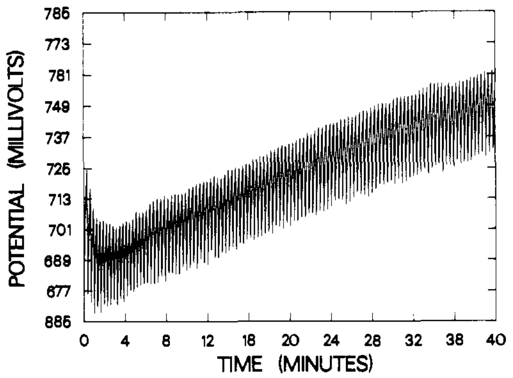

Figure 5. Air flow 0.085 cm^3/(min mL), 100 °C, 0.02 M Co^{2+}, 0.004 M Br^-, 0.75 M benzaldehyde.

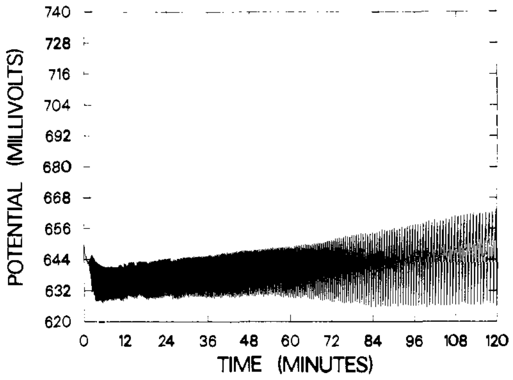

Figure 6. Air flow 0.085 cm^3/(min mL), 70 °C, 0.01 M Co^{2+}, 0.004 M Br^-, 0.75 M benzaldehyde.

by optimizing the other variables. Higher temperatures increase the oscillation frequency dramatically (Figure 5). The frequency increases about 0.2 cycles/min at 55 °C to 3.2 cycles/min at 100 °C. The rate of increase in average potential is also higher at 100 °C, but the rate of decrease in frequency is very small.

Cobalt Concentration. Reducing the cobalt concentration from 0.02 to 0.01 M had a large effect (Figure 6). The oscillations started at a very low amplitude, 2–3 mV, and a high frequency. Eventually the amplitude increased to the normal 50–60 mV, and after 3 h the cycles were very similar to those observed for the standard conditions. Increasing the cobalt concentration from 0.02 to 0.04 M had only a modest effect, the frequency increasing slightly.

Benzaldehyde Concentration. When the benzaldehyde concentration was reduced from 0.75 to 0.39 M, irregular oscillations occurred for about 30 min. At higher concentration, 1.5 M, the amplitude was much smaller, 15–16 mV, and the frequency much greater (Figure 7).

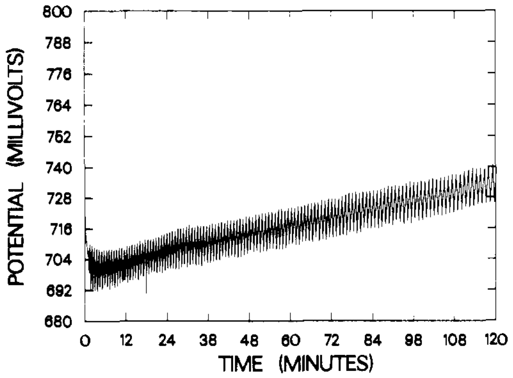

Figure 7. Air flow 0.085 cm^3/(min mL), 70 °C, 0.02 M Co^{2+} 0.004 M Br^-, 1.5 M benzaldehyde.

Bromide Concentration. Varying the bromide concentration had only a modest effect. As the bromide was increased from 0.002 to 0.008 M, the only effect was an increase in frequency from 0.12 to 0.38 cycles/min over the first 120 min.

Experimental Section

The oscillating reactions were carried out in a 250-mL round-bottom flask with a standard glass stirring rod, Teflon (DuPont) blade, and condenser. Heat was supplied with a 250-mL heating mantle inside a 1-L mantle. The outside mantle was operated at a constant voltage and acted as a background heater. The 250-mL mantle was set at 15 V and controlled by a thermister temperature controller with the probe in the solution. Temperature was maintained to ±0.5 °C.

A constant-temperature bath was unsatisfactory. The solution temperature is very dependent on air flow, heat of reaction, and stirring speed. A constant-temperature bath would not respond rapidly to small changes in these parameters.

The stirring speed was checked periodically with a General Electric Strobotac.

