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Oscillations and Bistability in Hydrogen–Platinum–Oxyhalogen Systems

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Abstract: Systems consisting of a bright platinum plate, hydrogen gas, and oxyanions, such as bromate, iodate, and chlorite, in aqueous sulfuric acid solution are found to exhibit two different stable steady states under some sets of identical experimental conditions, whereas under other conditions sustained oscillations appear at room temperature and in the absence of any external current. In the platinum-catalyzed oxidation of hydrogen by potassium bromate these oscillations are observed at concentrations of 0.03–0.1 M for bromate and 0.6–1.5 M for sulfuric acid in unstirred solutions or at higher acidity (2.0 M) if the solution is stirred gently. In the presence of one-electron redox couples, such as Ce(IV)/Ce(III), Mn(III)/Mn(II), V(V)/V(IV), Fe(III)/Fe(II), and Ag(I)/Ag, the oscillation can be maintained even under strong mechanical stirring. Under certain conditions, where the reaction fails to oscillate, bistability may appear. The iodate–hydrogen–acid–platinum system shows bistability as well, and some experiments suggest that oscillation may also occur. Chlorite gives rise to bistability at slightly lower acidity than bromate and iodate, and shows oscillation at significantly higher pH. In these systems, the oscillations and bistability are a surface rather than a bulk phenomenon. The essential role of such physical parameters as surface area, speed of stirring, etc., in giving rise to these phenomena is noted. A plausible explanation for the oscillation is suggested. Efforts to produce oscillation or bistability with chlorate, bichromate, and permanganate ions were unsuccessful.

Introduction

Among the known oscillatory chemical reactions, bromate-driven oscillators exhibit the most versatile nonmonotonic behavior. Temporal and spatial oscillations as well as bistability have been observed and the basic mechanisms of these phenomena are now considered to be well understood.

In the various bromate oscillatory systems (bromate ion–organic substrate–catalyst–acid), the reduction of bromate ion must take place in the same way. The chemistry of this process is clear.[2] However, the oxidative bromination reaction is different for each organic substrate. Because of the large variety of possible intermediates, the detailed chemistry of the oxidation and bromination is rather obscure. In order to reveal more about the role of the reducing agent in the oscillating system, substrates as simple as possible should be found. In principle, inorganic compounds would be the best candidates.

The substrates known so far to give rise to oscillation are either aliphatic carboxylic acids and ketones[3] or phenol and aniline derivatives.[4] No inorganic compound has yet been shown to be capable of replacing the organics in bromate oscillators. In this paper we report the first example of such a system. Hydrogen gas reacts with bromate in an oscillatory fashion in the absence and in the presence of aqueous metal ion catalysts. Our system might be regarded as a version of the Belousov–Zhabotinsky (B–Z) reaction with platinum playing the role of catalyst and hydrogen replacing the organic substrate. However, though there are some common features, an essential difference must be emphasized. The oscillatory process takes place on the surface of the platinum and no oscillation is observed in the bulk of the solution. Although we have found the simplest substrate from the chemical point of view, the heterogeneous processes introduce new complexities into the mechanistic analysis.

The reaction between hydrogen and bromate in the presence of platinum is oscillatory only in a narrow concentration range and under particular physical conditions. A certain change in these parameters can cause the platinum surface to attain either a low or a high steady potential value. There are some sets of experimental conditions with which either of these two states can be attained under *the same* external constraints (reactant concentrations, gas flow and stirring rates, electrode surface area, etc.). Which state is reached in response to the constraints depends upon the past history of the system; the system is bistable.

Investigations with other oxyhalogen ions show that chlorate ion is inert to hydrogen while iodate and chlorite behave in much the same way as bromate.

Experimental Section

The variation in potential of several platinum electrodes was monitored by a double channel Kipp & Zonen BD 9 recorder (input resistance 1–20 MΩ). The electrodes (Radelkisz OP 6123 type and some others prepared by ourselves with surfaces, of 12, 6, 4, 2, 1, 0.5, 0.25 cm^2 and platinum wire) were connected against a Hg/Hg_2SO_4, K_2SO_4 reference electrode (Radiometer Copenhagen Type 601), which has a potential of 0.6158 V with respect to a standard hydrogen electrode. In an attempt to follow the change in the bromide ion concentration, a bromide selective electrode (Orion, Model 94-35A) was used. A thermostated reaction vessel of volume 150 cm^3, equipped with a magnetic stirrer, was employed. High-purity hydrogen was taken from a gas cylinder and introduced into the solution through a gas inlet, which had a glass filter at the end to ensure the uniform distribution of the gas.

