Inorg. Chem. **1994**, *33*, 2077–2078 **2077**

A Family of Magnetic Field Dependent Chemical Waves[1]

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Received November 9, 1993

Effects of chemical waves, such as heart beats and chemotaxis, are familiar; yet, examples of pure chemical waves that might model or produce such effects are rare. In our effort to design prototypes of chemical oscillators and waves, we have studied reactions autocatalytic in H^+ or OH^-.[2] If, in addition to a net change in pH, these reactions produce a net change in magnetic moment, a chemical wave should result, whose direction of propagation is dependent on the gradient of an imposed magnetic field.[3] We now report the existence of a family of such chemical waves that are easily handled and amenable to further study.

To increase the number of known chemical waves, we investigated the complex interaction between (ethylenediaminetetraacetato)cobalt(II) ($\mathrm{Co^{II}EDTA^{2-}}$) and hydrogen peroxide, which yields $\mathrm{Co^{III}EDTA^-}$ and O_2.[4] Production of $\mathrm{Co^{III}EDTA^-}$ occurs through a reaction (eq 1) catalyzed by OH^- and is therefore

$$\mathrm{2Co^{II}EDTA^{2-} + H_2O_2 \rightarrow 2Co^{III}EDTA^- + 2OH^-} \quad (1)$$

autocatalytic. Production of O_2 occurs through the $\mathrm{Co^{II}EDTA^{2-}}$-catalyzed disproportionation of hydrogen peroxide into water and dioxygen.

Mechanistically, reaction 1 requires penetration of a peroxo ligand into the Co(II) inner coordination sphere. This process is inherently sluggish, because dissociation of the first EDTA dentate site is slow. Hydroxide ion readily penetrates the inner coordination shell,[5] substituting for an EDTA dentate site, labilizing chelate ring opening, and facilitating further substitution. Since OH^- is a product, this step causes reaction 1 to be autocatalytic.

To determine the minimum chelate denticity for this effect, we systematically investigated the hydrogen peroxide oxidation of several different multidentate complexes of iron(II) and cobalt(II) ions. We found iron(II) ion reactions to occur too rapidly, for example with EDTA, or not to occur at all, as with *o*-phenanthroline and bipyridyl ligands. For cobalt(II) ion, reactions with ligands of increasing denticity (number in parentheses) 2,2′-bipyridyl (2), aspartate (3), nitrilotriacetate (4), ethylenediamine-*N*,*N*′-diacetate (4), and *N*-(2-hydroxyethyl)-ethylenediaminetriacetate (5) were rapid and often resulted in precipitation (*e.g.*, aspartate and nitrilotriacetate). In addition to EDTA (6), we found propagating wave fronts with 1,2-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate (6) (PDTA), (±)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetate (6) (CDTA), and triethylenetetraminehexaacetate (10) (TTHA). Therefore, 6-fold or higher coordination appears to be required for wave propagation. The three principal requirements that must be met to ensure a propagating wave front for hexadenate complexes are as follows: (1) the uncatalyzed reaction should not be too fast, (2) the reduced complex should be stable in air, and (3) the stability constant of the oxidized complex should be high enough to avoid OH^- precipitation.

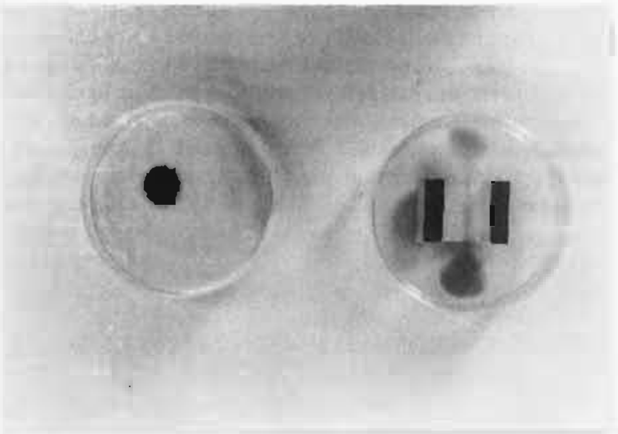

Figure 1. Chemical waves in unstirred solutions of $\mathrm{Co^{II}PDTA^{2-}}$ and hydrogen peroxide. A circular wave in the absence of an external magnetic field appears in the left dish. Dark rectangles under the right dish are the poles of a horseshoe magnet. Before initiation the pH in both dishes was 4.13 (unbuffered). A drop of 0.1 M NaOH solution was used to initiate the reaction. Chemical composition is the same in both Petri dishes: $\mathrm{[Co^{II}PDTA^{2-}]_0}$ = 0.02 M; $\mathrm{[H_2O_2]_0}$ = 0.08 M. The photo was taken 43 min after addition of the drop of NaOH solution.

