Pedagogic Interest of the H_2O_2, Cu^{2+}, SCN^-, OH^- Oscillating Reaction

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Abstract: Chemical reactivity is generally taught by considering the chemical properties of the reacting entities (acid–base, oxidation–reduction, complexation, and precipitation) and the values of the corresponding equilibrium thermodynamic constants (K_a, E^o K_d, K_s). This approach, however, is not well-suited to the dynamic chemical systems that are often encountered in industrial and environmental chemistry where nonequilibrium conditions prevail. In this respect, oscillating reactions are a good illustration of the limits of equilibrium thermodynamics and show the need for a complementary dynamic nonequilibrium study. We describe here an oscillating reaction that is easy to carry out in an inorganic chemistry practical class as it uses common reactants (H_2O_2, KSCN, $CuSO_4$, NaOH). This example should enable students to obtain a more realistic grasp of chemical reactivity based on a comprehension of coupled reaction processes, similar to those encountered in population dynamics or in enzymatic regulation.

Introduction

Complex chemical reactions are encountered in a variety of situations that include industrial processes, the environment, and biological systems. Although chemical reactions take place under nonequilibrium conditions, chemical reactivity is usually taught in courses within the framework of equilibrium thermodynamics. For example, in aqueous solution, the possible reactions: acid–base, oxidation–reduction, complexation, and precipitation, are more readily characterized by their corresponding equilibrium thermodynamic constants (K_a, E^o, K_d and K_s) rather than by their kinetic rate constants. This approach, which deals with the individual properties of species and processes, is the backbone of classical chemistry teaching; however, it is not adapted to a comprehension of the dynamic behavior of complex reaction systems where species and processes are always coupled. To comprehend the dynamic properties of a complex reaction system in nonequilibrium conditions, another approach based on the collective properties of the mechanism is required. Although the equilibrium and nonequilibrium approaches are complementary, they are generally dealt with in quite separate courses. To try to fill the gap between these two different approaches, chemical oscillating reactions are particularly useful as pedagogical tools [1–3].

The rather spectacular and attractive features of these systems have commonly been exploited as illustrations of oxidation–reduction reactions in aqueous solution [4, 5]; however, the origin of these oscillations is not readily interpretable in terms of the individual properties of the entities involved. An oscillating reaction involves several intermediates, and oscillations stem from the periodic variations in their concentrations. The comprehension of the phenomenon requires analysis of the individual chemical properties of the reacting species along with an overall analysis of the reaction processes and the couplings between them.

The analysis of the oscillating reaction from readily obtainable reactants (hydrogen peroxide, Cu(II) sulfate, potassium thiocyanate and sodium hydroxide) [6], represents a good illustration of the equilibrium and nonequilibrium approaches. This reaction is of particular pedagogic interest as it can be readily carried out in an inorganic chemistry practical class. The fundamental chemistry of the starting compounds is described in most textbooks. Moreover, the reaction mechanism has now been studied in some detail by Luo et al. [7], and a realistic kinetic scheme is available. We analyze here the properties of the starting compounds taken individually and then study the collective processes and the couplings between the reactions underlying the kinetics of the oscillating system using the realistic reaction mechanism that has been already published. We show the complementary nature of the two approaches: the first may be qualified as "systematic" as it deals with individual equilibrium properties of the starting compounds, while the second can be referred to as "systemic" as it deals with the overall dynamic properties of the kinetic network.

Conducting and Recording the Reaction

After mixing 0.5 mL volumes (in a 1cm × 1cm quartz cuvette thermostated at 25 °C and fitted with a magnetic stirrer) of aqueous solutions of the four starting compounds (H_2O_2, Cu^{2+}, SCN^- and OH^-) at the following concentrations: H_2O_2, 10 volumes; $CuSO_4 \cdot 5H_2O$ (MW = 249.68), 0.1 g L^{-1}; KSCN (MW = 97.18): 10.69 g L^{-1}; and NaOH (MW = 40): 5.6 g L^{-1}, the solution turns alternately yellow and transparent. These oscillations last for around an hour. The oscillations can be recorded conveniently by UV–vis spectroscopy at $\lambda = 400$ nm in a diode-array spectrophotometer or by potentiometry (in this last case use a beaker and 10 mL of each mother solution with a platinum recording electrode and saturated calomel electrode as reference). In both cases, the initial concentrations of the reactants in the medium are respectively: H_2O_2: 0.25 mol L^{-1}, Cu(II): 1×10^{-4} mol L^{-1}, SCN^-: 0.028 mol L^{-1} and OH^-: 0.035 mol L^{-1}. To succeed with the experiment, accurate concentrations are necessary; the copper concentration is the most critical.
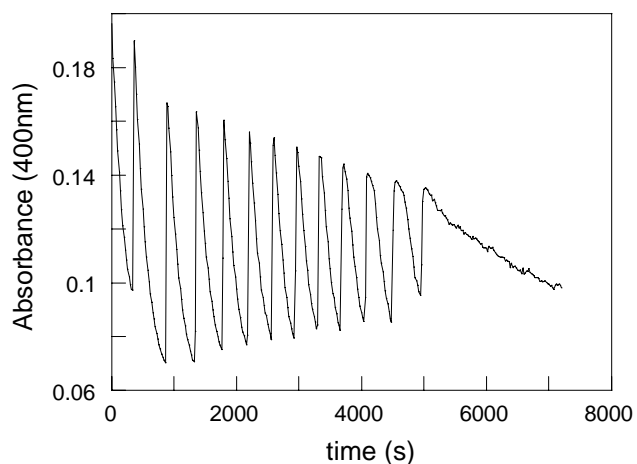
Figure 1: Recording of the oscillations by absorption spectroscopy at $\lambda = 400$ nm in a diode-array spectrophotometer in a 1cm × 1cm quartz cuvette thermostated at 25 °C and fitted with a magnetic stirrer.
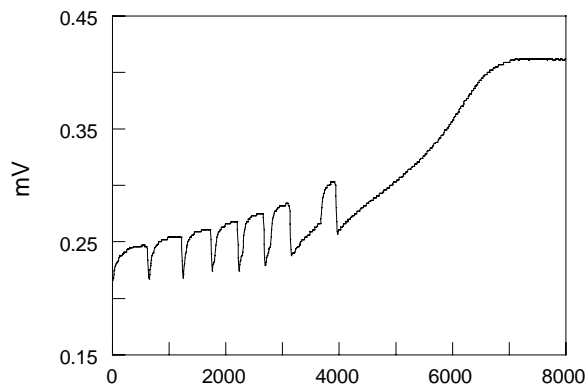