The redox potential was measured with an Orian pH Meter using a standard Ag/AgCl reference electrode and platinum sensing electrode. The output from the pH meter was stored in a DEC PDP-10 computer. Data were taken at 0.5 points/s.

Benzaldehyde was purified according to Fieser.[8] However, benzaldehyde from unopened bottles and even material that contained crystals of benzoic acid gave oscillating reactions.

Registry No. Benzaldehyde, 100-52-7; $Co(CH_3COO)_2$, 71-48-7; NaBr, 7647-15-6.

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A New Type of Bromate Oscillator: The Bromate–Iodide Reaction in a Stirred-Flow Reactor[1]

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Abstract: Sustained oscillations and bistability have been observed in the reaction between bromate and iodide in acidic solution in a stirred tank reactor at 25 °C. This reaction appears to be the first bromate oscillator that requires a mechanism more analogous to that of chlorite oscillators than to that of other bromate systems such as the Belousov–Zhabotinskii reaction.

Bromate oscillators are by far the most thoroughly studied and best understood family of homogeneous oscillating chemical reactions. Noyes[3] has formulated an overall mechanistic scheme to explain the behavior of several subgroups within this family.

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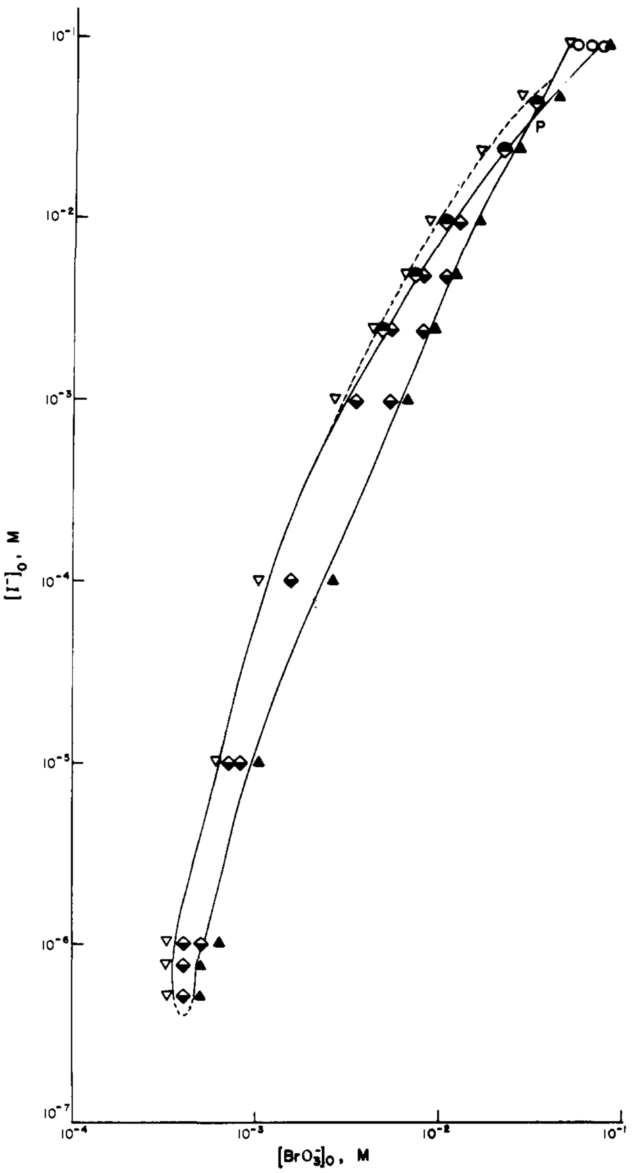

Figure 1. Phase diagram in the $[BrO_3^-]_0$–$[I^-]_0$ plane with flow rate $k_0 = 0.012\ s^{-1}$, $[H_2SO_4]_0 = 1.5$ M, $T = 25$ °C: (▽) low potential (high I_2) steady state, (▲) high potential (low I_2) steady state, (◆) bistability between oscillatory and low-potential states, (◆) bistability between high- and low-potential steady states, (○) oscillatory state.

The key to that mechanism is the ability of the system to switch rapidly between a state dominated by a radical, autocatalytic process and one dominated by nonradical reactions as the concentration of a control species, usually Br^-, passes through a critical level. The recent discoveries using flow reactor (CSTR) techniques of further classes of bromate oscillators including purely inorganic systems[1,4] have broadened the scope of bromate oscillation without necessitating any essential modification of the underlying mechanism.

