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The Bromate–Sulfide System. A Particularly Simple Chemical Oscillator[†]

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In a batch system, elementary bromine rapidly oxidizes the sulfide ion, HS^-, mostly to elementary sulfur and only a little further even though the redox potentials suggest the sulfide could be oxidized all the way to sulfate, SO_4^{2-}. A stoichiometric excess of acidic bromate, BrO_3^-, does oxidize batch sulfide all the way to sulfate. The potential of a platinum electrode in such a system exhibits two successive autocatalytic rises with an intervening plateau; visible evidence of elementary bromine does not appear until the start of the second rise. In a flow reactor, this ostensibly simple system exhibits oscillations with constant periods but somewhat erratic amplitudes. We are initiating a study to elucidate the mechanism of the reaction, which seems to differ in behavior from bromate-driven oscillators involving elements other than sulfur.

Introduction

Bromate is a strong oxidant which can generate oscillations with a number of reducing substrates, most of which are organic compounds. Often a metal ion is also necessary as a one-equivalent redox catalyst.

Thermodynamic considerations indicate that sulfur compounds with oxidation number less than +6 can all be oxidized to sulfate even by rather mild oxidants, but the mechanisms may be quite complex. When oscillatory behavior is observed, one-equivalent catalysts are often needed. Examples of such catalyzed oscillators with sulfur substrates include the air oxidation of alkaline sulfide to polysulfide catalyzed by methylene blue,[1] the oxidation of thiosulfate by hydrogen peroxide catalyzed by copper(II),[2] and the oxidation of sulfite by bromate catalyzed by manganese(II).[3] Orbân and Epstein[4] have also observed uncatalyzed oscillations involving sulfide and hydrogen peroxide under conditions such that the pH oscillated to both sides of neutral.

One of us has recently discovered oscillatory systems based on bromate oxidation of thiourea,[5] $(NH_2)_2CS$, and of thiocyanate ion,[6] SCN^-, with no other species except acid. Although these oscillations did not require catalysts, the chemistry was potentially complicated by reactions of compounds of carbon and nitrogen. It occurred to us that similar behavior might be observed with only bromate and sulfide and that such a system would be the simplest possible bromate-driven oscillator involving sulfur chemistry. Our objective has been attained.

Experimental Section

The following analytical-grade chemicals were used without further purification: sodium bromate (Matheson Coleman and Bell), sodium sulfide (Fisher), perchloric acid 69–72% (Baker), and sodium perchlorate (EM Science). The continuously stirred tank reactor (CSTR) experiments were carried out in a plexiglass reactor of volume 30.0 cm^3 prepared at Brandeis University. The stirring rate (magnetic stirrer) was maintained constant throughout the flow studies. The reactor was fed by a Sage 375A peristaltic pump through three inlet tubes. Each tube carried a separate stream of perchloric acid, sodium bromate, or sodium sulfide. The reaction was followed by measuring the potential of a platinum electrode against a Radiometer K601 $Hg|Hg_2SO_4|K_2SO_4$ reference electrode. The batch experiments were carried out in the same reactor with the Sage pump disconnected. The ionic strength in the batch experiments was maintained at 0.2 M with sodium perchlorate. The reactor was filled initially at the highest pump speed, and the speed was reduced or again increased in steps while the different oscillatory states were noted. Laboratory temperature was about 22 °C.

Batch Reactions. Bromine and sulfide in mild acid reacted almost instantaneously to form a dispersion of elemental sulfur as shown in process A. Although bromine is a strong enough

$$Br_2 + HS^- \rightarrow S(s) + 2Br^- + H^+ \qquad (A)$$

oxidant to continue the reaction to sulfate, we did not observe qualitative evidence of much further reaction. This limited reaction is in contrast to the behavior of thiourea; both bromine[7] and the still weaker oxidant iodine[8] oxidize the sulfur in thiourea all the way to sulfate.

When sulfide was in stoichiometric excess, it reacted with acidic bromate to produce a clear yellow solution which apparently contained polysulfides, S_x^{2-}. A test with barium ion indicated that some sulfate was also formed. The reaction is obviously complex with no unique stoichiometry.

When bromate was in excess of sulfide, the solution remained clear at all times. The color of elementary bromine eventually appeared, but only after an induction period. The presence of sulfate was indicated by a test with barium ion. We anticipate that bromate should oxidize all oxysulfur compounds cleanly to sulfate and that the overall stoichiometry should be that of process B.

$$5HS^- + 8BrO_3^- + 3H^+ \rightarrow 5SO_4^{2-} + 4Br_2 + 4H_2O \qquad (B)$$

Even if the stoichiometry is clean, the dynamics are complex. Figure 1 shows the trace of the potential of a platinum electrode in such a system. This behavior is similar to that of thiocyanate with bromate[6] and indicates a double autocatalysis with appearance of bromine as a kind of "clock" reaction. This peculiar behavior encouraged us to search for oscillatory behavior in a flow reactor.