The concentrations of the reagents varied up to 3.0 M for sulfuric acid, and between 0.03 and 0.1 M for potassium bromate, 0.0001 and 0.01 M for potassium iodate, and 0.001 and 0.02 M for sodium chlorite. Metal ion concentrations were between 10^{-3} and 10^{-4} M with the exception of silver ion, of which 10^{-5} M or less was added.

The experiments were carried out as follows. First a hydrogen electrode was established in the reaction vessel by introducing a hydrogen gas stream into a sulfuric acid–water mixture under constant stirring. When the equilibrium potential at the platinum was attained, the second component, the oxyhalogen ion, was added. The potential of the platinum electrode was followed at different chemical compositions and physical conditions.

Results

Bromate–Hydrogen–Platinum–Acid System. Reaction mixtures composed of 0.6–1.5 M sulfuric acid and 0.03–0.1 M potassium bromate showed potential oscillations immediately after the magnetic stirrer was switched off. The gas stream had to be slow if the surface of the platinum was small (<1 cm^2), but a stronger stream could be applied with larger electrode surfaces. The oscillations could be suppressed and started again by switching the magnetic stirrer on and off. If the surface area of the platinum was very large (>10 cm^2), the oscillations could be maintained in a mildly stirred reaction mixture as well.

A typical redox potential vs. time curve is presented in Figure 1. The experimental conditions are indicated in the caption. The

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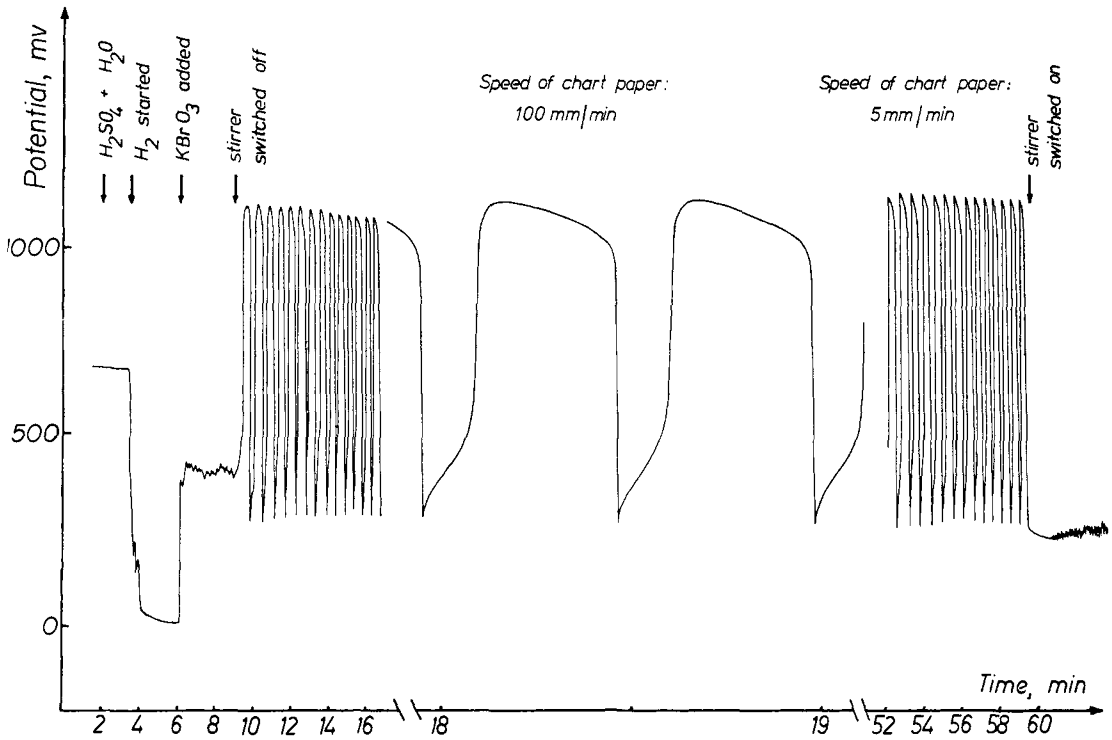

Figure 1. Potential oscillations in an unstirred hydrogen gas, potassium bromate (0.077 M), and sulfuric acid (1.15 M) reacting system: temperature, 20 °C; surface of platinum electrode, 1.0 cm^2. Potential values are with respect to a standard hydrogen electrode.

shape of the oscillatory trace is shown in the central part of the curve. The sustained oscillations proceed for hours. Switching off the hydrogen gas stream terminates the oscillations immediately.