We report here the discovery of a new bromate oscillator, the reaction between bromate and iodide in a CSTR, which appears to fall outside the realm of previously reported bromate oscillators. It seems, rather, to resemble the chlorite–iodide oscillator discussed by Dateo et al.[5] The reaction may also be viewed as the first or minimal[4] member of a family of uncatalyzed[6] inorganic bromate oscillators.

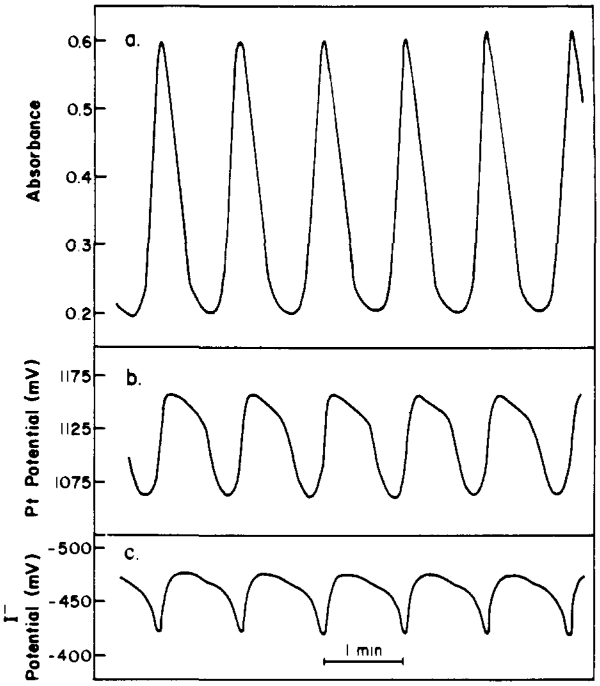

Figure 2. Typical oscillations in the bromate–iodide reaction with $k_0 = 0.012\ s^{-1}$; $[BrO_3^-]_0 = 0.005$ M, $[I^-]_0 = 0.005$ M, $[H_2SO_4]_0 = 1.5$ M, $T = 25$ °C: (a) absorbance at 460 nm, (b) potential of Pt electrode, (c) potential (uncalibrated) of iodide-sensitive electrode.

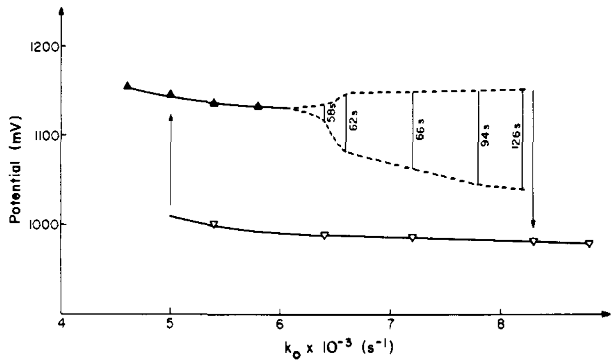

Figure 3. Hysteresis in the transition between steady states (symbols as in Figure 1) and oscillatory state as a function of flow rate k_0 with $[BrO_3^-]_0 = 0.005$ M, $[I^-]_0 = 0.005$ M, $[H_2SO_4]_0 = 1.5$ M, $T = 25$ °C. Envelopes of vertical segments show upper and lower limits of platinum electrode potential in the oscillatory state. Numbers next to these segments indicate period of oscillation in seconds. Arrows show spontaneous transitions between states.

The experiments were performed in a thermally regulated (25.0 ± 0.1 °C) CSTR of volume 21.5 cm^3 with no free surface. The responses monitored were the optical density at 460 nm and the potentials of a platinum and of an iodide-sensitive electrode against a mercurous sulfate reference electrode.

In Figure 1 we show the phase diagram of the system at a fixed residence time of 82 s. We observe two different regions in which there exists a single stable stationary state. Between these at low input concentrations we find two regions of bistability, one between the two stationary states and a second in which both the low-potential state and an oscillatory state are stable. At higher input concentrations, the bistability phenomena vanish and only the oscillatory state remains. Typical oscillatory traces are shown in Figure 2.

The oscillations in the multistable region arise as the high-potential state becomes unstable, leading to a supercritical Hopf

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(1) Part 15 in the series Systematic Design of Chemical Oscillators. Part 14: Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5918–5922.

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bifurcation.[7] This behavior, illustrated in Figure 3, resembles but is not identical with the subcritical Hopf bifurcation and resulting bistability between a stationary and an oscillatory state found in the chlorite–iodide system.[5]

If the iodide and bromate input concentrations are increased still further, we reach a critical point P at which the two stationary states simultaneously become unstable. Beyond this point, the oscillatory state is the only stable one. This region of oscillatory monostability widens, in accordance with the cross-shaped diagram model,[5,8] as the input concentrations are increased. Quantitative measurements in this range are hampered, however, by significant iodine precipitation.

