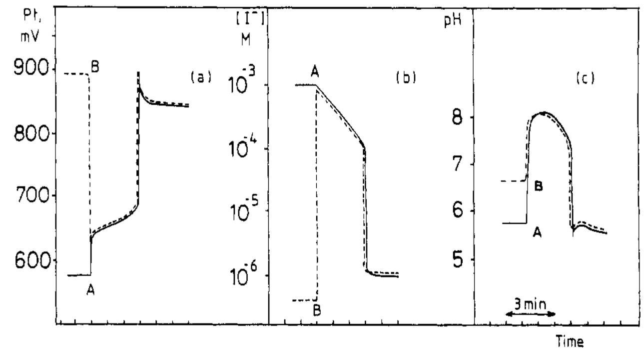

Figure 3. Batch behavior of the bromite–iodide reaction $[BrO_2^-]_0 = 2 \times 10^{-3}$ M, $[I^-]_0 = 1 \times 10^{-3}$ M: (a) potential of Pt electrode; (b) iodide concentration; (c) pH. The reaction was initiated either by adding bromite at point A (solid curve) or by adding iodide at point B (dashed curve).

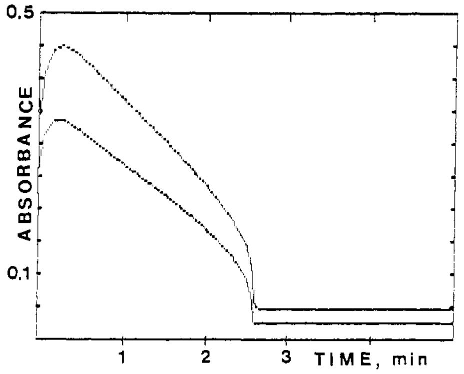

Figure 4. Absorbance at 353 nm (lower curve) and at 288 nm (upper curve) for the batch bromite–iodide reaction with initial conditions as in Figure 3. Path length = 1.0 cm.

High sensitivity of a chemical process to stirring rate can arise from the presence of bulk inhomogeneities and/or surface effects. For example, the Br_2–H_2 reaction is oscillatory in a CSTR only if a platinum surface is present,[13] and the oscillations are strongly dependent on the stirring rate. To assess the possibility of surface catalysis by the Pt electrodes, we performed experiments in which two Pt electrodes of very different surface areas (0.5 cm^2 and 8 cm^2) were utilized. We monitored the potential changes of both electrodes simultaneously and obtained synchronous oscillations in both circuits. This result and the observation that oscillations in pH and $[I^-]$ persist when the Pt electrode is removed from the reactor appear to preclude the possibility of oscillations induced by the Pt surface.

Batch Experiments. In addition to the above CSTR experiments, we performed a number of experiments in a batch (closed system) configuration in an effort to gain further insights into the behavior of the bromite–iodide system. Typical results obtained by observing the potentials of Pt, glass, and iodide-selective electrodes are shown in Figure 3. Absorbance traces for the batch reaction at wavelengths characteristic for I_3^- appear in Figure 4.

The potentiometric traces show that the bromite–iodide batch system behaves as a typical clock reaction. With bromite in excess over iodide, as in Figures 3 and 4, the iodide is consumed completely, at about 3 min for these concentrations, and the reaction terminates. The pH rises to about 9 immediately after mixing, then declines slowly until it undergoes an autocatalytic drop at the end of the reaction. The absorbance curve, Figure 4, shows rapid formation of about 1.2×10^{-5} M I_3^-, which is then further oxidized in a slow process. A pale yellow color (blue in the presence of starch) is apparent until it disappears with the rapid transition at 3 min. We note that the maximum concentration of triiodide formed is only a few percent of the stoichiometric amount. Spectra of the reaction mixture between 280 and 500 nm were taken every 10 s for 5 min, but no characteristic absorbances were observed other than the transient spectrum of I_3^-.

We define the reaction time for the batch reaction as the time from mixing the reagents to the maximum in the Pt potential (or equivalently to the minimum in $[I^-]$, pH, or absorbance). This time is insensitive to

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[9] Dateo, C. E.; Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 504.

[10] Alamgir, M.; De Kepper, P.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 2641.

[11] Menzinger, M.; Boukalouch, M.; De Kepper, P.; Boissonade, J.; Roux, J.-C.; Saadoui, H.; *J. Phys. Chem.* **1986**, *90*, 313.

[12] Menzinger, M.; Dutt, A. K. *J. Phys. Chem.* **1990**, *94*, 4510.