A study was made of the effect of one-electron redox couples on the behavior of the oscillating hydrogen gas–acidic bromate system. Besides the catalysts used in the classical B–Z reaction [$Ce(SO_4)_2$, $Ce(NO_3)_3$, $MnSO_4$, ferroin], several other compounds, such as $VOSO_4$, NH_4VO_3, $FeSO_4$, and $AgNO_3$, were tried and found to act as catalysts, i.e., to give rise to oscillations in the system under intensive mechanical stirring when the oscillation would cease in the absence of metal ions. Even after the hydrogen gas stream is switched off, an additional 10–20 potential oscillations occur. The oscillation was initiated by adding the metal ion to a well stirred acidic bromate–hydrogen gas system. The redox-couple-catalyzed oscillatory curves show somewhat different characteristics from those in Figure 1. The amplitude is smaller, the frequency is lower, and the shape of the oscillatory trace is spiked in the opposite direction.

The redox-couple-catalyzed oscillator has an induction period. If the oscillation is initiated with the oxidized form of the ion, the induction period is long and is marked by irregular, noisy oscillations with a very high frequency and increasing amplitude. This aperiodic behavior then evolves into sustained, regular, undamped oscillations. A potential trace vs. time in the presence of cerium(IV) ions is shown in Figure 2. The curve with VO_3^- added (10^{-3} M) is similar in appearance, but a longer induction period, a lower frequency, and a smaller amplitude were observed.

If the oscillation is initiated with the reduced form of the redox couple, the induction period is usually short and free from the "chaotic" behavior. The oscillatory part of the reaction resembles that seen when the oxidized form of the redox couple is employed. As an example, the vanadium(IV)-initiated oscillation is presented in Figure 3. Manganese(II), cerium(III), and iron(II) ions result in similar oscillatory traces. The shorter induction period obtained with the reduced metal ion suggests this form to be active as the catalyst. The oxidized state must, at least partly, be reduced by hydrogen either in a homogeneous reaction or at the platinum surface to initiate oscillations. The slow rate of the reduction results in a long induction period.

Silver ion has a special effect. If 10^{-5} M silver ion is added to the stirred reaction mixture (composition as shown in Figure 1), the oscillation starts immediately. Further addition stops the oscillation. If the silver ion concentration is then decreased by introducing an equivalent amount of bromide ion, the system is ready to oscillate again. In the unstirred oscillatory mixture silver ions increase the frequency. (Silver ions can make the platinum electrode unusable because of the formation of a silver/silver bromide electrode on the surface. The platinum can be regenerated by soaking it in 10% potassium cyanide solution.)

The effects of oxygen, bromide ion, bromine, hypobromous acid, and iodide ion were also studied. Introducing oxygen gas into the oscillating system stopped the potential oscillation. Runs with nitrogen bubbling led to the same results. Thus these transitions may be attributed to the effect of increasing the stirring of the solution by the additional gas stream. Experiments carried out by carefully excluding dissolved oxygen showed no difference either in the amplitude or in the frequency of the oscillation from reactions exposed to air. Bromide ion, bromine, and iodide ion proved to be inhibitors above 10^{-5} M concentration, but oscillations were observed at 10^{-4} M hypobromous acid. Further amounts of HOBr terminated the oscillation.

The results described in the previous section were found in solutions 0.6–1.5 M in sulfuric acid. At a sulfuric acid concentration of 2.0 M (other conditions as in Figure 1), oscillations appeared only within a definite range of stirring. At the lower end of the range the waveform resembled that of Figure 1, while close to the upper limit, profiles like that in Figure 3 were observed. At stirrer speeds below the oscillatory range the potential rose to a constant high value, while a low steady potential was attained above this range. Further increasing the acid to 3.0 M led to a high constant potential level even at strong stirring.