While the mechanism for this system remains to be worked out, two different schemes can be envisioned that would lead to oscillation. Iodide could reduce enough bromate to bromide to provide a source of that essential species, while simultaneously generating the 1-equiv redox couple required for the autocatalytic production of $HBrO_2$, which drives the key process in the mechanisms of other bromate oscillators.[3] Some higher oxidation states of iodine such as I, HIO, IO, HIO_2, or IO_2 would presumably play the important role of the redox couple.

Alternatively one may invoke a mechanism similar to that of the chlorite–iodide oscillating system. Preliminary work suggests that such a mechanism will involve a key binuclear intermediate $IClO_2$ in the ClO_2^-–I^- reaction and probably $IBrO_2$ in the present one.

It is somewhat surprising that earlier rate studies of the iodide–bromate reaction in a closed system give no indication of autocatalytic or even complex kinetics. Barton and collaborators[9,10] obtain a rate law

$$\frac{-d[BrO_3^-]}{dt} = k[H^+]^2[BrO_3^-][I^-] \qquad (1)$$

with a stoichiometry

$$BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O \qquad (2)$$

Since all other homogeneous oscillators discovered thus far involve some form of autocatalysis, it seems worth reinvestigating reaction 2, especially in view of a reported induction period[11] before it proceeds. The iodine–bromate reaction, which proceeds through a series of intermediates,[12] also appears to merit further study in this connection.

The iodide–bromate reaction can be augumented by the addition of a flow of Mn^{2+} to give a system that has two different oscillatory and three different stationary states. Details of this and related bromate oscillators will appear in a forthcoming publication.

Acknowledgment. This work was supported by National Science Foundation Grants CHE 7905911 and CHE 8204085. We thank Kenneth Kustin and György Bazsa for helpful comments.

Registry No. BrO_3^-, 15541-45-4; I^-, 20461-54-5.

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Reduction of Carbon Monoxide by Binuclear Tantalum Hydride Complexes

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Abstract: $[TaCp'Cl_2H]_2$ ($Cp' = \eta^5\text{-}C_5Me_4Et$) reacts with CO to give yellow, crystalline $Ta_2Cp'_2Cl_4(H)(CHO)$; the hydride bridges the two metals as does the side-on bonded formyl fragment. When PMe_3 is added to $Ta_2Cp'_2Cl_4(H)(CHO)$ the formyl C–O bond is broken to give $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$. The reaction of a mixture of $[TaCp'Cl_2H]_2$ and $[TaCp'Cl_2D]_2$ with CO followed by PMe_3 to give only a mixture of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ and $Ta_2Cp'_2Cl_4(D)(O)(CDPMe_3)$ suggests that the dimer does not fragment when it reacts with CO. This was confirmed by a crossover experiment involving $[TaCp'Cl_2H]_2$ and $[TaCp^sCl_2H]_2$ ($Cp^s = \eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2$). $[TaCp'Cl_2H]_2$ forms a green, diamagnetic pyridine adduct that contains two inequivalent hydride ligands. $[TaCp'Cl_2H]_2$ forms an unstable, purple CO adduct that shows a terminally bound CO band ($\nu_{CO} = 1939\ cm^{-1}$) and two different hydride bands ($\nu_{MH} = 1560$ and $1599\ cm^{-1}$) in the IR spectrum of a thin film at −78 °C, and a singlet ascribed to the carbonyl carbon atom at 238 ppm in the ^{13}C NMR spectrum. $[TaCp'Cl_2H]_2(CO)$ decomposes rapidly in solution or in the solid state at −30 °C to give $Ta_2Cp'_2Cl_4(H)(CHO)$ quantitatively. Methane is formed in $\sim$70% yield when $Ta_2Cp'_2Cl_4(H)(CHO)$ is treated with $AlCl_3$ under molecular hydrogen. Methanol is formed in high yield when $Ta_2Cp'_2Cl_4(H)(CHO)$ is hydrolyzed with aqueous HCl.

There is a lively interest in the selective reduction of carbon monoxide to a product containing two or more carbon atoms.[1] It is thought that such selectivity is more likely with a homogeneous catalyst, and that the reduction product will likely still contain at least one oxygen atom.[2] The best example so far of some degree of selectivity to a two-carbon product is the Rh-catalyzed reduction of CO to ethylene glycol.[2g]

Although there have been many elegant studies of the chemistry of formyl complexes and other likely intermediates in systems in

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