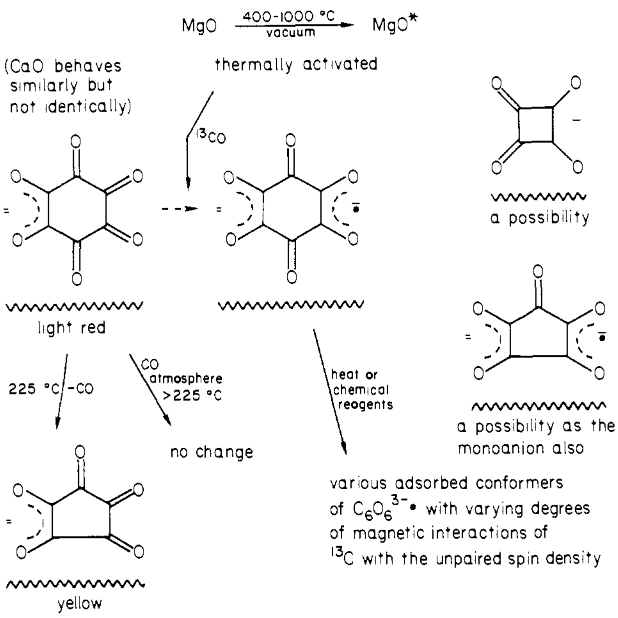
Scheme I



Adsorption of CO onto thermally activated MgO or CaO also leads to the formation of several adsorbed, paramagnetic radical anions. Although these species may be colored, their concentrations are much lower than the dianion species discussed above, and therefore color is not indicative of their presence (2–10% of the adsorbed CO yield paramagnetic species). The formation of the anion radicals is preceded by formation of the colored dianions.

A variety of considerations, including ESR spectral evidence, spectral computer simulations, and chemical treatments, lead us to the conclusion that the most common radical anion is the $C_6O_6^{3-}\cdot$ species, which is probably formed from $C_6O_6^{2-}$. The surface adsorption state of this species is such that only two carbons strongly interact with the unpaired spin density. Upon treatment of this trianion radical with heat, oxygen (slow addition), CO_2, H_2O, HCl, or NH_3 it is converted to a different adsorbed state where different magnetic interactions occurs but in which no gross chemical changes have occurred (new bond formations or bond cleavages). It is also possible that some smaller ring species form. These ideas are illustrated in Scheme I.

Apparently the added reagents adsorb on the MgO or CaO surface near the $C_6O_6^{3-}\cdot$ species and cause a change in its conformational state, either by changing the electronic properties of the basic surface or simply by crowding the $C_6O_6^{3-}\cdot$ species. Neither the dianions or trianions are affected by adding relatively nonreactive substances (at 25 °C) such as H_2, CH_4, N_2, C_2H_4, or $C_6H_5CH_3$. In fact, the activated MgO can be placed in a bath of pure toluene followed by CO addition, and both colored dianions as well as paramagnetic trianions form without toluene interference.

Experimental Section

Materials. The preparation of MgO samples has been described previously.[28,34] A single source of calcium oxide was obtained from ROC/RIC listed as 99.99% pure. CO (Linde, 99.999%) was passed through a 77 K cold trap just prior to adsorption on the oxide samples. ^{13}CO (Prochem Isotopes, 98% ^{13}CO, 2% ^{12}Co) was passed over a freshly regenerated BASF-R3-11 deoxygenation catalyst and then through a −196 °C trap just prior to adsorption.

EPR Spectroscopy. Two spectrometers were used, a Bruker ER-420/10V and a Varian V-4502. The Bruker instrument was used to obtain all ^{13}C data, and experimental parameters have been reported previously.[28]

Sample Preparations. The oxide samples were washed with boiling distilled water for 1 h, recovered by hot filtration, and dried in air at 110 °C for ~6 h, and the samples were stored in vials awaiting thermal activation. Each oxide sample was chopped (not ground since grinding produced higher concentrations of paramagnetic defects) into small pieces <1.5 mm. About 100 mg was placed in a 10–15-cm quartz cell equipped with a graded Pyrex seal to a high vacuum stopcock (4 mm). The cell was evacuated slowly and heating was begun very slowly. About 2.5 h was needed to attain 380–400 °C, and then several more hours were needed to slowly reach the desired temperature. The extremely slow heating was necessary to avoid violent degassing of the oxide sample. The desired temperature was maintained for about 14 h and followed by cooling to room temperature. Typical pressures at the conclusion of this process were 2×10^{-6} torr.