With a sulfuric acid concentration equal to or less than 0.5 M, no oscillations are observed. However, in solutions of 0.5 M acid and 0.01–0.1 M potassium bromate the oxidation of hydrogen gas on the platinum surface may give rise to two different steady states under the same experimental conditions; i.e., bistability appears. When the reaction is started as described earlier, a low steady potential (SS_{red}) of the platinum electrode is obtained. A perturbation of this state can induce a transition to a high constant value (SS_{ox}), which differs from the previous state by about 1000 mV. The transition between SS_{red} and SS_{ox} can be accomplished in several ways. Application of a positive external potential to the system in the reduced state causes the potential of the platinum

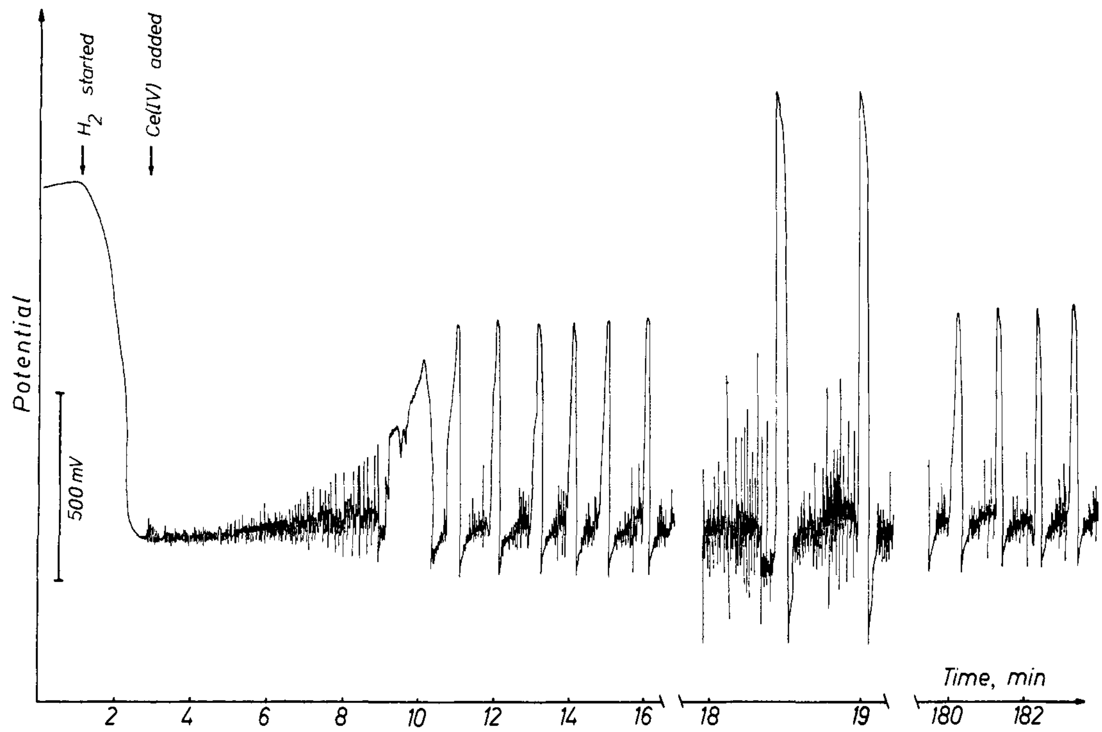

Figure 2. Potential oscillations in a stirred hydrogen gas, potassium bromate (0.077 M), sulfuric acid (1.15 M), and Ce^{4+} (10^{-3} M) reacting system. The experimental conditions are as in Figure 1.