Behavior in a Flow Reactor. Solutions of bromate, sulfide, and perchloric acid were introduced in three streams into a CSTR. The potential of a platinum electrode behaved somewhat erratically even when the residence times in the reactor clearly put the cell contents on the flow or on the thermodynamic branch. Intermediate flow rates generated the sort of behavior shown in Figure 2. The oscillations have amplitudes of about 200 mV and exhibit fairly regular periods even though the amplitudes are quite erratic. We are not presently in a position to explain the types of extreme sensitivity which lead to such erratic behavior but can speculate that the presence of ill-defined colloidal sulfur may contribute to the obvious lack of complete control of the system.

An electrode intended to measure bromide ion exhibited small

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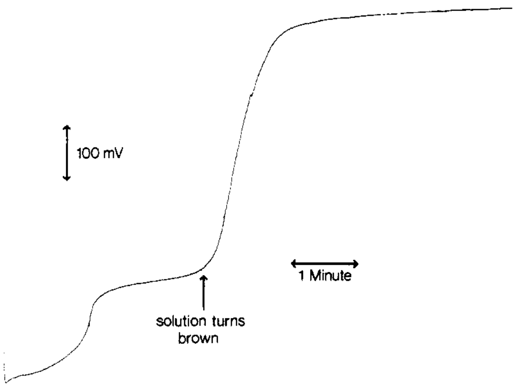

Figure 1. Trace of the potential of a platinum electrode in a batch reactor. Composition at time zero was $[BrO_3^-] = 0.03$ M, $[Na_2S] = 8 \times 10^{-4}$ M, $[HClO_4] = 0.05$ M. Note the two autocatalytic rises.

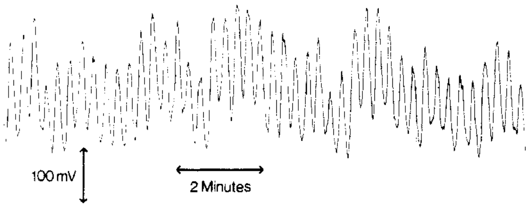

Figure 2. A train of oscillations in electrode potential in the CSTR reactor with residence time 48 min. Concentrations which would have existed in the reactor if there had been no chemical change were $[BrO_3^-] = 0.033$ M, $[Na_2S] = 0.001$ M, $[HClO_4] = 0.05$ M.

regular "blips" in a direction of decreasing bromide when the platinum electrode was more positive. The amplitude was only a few millivolts. Sulfide ion interfered badly with the measurement of bromide with such an electrode, and the observations serve only to support the conclusion that the contents of the reactor was oscillating with a regular period in spite of the erratic amplitudes in Figure 2.

The concentration of acid in Figure 2 was so much greater than that of sulfide that the pH could not oscillate significantly, unlike the situation for oscillations in the peroxide–sulfide system.[4]

Discussion

This system requires only one oxyanion and a mononuclear reductant in addition to acid. The only oscillator we are aware of with comparable simplicity of feed reactants is the bromate–iodide system observed by Alamgir et al.[9]

The behavior of this bromate–sulfide system is obviously complex, and we are undertaking further studies to elucidate the mechanism. We are particularly intrigued by the prospect that this system may differ from the previously known bromate-driven oscillators which do not involve sulfur chemistry. In those systems, BrO_3^- and Br^- are in competition for $HBrO_2$, and the bromate step initiates autocatalytic generation of the one-equivalent oxidant BrO_2. Although a bromide ion electrode will not function in a sulfide solution, we anticipate that the solution in Figure 2 contains so much bromide at all times that $BrO_2^{\bullet}$ is not an important actor in the obviously complex chemistry.

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Energy Gap and Bond Length Alternation in Heterosubstituted Narrow Gap Semiconducting Polymers

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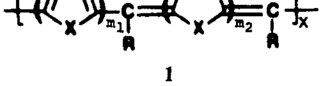
Modified polythiophenes $[-(C_4SH_2)—CH{=}(C_4SH_2){=}CH-]_x$ with bridging —CH═ groups have been suggested to possess small energy gaps. Based on MNDO geometry optimizations for the infinite polymer, it is found, that the bond length alternation along the C–C backbone of the polymer is similar to, but modified relative to, that of polyacetylene, $(CH)_x$ or PA. The presence of aromatic and quinoid groups is a consequence of the fact that an *odd* number (namely one) of —CH═ groups bridges the two types of rings. Heterosubstitution has no significant effect on the gap, because the HOMO and LUMO are perturbed identically in the first-order perturbation theory. Due to small differences in the shift in second order, however, some analogous polymers may have even smaller gaps.

Engineering of energy gaps in semiconductors, specifically designing conducting conjugated polymers with small energy gaps, E_g, has attracted considerable attention.[1–13] It has been argued that in these quasi-one-dimensional polymers nuclear relaxation is fundamentally important to explain doping effects,[10] charge transfer, and also nonlinear optical properties.[14] Jenekhe[9] has recently suggested that the modified polythiophenes (**1**) should be excellent candidates as small E_g polymers. In this study we predict the gap of this system and elucidate the role of nuclear



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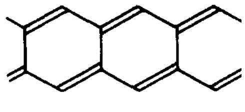

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