When large samples of thermally activated MgO or CaO were required, a special apparatus was necessary. A quartz bulb with a graded Pyrex seal was connected to a glass frit and then to the vacuum system. A frit bypass tube with a stopcock was also necessary. Upon heating of the sample (up to 2 g could be used) the glass frit prevented loss of sample to the vacuum system on the numerous occasions that violent degassing (powder flying about) took place. Very slow heating was necessary, and after the system had stabilized the by pass valve was opened. Pressures about 1×10^{-5} torr could be attained.

After cooling to room temperature the oxide samples were treated with ^{12}CO or ^{13}CO, usually at 150 torr. The CO atmosphere usually remained over the sample for several weeks as radical anion growth took place. Then ESR studies were carried out, the CO atmosphere was removed, and desired chemical reagents were added, always in excess, on a vacuum system.

Acknowledgment. Support of the Department of Energy and the DOW Chemical Co. is acknowledged with gratitude.

Registry No. CO, 630-08-0; CaO, 1305-78-8; MgO, 1309-48-4; $C_6O_6^{2-}$, 28737-41-9; $C_5O_5^{2-}$, 15110-70-0.

A New Type of Oscillating Reaction: Air Oxidation of Benzaldehyde

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Abstract: During the air autoxidation of benzaldehyde catalyzed by cobalt and bromide, the solution oscillates between pink and dark brown. The color changes correspond to redox potential changes and can occur for several hours.

Several homogeneous liquid-phase reactions that oscillate between two states have been studied recently. The underlying mechanism for this seemingly odd behavior is now understood for several of these reactions.[1,2] The most thoroughly studied types

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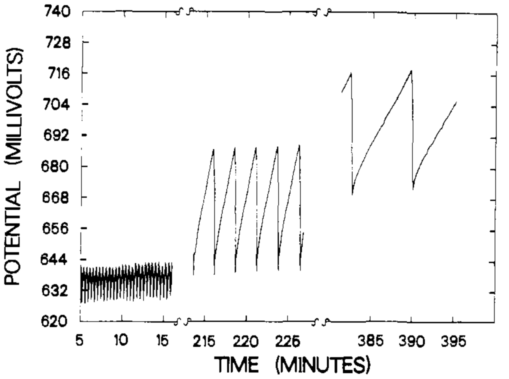

Figure 1. Air flow 0.085 cm^3/(min mL), 70 °C, 0.01 M Co^{2+}, 0.004 M Br^-, 0.75 M benzaldehyde.

are all related. The Belousov–Zhabotinsky reaction is the cerium-catalyzed bromate oxidation of malonic, or a similar acid.[3,4] The Bray–Liebhafsky is the decomposition of hydrogen peroxide catalyzed by iodic acid.[5,6] Briggs and Rauscher[7] have combined the two by reacting acidic iodate, hydrogen peroxide, manganous salt, malonic acid, and starch indicator, which oscillates between colorless and black.

A new reaction has been discovered that exhibits dramatic color changes between pink and brown/black and continues for many hours under ideal conditions. The oscillations occur during autoxidation of benzaldehyde in 90/10 acetic acid/water (w/w) solvent catalyzed by cobalt and bromide. Oscillations have been observed for over 16 h and 800 cycles.

The color change is accompanied by a change in the redox potential of between 5 and 60 mV, depending on conditions. The pink corresponds to a low Co(III)/Co(II) ratio, while the brown/black corresponds to a high Co(III)/Co(II) ratio, or to a Co(III)Br complex. The oscillations are reproducible with or without the electrodes, eliminating possible effects of platinum and silver chloride from the electrodes.