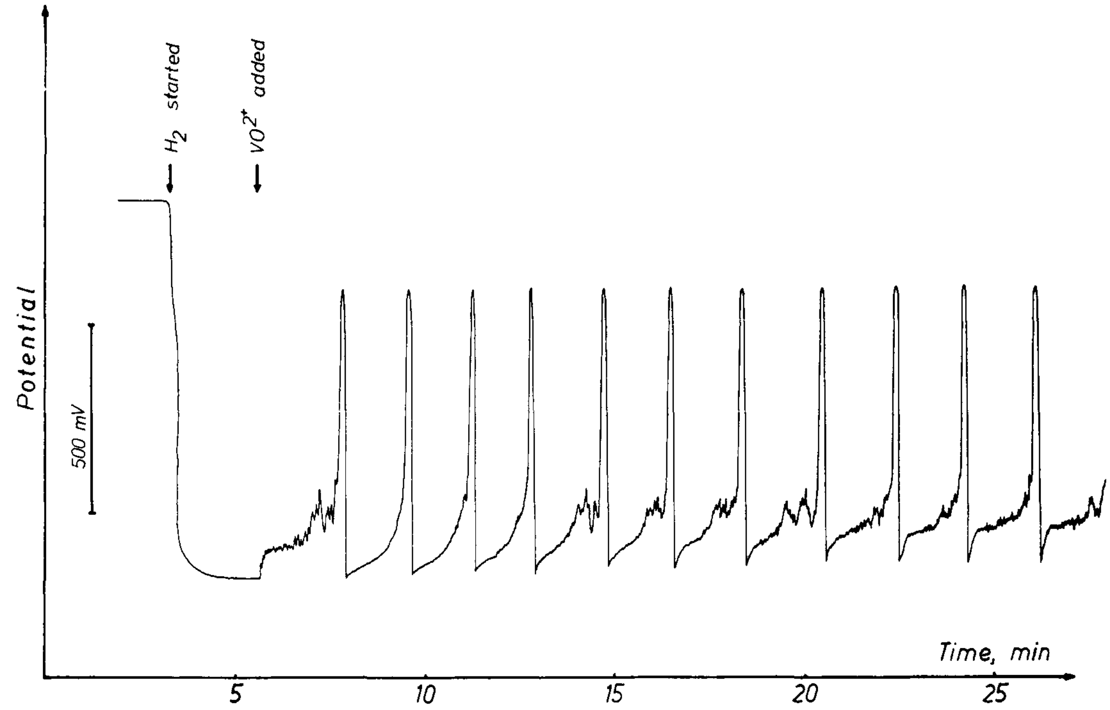

Figure 3. Potential oscillations initiated with VO^{2+} (10^{-4} M). The experimental conditions are as in Figure 1.

electrode to rise. If the magnitude of the external voltage is large enough and if it is applied for a sufficiently long time, the system remains in SS_{ox} when the source is removed. If the voltage is too low or is applied for too short a time, the system returns to SS_{red} on disconnecting the source. Transitions from SS_{ox} to SS_{red} may be induced by application of a negative external potential. The $SS_{red} \rightarrow SS_{ox}$ transition can also be achieved by temporarily turning off the stirrer. When the stirring rate is restored to its original value, the system remains in SS_{ox}. It can be returned to SS_{red} by temporarily increasing the stirring rate. The $SS_{red} \rightarrow SS_{ox}$ transition is quite rapid, but longer stirring perturbations are required to induce the reverse transition. Touching the electrode surface with an iron or a copper wire also induces the $SS_{ox} \rightarrow SS_{red}$ transition. It is important to note that at a given chemical composition the potential values for SS_{red} and SS_{ox} are independent of the way the perturbation is carried out.

At low acid concentration (<0.2 M) no oscillations or bistability were found in the concentration range of 0.0005–0.1 M for bromate.

Iodate–Hydrogen–Platinum–Acid System. In the classical Belousov–Zhabotinsky oscillatory reaction, the bromate ion is of essential importance. Oscillations have been observed in modified systems in which all components, with the single exception of bromate, have been replaced by other species. In the Bray–Liebhafsky and Briggs–Rauscher reactions iodate plays a role similar to that of bromate in the B–Z system. Molecular hydrogen

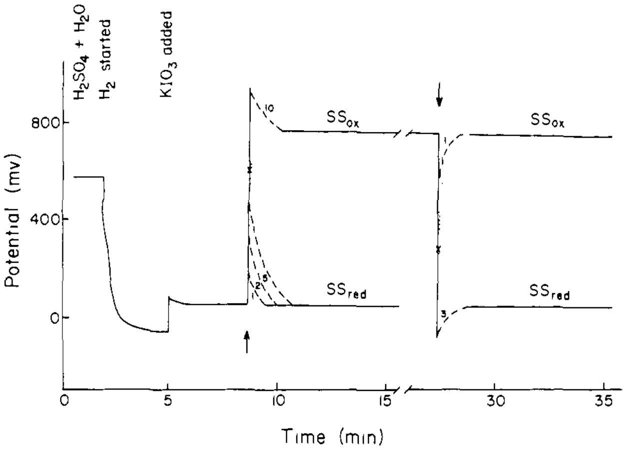

Figure 4. Plot of potential vs. time in a hydrogen gas–potassium iodate (0.0005 M)–sulfuric acid (0.2 M) system. The transitions were induced by a potential perturbation. (For explanation see text.)