[13] Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1981**, *103*, 3723.

the stirring rate but shows a sharp dependence on the initial pH. For example, when the pH's of the iodide solution before addition of bromite were 2.94, 3.68, 5.26, and 6.55, the reaction times were 15 s, 1.5 min, 3.0 min, and 4.5 min, respectively. The reaction time also depends upon the initial reactant concentrations, decreasing with $[BrO_2^-]$ and increasing with $[I^-]$. Addition of even small amounts of I_2 to the initial reaction mixture sharply decreases the reaction time, and the reaction becomes instantaneous if the initial $[I_2]$ is above about 10^{-5} M.

Discussion

The kinetics of the bromite–iodide reaction have been studied in buffered solution with a large excess of I^- over BrO_2^- by Ferranti and Indelli[14] using stopped-flow methods. Under these conditions, bromite ion is reduced in a very fast reaction with the stoichiometry of eq 1:

$$BrO_2^- + 4I^- + 4H^+ \rightarrow Br^- + 2I_2 + 2H_2O \tag{1}$$

The reaction was found to be first order in BrO_2^-, I^-, and H^+:

$$v_1 = k[BrO_2^-][I^-][H^+] \tag{R1}$$

Lee and Lister[15] also investigated the kinetics and mechanism of this reaction with excess iodide, but in highly alkaline (pH $\geq$ 13) solution. The overall stoichiometry was found to be

$$3BrO_2^- + 2I^- \rightarrow 3Br^- + 2IO_3^- \tag{2}$$

and the data were consistent with a rate law first order in each of the reactants. With initial concentrations $[BrO_2^-] = 6.5 \times 10^{-3}$ M, $[I^-] = 1 \times 10^{-1}$ M, they deduced that the intermediate hypoiodide and triiodide ions built up to levels of about 10^{-3} and 10^{-5} M, respectively. These species were then presumed to react further to yield the final products:

$$IO^- + 2I^- + H_2O = I_3^- + 2OH^- \tag{3}$$

$$BrO_2^- + I^- \rightarrow BrO^- + IO^- \tag{4}$$

$$BrO^- + I^- \rightarrow Br^- + IO^- \tag{5}$$

$$BrO_2^- + IO^- \rightarrow Br^- + IO_3^- \tag{6}$$

No kinetic studies of the bromite–iodide reaction are available under excess bromite conditions similar to those which give oscillations in the CSTR. Kern and Kim[16] have investigated the analogous ClO_2^-–I^- with chlorite in excess. The stoichiometries they find are those of eq 1 and 2 with ClO_2^- replacing BrO_2^-. The rate expression for the chlorite–iodide reaction was found to be

$$v = k_1[ClO_2^-][I^-][H^+] + k_2[ClO_2^-][I_2]/[I^-] \tag{R2}$$

with rate-determining steps (7) for the first term and (8) for the second:

$$HClO_2 + I^- \rightarrow HOCl + IO^- \tag{7}$$

$$HClO_2 + HOI \rightarrow HIO_2 + HOCl \tag{8}$$

As eq R2 shows, Kern and Kim found both autocatalysis by I_2 and inhibition by I^- in the chlorite–iodide reaction. Our batch experiments on the bromite–iodide system suggest that both these phenomena also occur in the BrO_2^-–I^- reaction.

The similarities in the stoichiometry, kinetics, and dynamical behavior of the ClO_2^-–I^- and BrO_2^-–I^- reactions suggest that we might borrow some ideas from what is known about the mechanism of the chlorite–iodide system[17] in an attempt to account for the oscillatory behavior of the present system. One must, however, bear in mind a significant difference between the two systems. The chlorite–iodide reaction shows oscillations in solutions buffered at pH $\approx$ 2, while the bromite–iodide system oscillates only in unbuffered solution and at considerably higher pH. One or more protonation equilibria must play a more pronounced role in the bromite than in the chlorite system. The BrO_2^-–I^- reaction appears to be a true pH oscillator[18] in the sense that H^+-producing and -consuming processes and the concomitant changes in pH provide the switch between the two sets of reactions that comprise the oscillatory cycle.

We are not able at this stage to propose a detailed mechanism to account for the oscillatory behavior of the BrO_2^-–I^- flow system. Some insights, however, may be gained from examination of our batch experiments. The rapid initial pH jump from about 6 to 9 corresponds to the reaction

$$BrO_2^- + I^- + 2H^+ \rightarrow HOI + HOBr \tag{9}$$

The pK_a values of HOI and HOBr are 11 and 8.7, respectively, so we write these species in their protonated forms at pH < 9. The pale yellow color that accompanies the pH rise results from formation of I_3^-, presumably via eq 10:

$$HOI + 2I^- + H^+ \rightleftarrows I_3^- + H_2O \tag{10}$$

From the low $[I_3^-]$ observed, we conclude that the equilibrium in reaction 10 lies to the left.