The temperature increases by 0.1–0.3 °C when the potential drops rapidly from high to low levels. A corresponding change in temperature during the increase in potential has not been observed because the increase in potential is slow, and temperature changes due to reaction are masked by the heat flow required to maintain the solution at a constant temperature.

A typical plot of oxidation potential vs. time is shown in Figure 1.

The color changes can be demonstrated by mixing the reagents in a small beaker on a hot plate with a magnetic stirrer. A 50-mL portion of 0.026 M $Co(CH_3COO)_2{\cdot}4H_2O$ in 90/10 acetic acid/water (w/w) and 10 mL of 0.026 M NaBr in 90/10 acetic acid/water are heated to 70 °C with a stream of air added beneath the surface with a glass tube. When 5 mL of benzaldehyde is added, the solution turns from pink to brown and then oscillates between the two colors. Occasionally an induction period is observed.

Controlled conditions must be used to obtain reproducible results. The air must be added through a frit, the stirring must be vigorous, and the concentration must be maintained by condensing the solvent.

The cycle frequency and amplitude range widely depending on conditions (Figures 1 and 3–7). However, the general shape of each cycle is the same. The potential increases slowly, corresponding to a slow change to brown or black, and then falls quickly corresponding to a change to pink (Figure 2). Several other trends are reproducible. The oscillation frequency always decreases with time (Figure 1), and the average potential increases with time, sometimes after a small decrease at the beginning of the reaction.

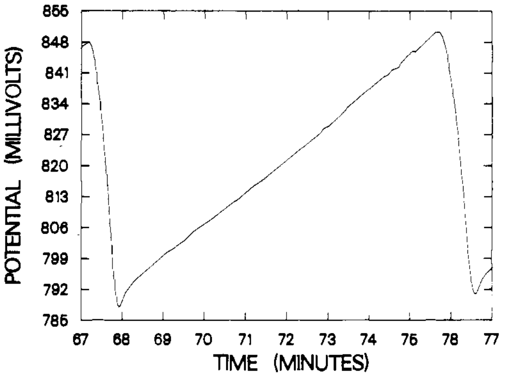

Figure 2. Air Flow 0.085 cm^3/(min mL), 70 °C, 0.02 M Co^{2+}, 0.004 M Br^-, 0.75 M benzaldehyde.

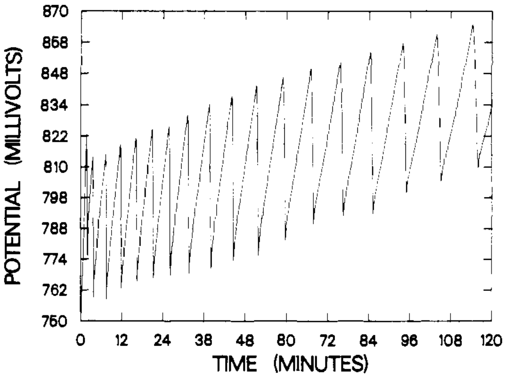

Figure 3. Air flow 0.085 cm^3/(min mL), 70 °C, 0.02 M Co^{2+}, 0.004 M Br^-, 0.75 M benzaldehyde.

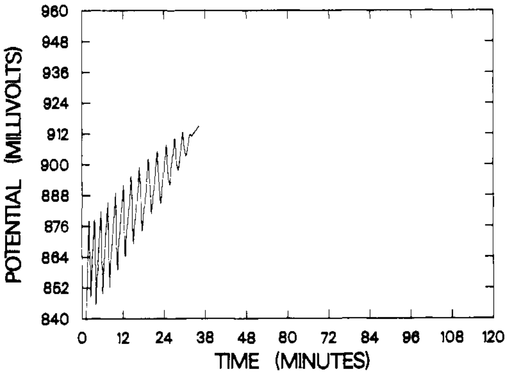

Figure 4. Air flow 0.65 cm^3/(min mL), 70 °C, 0.02 M Co^{2+}, 0.004 M Br^-, 0.75 M benzaldehyde.