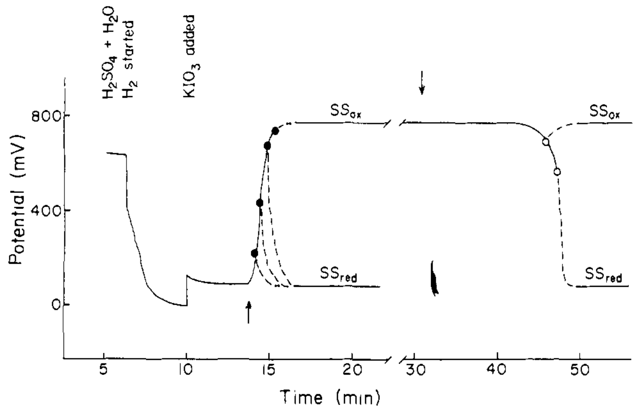

Figure 5. Plot of potential vs. time in a hydrogen gas–potassium iodate (0.0005 M)–sulfuric acid (0.2 M) system. The transitions were induced by perturbation of the stirring speed. (For explanation see text.)

is known to reduce iodate in aqueous solution;[5] therefore, one might expect similar behavior in the platinum–hydrogen–acid system when bromate is replaced by iodate.

At concentrations of 0.1–0.5 M sulfuric acid and 0.0002–0.0005 M iodate bistability appeared. The difference in potential between the two states of the platinum surface was about 700 mV. Perturbation by an external potential caused a rapid transition in either direction. Perturbation by temporarily changing the intensity of stirring gave a rapid transition from SS_{red} to SS_{ox}, but required even a longer time than was observed in the bromate system to go from SS_{ox} to SS_{red}. Again, the potentials of the two states are independent of the mode of perturbation employed to reach them. Figures 4 and 5 illustrate the change in potential of the platinum electrode during the perturbation experiments.

In Figure 4 the arrows show the points at which a 1-V potential was imposed on the platinum electrode for the time (in seconds) indicated on the dotted lines. The crosses show approximately the threshold values of the increasing external potential imposed for a fixed time, at which the state turns to SS_{ox} or SS_{red}. Notice that threshold values for induced transitions in one direction differ significantly for those in the opposite direction. This is consistent with the behavior of a multidimensional system.[6] The results of varying the stirring rate are shown in Figure 5. The upward arrow indicates the point at which the stirring was stopped until the potential reached the values marked by the full circles. At the downward arrow the stirring rate was increased sharply. At the times indicated by the open circles the original stirrer speed was restored.

At iodate concentrations of less than 0.0002 M, state SS_{red} was attained even when the acid concentration exceeded 1.0 M. With more than 0.001 M iodate, state SS_{ox} could not be transformed to SS_{red} even when the sulfuric acid concentration was as low as 0.1 M.

A rather wide range of reagent concentrations was tried without finding sustained oscillation. At 0.5 M sulfuric acid and 0.0005 M iodate several oscillations of about 400-mV amplitude were observed with careful adjustment of the stirring speed. The poor reproducibility of the oscillation suggests that the oscillatory range of composition must be rather narrow and considerably more sensitive to the physical parameters than for the system containing bromate.

Chlorite–Hydrogen–Platinum–Acid System. While oscillators based on oxybromine and oxyiodine chemistry are known, no oscillation involving oxychlorine species has been reported previously. The system described above with strong stirring and rapid H_2 gas flow shows sustained complex oscillations of amplitude 400–500 mV with sodium chlorite concentrations of 0.001–0.01 M in the pH range 3–7. Even at the lowest chlorite concentrations employed, the oscillations persist for hours. Bistability is found in the same range of chlorite concentration at pH's between 1 and 2. We note that at higher acidity than this the decomposition of chlorite to yellow ClO_2 becomes quite noticeable.