After the maximum in pH is reached, the disproportionation of HOI begins:

$$3HOI \rightarrow 2I^- + IO_3^- + 3H^+ \tag{11}$$

As step 11 proceeds, the pH slowly decreases This step also retards the consumption of I^- by step 9. The bromite, still in excess, further reacts with HOI according to

$$BrO_2^- + HOI \rightarrow IO_2^- + HOBr \tag{12}$$

The protonation constants of the bromite and iodite ions are unknown, though pK_a for $HBrO_2$ has been estimated[7] to be about 6. Thus the XO_2^- species are probably unprotonated at the plateau of the pH versus time curve.[19] The further decrease in pH that results from eq 11 should lead to the protonation of the XO_2^- species. The sequence of reactions 12 and 13 coupled with protonation of iodite ion will then result in rapid, autocatalytic production of H^+.

$$HIO_2 + HOBr \rightarrow IO_3^- + Br^- + 2H^+ \tag{13}$$

This sequence causes the pH to drop and yields the products IO_3^- and Br^- found in the overall stoichiometry of eq 2.

Reactions 9–13 are likely to play a major role in the mechanism of oscillatory behavior in the bromite–iodide flow system. A full mechanism and computer simulations will require further information about the rates, kinetics, and protonation constants of the reactions and species involved. Such studies are now under way in our laboratories.

The bromite–iodide chemical oscillator possesses two features that differentiate it from other halogen-based oscillating reactions. The other oscillators characterized to date all oscillate in an acidic range of pH. The BrO_2^-–I^- reaction is the only halogen oscillator that operates around and above pH 7.

The other striking feature of this system is its extreme sensitivity to the rate of stirring. Only the chlorite–iodide reaction exhibits comparable sensitivity.[12,20] It has been suggested[12] that in the chlorite–iodide reaction in a CSTR, chlorite ions near the chlorite feedstream encounter a relatively high level of $[I_2]$ as compared with $[I^-]$ in the bulk and tend to react according to eq 14:

$$5ClO_2^- + 2I_2 + 4H_2O \rightarrow 5Cl^- + 4IO_3^- + 4H^+ \tag{14}$$

rather than according to the chlorite analogue of eq 1 as would be true if the mixing of the feedstreams occurred infinitely rapidly or if the feeds were premixed. This explanation may hold a fortiori

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[14] Ferranti, F.; Indelli, A. *Gazz. Chim. Ital.* **1972**, *102*, 117.

[15] Lee, C. L.; Lister, M. W. *Can. J. Chem.* **1979**, *57*, 1524.

[16] Kern, D. M.; Kim, C.-H. *J. Am. Chem. Soc.* **1965**, *87*, 5309.

[17] Citri, O.; Epstein, I. R. *J. Phys. Chem.* **1987**, *91*, 6094.

[18] Råbai, Gy.; Orbån, M.; Epstein, I. R. *Acc. Chem. Res.* **1990**, *23*, 258.

[19] The alternative estimate for pK_a($HBrO_2$) of about 4.9 (given by: Field, R. J.; Försterling, H.-D. *J. Phys. Chem.* **1986**, *90*, 5400) only reinforces this conclusion.

[20] Roux, J.-C.; De Kepper, P.; Boissonade, J. *Phys. Lett. A* **1983**, *97*, 168.

for the bromite–iodide reaction, since eq 1, which consumes H^+, will be further retarded by the much higher pH of the bromite system. The lack of stirring rate sensitivity in the batch bromite–iodide system is consistent with this view, since in the batch configuration it is not necessary for spatially separated feedstreams to mix. Menzinger and Dutt[11] also report spatial synchronization in the chlorite–iodide flow system, consistent with our observations in the bromite–iodide reaction.

In view of the many chlorite-based oscillators[21] that have been discovered in the past decade, one may wonder whether there are large numbers of bromite-based oscillating reactions waiting to be uncovered. The answer may depend upon how the oscillations in the present system actually arise, i.e., on the mechanism. It seems quite likely that one can construct oscillators analogous to the chlorite–iodide–oxidant systems[21b] by adding appropriate oxidizing agents to the present system. Such oscillators might be expected to be more robust, less sensitive to stirring, and perhaps even show batch oscillation.[21c] If, however, the existence of a stable bromine(IV) species is essential, as ClO_2 apparently is in the chlorite–iodide–malonic acid batch oscillator,[22] then the lower stability of BrO_2 may prevent observation of oscillatory behavior in the analogous bromite systems. Whether one can replace iodide ion with other species as has been done, for example, with several sulfur compounds in chlorite oscillators,[21d,e] may depend upon whether oscillation in the bromite system is attributable more to the autocatalytic effect of I_2 or to the inhibitory effect of I^-. The former effect will be much easier to duplicate with other reagents than will the latter. In any case, the search for new bromite oscillators should lead to a deeper understanding of the chemistry of this fascinating species.