A number of phenomenological studies have been made to assess the contribution of the various reactants and conditions. The representative figures all have the same time scale, except Figure 5, to make visual comparison easier. The conditions of Figure 3 are considered standard and all variables have been run at higher and lower values, although the plots are not shown for all of the experiments.

Changing conditions often have a dramatic effect, particularly on the frequency of oscillation.

Air Flow. The air flow to the reaction is a critical variable. The most stable oscillations occur at 0.085 cm^3 of air/(min mL of solution). At 0.65 cm^3/(min mL) the oscillations have a higher frequency, the average potential increases much more rapidly, and the oscillations die in about 30 min (Figure 4). At 0.033 cm^3/(min mL) erratic oscillations have been observed for several hours.

Temperature. Oscillating behavior can be observed between about 55 and 100 °C. It may be possible to expand these limits

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(1) Noyes, R. M.; Field, R. *Acc. Chem. Res.* **1977**, *10*, 273–280.
(2) Cooke, D. O. *Prog. React. Kinet.* **1977**, *8*, 185–229.
(3) Belousov, B. P. *Ref. Radiat. Med.* **1959**, 1958, 145.
(4) Zhabotinsky, A. M. *Dokl. Akad. Nauk* SSRR **1964**, *157*, 392.
(5) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 394.
(6) Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 896–911.
(7) Briggs, T. S.; Rauscher, W. C. *J. Chem. Educ.* **1973**, *50*, 496.

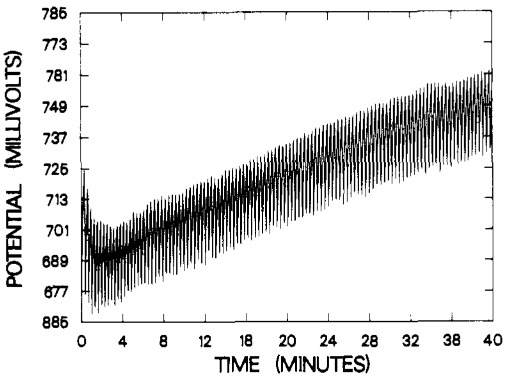

Figure 5. Air flow 0.085 cm^3/(min mL), 100 °C, 0.02 M Co^{2+}, 0.004 M Br$^-$, 0.75 M benzaldehyde.

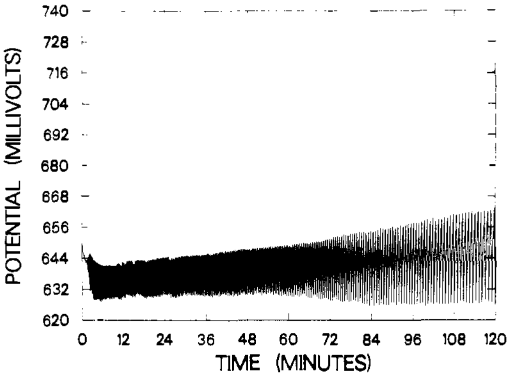

Figure 6. Air flow 0.085 cm^3/(min mL), 70 °C, 0.01 M Co^{2+}, 0.004 M Br$^-$, 0.75 M benzaldehyde.

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).

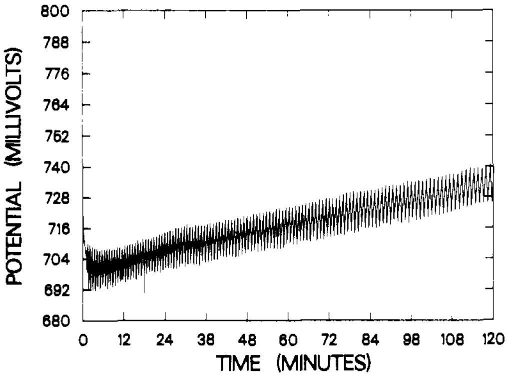

Figure 7. Air flow 0.085 cm^3/(min mL), 70 °C, 0.02 M Co^{2+} 0.004 M Br$^-$, 1.5 M benzaldehyde.

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$_3$COO)$_2$, 71-48-7; NaBr, 7647-15-6.

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(8) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1979.

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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