Experiments with Other Oxyanions. Experiments were also carried out with chlorate, bichromate, and permanganate ions. The reduction of $Cr_2O_7^{2-}$ and MnO_4^- in aqueous solution by molecular hydrogen has been reported by Halpern et al.[5,7] in the presence and in the absence of catalysts. Our preliminary experiments indicate that neither bistability nor oscillation appears in the system when bromate, iodate, or chlorite is replaced by these species.

Discussion

The hydrogen gas–acidic bromate system constitutes a heterogeneous oscillator. The hydrogen is introduced as a gas, the acidic bromate is in solution, and the reaction between these reagents takes place on a solid surface, i.e., on the platinum plate. Both physical and chemical processes contribute to the oscillations.

Many observations prove the essential role of the boundary surface in bringing about oscillatory behavior. These are as follows. (a) The characteristics of the oscillatory curve depend greatly on the size and the quality of the platinum surface (e.g., with a platinum wire electrode, because of the small surface, no oscillations could be produced), on the position of the platinum electrode in the reaction vessel, on the intensity of the hydrogen gas stream, on the pore size of the filter by which the gas is dispersed into the solution, on the speed of the magnetic strirrer, etc. (b) A bromide-selective electrode immersed in the reaction mixture shows no oscillations, while the platinum electrode does. (c) No color change in the bulk of the solution is observed during the oscillatory process when the redox couple is present. (d) Simultaneous recordings on a double-channel recorder with two platinum-reference electrode pairs give asynchronous oscillations even if the electrodes are the same in type, size, and position.

The above observations, particularly (b) and (d), as well as the catalytic properties of species which are ineffective in the B–Z reaction, strongly suggest that the oscillations in this system are not homogeneous bromate-driven oscillations of the type discussed by Noyes.[8] The fact that no external voltage or current source is required also differentiates this phenomenon from the electrochemical oscillations characterized by a number of workers.[9] Perhaps the closest analogues are to be found in the oscillatory gas-phase oxidations of ethylene[10] and carbon monoxide[11] at platinum surfaces.

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Since the major part of the reaction apparently takes place at or adjacent to the platinum surface, the system is in effect a flow reactor or pumped system[12] in which hydrogen gas, hydrogen ion, and bromate, iodate, or chlorite are brought at a constant concentration to the reaction volume (i.e., the platinum surface and adjacent boundary layer) by the combined effects of gas flow, stirring, and diffusion. The existence of both bistability and oscillation suggests that these systems may provide examples of the "cross-shaped phase diagram" of Boissonade and De Kepper[13] in which oscillation is closely related to the bistability phenomenon by an appropriate feedback. Bistability or sustained oscillation, which mutually exclude each other, may be observed depending on the values of various constraints. In this case the constraints may be either chemical ($[H^+]$, $[BrO_3^-]$, $[IO_3^-]$, $[ClO_2^-]$, p_{H_2}), or physical (stirring and gas flow rate, electrode surface area).

It would be premature to postulate a detailed mechanism for the behavior of the hydrogen gas–platinum–oxyhalogen systems at this point. However, several elements which may lead to oscillation and bistability can be suggested. We have observed bromine gas in the effluent of the bromate system. Bromine may be generated in the bulk of the reaction mixture or in the diffusion layer by either of two overall reactions:

$$2BrO_3^- + 2H^+ + 5H_2 \rightarrow Br_2 + 6H_2O \qquad (1)$$

or

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (2)$$

The major source of bromine presumably switches between eq 1 and eq 2 during the course of the oscillation. Analogous reactions may be written for the iodate system, in which case reaction 2 is the well-known (and autocatalytic) Dushman reaction.[14] Corresponding equations could also be written for the reaction with chlorite, but one should first resolve the question of whether the active species is ClO_2^- or ClO_2.