Acknowledgment. We thank Kenneth Kustin and Roberto Faria for helpful discussions. This work was supported by the National Science Foundation (CHE-9023294), by the Hungarian Academy of Sciences (OTKA 1/3 No. 2275), and by a U.S.-Hungarian cooperative grant from the NSF and the Hungarian Academy.

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(21) (a) Orbán, M.; De Kepper, P.; Epstein, I. R.; Kustin, K. *Nature* **1981**, *292*, 816. (b) Orbán, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5911. (c) De Kepper, P.; Epstein, I. R.; Orbán, M.; Kustin, K. *J. Phys. Chem.* **1982**, *86*, 170. (d) Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 431. (e) Alamgir, M.; Epstein, I. R. *Int. J. Chem. Kinet.* **1985**, *17*, 429.

(22) Lengyel, I.; Rábai, Gy.; Epstein, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 4606.

Photochemistry of Binuclear Ferraazetines: CO vs Alkyne Insertion

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Received June 3, 1991. Revised Manuscript Received September 16, 1991

Abstract: An investigation of the low-temperature matrix isolation photochemistry of ferraazetines, $Fe_2(\mu\text{-}CRCHNBu^t)(CO)_6$ (**1a**, R = H; **1b**, R = CH═CHPh) in rigid matrices is reported. Near-UV irradiation of **1a** and **1b** in CO-saturated methylcyclohexane (MCH) at 298 K yields ferrapyrrolinones **2a** and **2b**, $Fe_2\{\mu\text{-}CRCHNBu^tC(O)\}(CO)_6$, and in the presence of *tert*-butylacetylene, **1a** and **1b** form ferrapyridines **3a** and **3b**, $Fe_2(\mu\text{-}Bu^tCCHCRCH{=}NBu^t)(CO)_6$. The photoinduced insertion of CO and *tert*-butylacetylene occur at different positions in the ferraazetine metallacycle. CO insertion occurs between the Fe–N bond of the metallacycle whereas *tert*-butylacetylene insertion occurs between the Fe–C bond. At 15 or 8 K in MCH, 1:1 *tert*-butyl acetylene/MCH, or CO matrices, the primary photoprocess for **1a** and **1b** involves Fe–N bond cleavage to yield coordinatively unsaturated compounds **4a** and **4b**, respectively. Irradiation of **4a** in a MCH matrix gives bridging CO compound **5**, $Fe_2(\mu\text{-}CHCHNBu^t)(\mu\text{-}CO)(CO)_5$, which is formed by a CO ligand swinging from the adjacent Fe center to occupy the vacant coordination site created by the Fe–N cleavage. In a 1:1 *tert*-butylacetylene/MCH matrix, irradiation of **4a** at 98 K gives a *tert*-butylacetylene adduct **6**, $Fe_2(\mu\text{-}CHCHNBu^t)(CO)_6(Bu^tC{\equiv}CH)$. When warmed to 298 K, **6** inerts the *tert*-butylacetylene ligand to form **3a**. Irradiation of **4a** in a ^{13}CO matrix at 8 K gives CO insertion product **2a** with ^{13}CO incorporation at a terminal position with no evidence of incorporation at the carbonyl of the acyl ligand. When **4b** is irradiated in MCH at 15 K, compound **7**, $Fe_2\{\mu\text{-}C(CH{=}NBu^t)CHCHPh\}(CO)_6$, is formed. **7** derives from a ligand exchange of the $C{=}NBu^t$ group of the ferraazetine ring in **4b** for its pendant styryl group, CH═CHPh. When irradiated at 98 K or 298 K in MCH, **1b** forms **7** with no detectable intermediates and the photoconversion is much faster at these temperatures than at 15 K. At 298 K **7** quantitatively re-forms **1b** after 2 h in the dark.

Introduction

We report the low-temperature photochemistry of binuclear ferraazetines **1a** and **1b** with CO and *tert*-butylacetylene in solution and in rigid matrices at $T \leq 98$ K. It has been recently reported that the near-UV irradiation of **1a** at 298 K in the presence of CO (1 atm) produces ferrapyrrolinone **2** and in the presence of alkyne, **1a** forms ferrapyridine complex **3**, eqs 1 and 2.[1,2] The reaction between **1** and monosubstituted alkynes is general and quite regioselective with only one of two possible regioisomers being formed as product, eq 2. Compound **3** and its derivatives have proven useful in the development of a high-yield regioselective

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(1) (a) Mirkin, C. A.; Lu, K.; Snead, T. E.; Young, B. A.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 3800. (b) Mirkin, C. A.; Lu, K.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *18*, 7279.

(2) Mirkin, C. A.; Lu, K.; Snead, T. E.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 2809.

0002-7863/92/1514-1256\$03.00/0