Although wave front propagation may be observed in tubes, the most spectacular presentation is in thin unstirred layers. This arrangement also facilitates demonstration of the magnetic field effect. We rested a 10 cm-diameter Petri-dish on the poles of a strong permanent magnet (Edmund Scientific Co., N41,949 average gauss 2600). A pink paramagnetic, slightly acidic solution of the Co(II) complex is layered (1–2 mm depth) onto the bottom of the dish. Reaction is initiated in the solution space between the poles of the magnet by carefully adding a drop of 0.1 M NaOH. (A similar arrangement suffices to generate a traveling wave front in the absence of a magnetic field.) A circular wave front of dark blue then begins to propagate outward from the initiation site. After one min this region elongates between and parallel to the magnetic poles. After 15 min the narrow, rectangular zone between the poles terminates at either end in circular disks of dark blue (Figure 1).

In stirred reaction vessels, the EDTA reaction is fastest, and the CDTA reaction is slowest. For equimolar initial concentrations, the time required to complete the reaction would be approximately 1.2 times longer for PDTA and 12 times longer for CDTA than for EDTA. During the reaction, bubbles of escaping O_2 gas are observed.

The following mechanism with two Co(II)-containing intermediates can explain these results. A mixed peroxo-chelating agent Co(II) complex ($\mathrm{Co^{II}YHO_2^{3-}}$, Y is a hexadentate or higher denticity ligand) is formed in an OH^--catalyzed reaction (eq 2).

$$\mathrm{Co^{II}Y^{2-} + H_2O_2 \xrightarrow{OH^-} Co^{II}YHO_2^{3-} + H^+} \quad (2)$$

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$$\mathrm{Co^{II}YHO_2^{3-} + Co^{II}Y^{2-} + H_2O \rightarrow 2Co^{III}Y^- + 3OH^-} \quad (3)$$

$$\mathrm{Co^{II}YHO_2^{3-} + H_2O_2 \xrightarrow{OH^-} Co^{II}Y^{2-} + O_2 + H_2O + OH^-} \quad (4)$$

This step is fastest for EDTA, slowest for CDTA. When this intermediate reacts with an unsubstituted chelate complex such as $\mathrm{Co^{II}EDTA^{2-}}$, a dicobalt complex intermediate and $\mathrm{OH^-}$ are formed.[5] The dicobalt complex intermediate decomposes yielding a Co(III) complex and $\mathrm{OH^-}$ (eq 3). Reaction between the first intermediate and a second peroxide leads to disproportionation of H_2O_2 and release of, for example, $\mathrm{Co^{II}EDTA^{2-}}$ (eq 4).

A qualitative explanation of the magnetic field effect is based on the different behavior of para- and diamagnetic ions in these fields. Paramagnetic Co(II) ions react in the space between the magnetic poles, because of the initially added hydroxide ion there. As the Co(II) ions disappear from this space, due to reaction, a concentration gradient is set up which is augmented by the paramagnetic attraction. The combined driving forces of concentration gradient and magnetic attraction cause the Co(II) ions to move into the space between the magnetic poles where they continue to react. Diamagnetic Co(III) ions, produced by the reaction, are repelled by the magnetic field. These ions move away from the reaction space, in either of two exit directions determined by the symmetry of the magnetic field, and therefore accumulate in initially circular dark blue traveling waves at opposite sides of the dish.

This family of magnetic field dependent chemical waves offers a simple, reproducible chemical system interesting in its own right and one which may serve as a dynamical model of magnetotaxis[6] and other magnetochemical effects.[7]

Acknowledgment. We thank Irving R. Epstein for a critical reading of this manuscript. This work was supported by Research Grant CHE-9023924 and U.S.-Hungarian Cooperative Grant INT-8921816 from the National Science Foundation and Research Grant 3065 from the Hungarian Science Foundation (OTKA).

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