Chemisorbed atomic hydrogen has been found by electrochemical measurements[15] to exist in two or more forms on platinum surfaces in aqueous solution. Molecular halogens are also strongly adsorbed on platinum. If two distinct chemisorbed hydrides were to be present and if the free halogen (or some halogen-containing species like HOBr, HOI, or ClO_2) were to compete with hydrogen for sites and react with hydrogen at only one of the two types of platinum surface sites, then oscillation could result from a mechanism similar to that of Vayenas et al.[16] in which ethylene reacts in an oscillatory fashion with one of two surface platinum oxides. Alternatively, oscillations and bistability may arise from competition between molecular halogen and hydrogen adsorption where one or both species are adsorbed in such a way that the activation energy for desorption varies with the amount adsorbed. Such cooperativity is thought to be quite common in gas–metal adsorption reactions.[17] These possibilities will be explored quantitatively in further studies.

In either case the bromate oscillation might proceed as follows. Dissolved H_2 initially equilibrates on the platinum surface. This point corresponds to the lowest potential in Figure 1. When the bromate is added, Br_2 is produced by reaction 1 and diffuses to the platinum surface where it is adsorbed. An electron transfer reaction, such as

$$H_{ads} + Br_{ads} \rightleftarrows H^+_{(aq)} + Br^-_{(aq)} \qquad (3)$$

then removes much of the adsorbed hydrogen and bromine, bringing the system to its maximum potential. In the neighborhood of the surface, the bromide ion reacts via eq 2 to produce Br_2, which either readsorbs or is carried off by the gas stream at a rate dependent upon the gas flow rate and the stirring speed. Since the H_2 diffuses significantly faster than any of the halogen-containing species, the restoration of the bromate (and bromine) level in the diffusion layer is delayed compared to that of the hydrogen. Thus the adsorbed hydrogen can be largly replenished, lowering the potential, until enough bromine can reach the surface to reinitiate reaction 3 and raise the potential again.

The inhibitory effects of added Br^-, Br_2, HOBr, and I^- then result from these species occupying the platinum sites at the expense of hydrogen. We note that when oscillation is prevented by addition of these species, the observed constant high potential is at or above the upper limit of oscillation, corresponding to low adsorbed hydrogen, and that the electrode may be reactivated for oscillation by soaking it in an acidic concentrated ferrous sulfate solution or by electrolysis.

The added redox couples, many of which do not catalyze the B–Z oscillations, do not appear to produce bulk oscillations. They may serve as electron-transfer catalysts for some reaction, such as eq 3, occurring at or near the platinum surface. Apparently, it is the reduced form of the couple which is catalytically active, which suggests that the metal ion acts by transferring electrons to the adsorbed bromine atom. By speeding up this step, the redox couple might allow the system to remain in the oscillatory range even in the presence of stirring, which will effectively speed diffusion and reduce the thickness of the boundary layer, though not to zero. Alternatively, the redox couple might catalyze the reduction of bromate to bromide in the bulk, thereby adjusting the bromine concentration to a level capable of supporting sustained oscillation at the stirring rate employed.

While the hydrogen–platinum–acidic bromate system does indeed constitute a purely inorganic bromate oscillator, its contribution to our understanding of the general class of bromate oscillators must await a clearer picture of the role of surface phenomena in heterogeneous oscillators.

We have found poor reproducibility in the oscillatory reaction between iodate, platinum, and hydrogen. This may be due to blocking of the sites by strong adsorption of iodide ion or iodine on platinum. Iodide has been shown to be an inhibitor in the reduction of many organic compounds by hydrogen on a platinum catalyst, whereas other halide ions had little inhibitory effect.[18]

Bistability in the homogeneous oxidation of cerium(III) by acidic bromate in a continuously stirred tank reactor has been observed by Geiseler and Föllner,[19] and the chemical processes responsible for bistability in that system are well characterized.[20] The origin of the bistability in the present systems is less clear, though either a two-site or a cooperative adsorption mechanism lends itself to the existence of both a high hydrogen (SS_{red}) and a low hydrogen (SS_{ox}) stable steady state under the appropriate physical conditions and concentrations.

The above model is quite crude, but we believe that its essential elements—the crucial role of the platinum surface, the existence of multiple adsorption sites and/or cooperative binding, the competition for sites between hydrogen and a halogen or halogen-containing species, the importance of diffusion and the role of redox couples as electron transfer catalysts—contain the key to understanding these systems. In addition to quantitative modeling, experiments using rotary disk electrodes to simplify the diffusion effects or low-angle photon scattering to monitor the surface states would be of considerable value.

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