Figure 2: Recording of the oscillations by potentiometry with a platinum recording electrode and saturated calomel electrode as reference. Experimental concentrations are similar to those in Figure 1.

Because the reaction is conducted in a closed reactor into which all required starting compounds are introduced, the oscillations cease when the reagents are partially consumed, that is, when the reaction system is sufficiently close to thermodynamic equilibrium. To account for this fascinating phenomenon the reaction mechanism must be considered in detail, but before analyzing the mechanism as described in the literature, let us enumerate the main chemical equilibrium properties of the individual reactants.

Systematic Study of the Individual Equilibrium Chemical Properties of the Starting Compounds H_2O_2, Cu^{2+}, SCN^-, OH^-

In this paragraph we will consider only the best-described properties of each of the starting compounds.

Hydrogen Peroxide, H_2O_2. *Redox Properties.* H_2O_2 forms part of two redox systems corresponding to the exchange of two electrons:

$$H_2O_2/H_2O \qquad E°_1 = 1.78 \text{ V}$$

$$O_2/H_2O_2 \qquad E°_2 = 0.68 \text{ V}$$

A thermodynamic consequence of the existence of the two redox systems is the dismutation of hydrogen peroxide:

$$H_2O_2 + H_2O_2 \rightleftharpoons O_2 + 2 H_2O \qquad K_{dism} = 4.6 \times 10^{36}$$
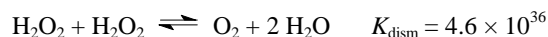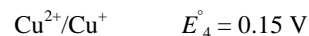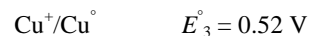
Although the dissociation is quasicomplete, the reaction is very slow in the absence of catalyst. Hydrogen peroxide may behave as either an oxidizer or a reducer, or on the other hand may dissociate.
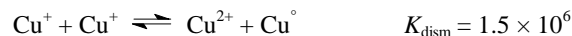
Acid–Base Properties. Hydrogen peroxide is also a weak Brönsted acid. This property tends to be overshadowed by its redox properties, and so has often been overlooked:

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+ \qquad K_a = 2.5 \times 10^{-12}$$
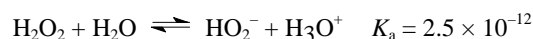
Cupric Ion, Cu^{2+}. *Redox Properties.* With respect to its redox properties, the cupric ion (Cu^{2+}) is either associated with copper metal ($Cu°$) or the cuprous ion (Cu^+). Cu^{2+} is stable in aqueous solution, but the cuprous ion Cu^+ (like H_2O_2) undergoes a dismutation. The standard potentials of the corresponding redox systems for exchange of a single electron are:

$$Cu^+/Cu° \qquad E°_3 = 0.52 \text{ V}$$

$$Cu^{2+}/Cu^+ \qquad E°_4 = 0.15 \text{ V}$$

consequently:

$$Cu^+ + Cu^+ \rightleftharpoons Cu^{2+} + Cu° \qquad K_{dism} = 1.5 \times 10^6$$

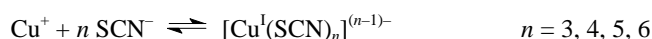This means that cuprous ions (Cu^+) will not be found in aqueous solution unless they are stabilized by complexation.

Lewis Acids. Cu^{2+} and Cu^+ ions are both Lewis acids, which may bind ligands such as SCN^-. There are four copper(II) thiocyanate complexes: $[Cu^{II}(SCN)]^+$, $[Cu^{II}(SCN)_2]$, $[Cu^{II}(SCN)_3]^-$, and $[Cu^{II}(SCN)_4]^{2-}$ with pK_d: 1.7; 2.5; 2.7, and 3.0, respectively. The cuprous ion may also complex with SCN^- forming the Cu(I) thiocyanate complexes: $[Cu^{I}(SCN)_3]^{2-}$ $[Cu^{I}(SCN)_4]^{3-}$, $[Cu^{I}(SCN)_5]^{4-}$, and $[Cu^{I}(SCN)_6]^{5-}$ with pK_d: 9.9; 10.1; 9.6, and 9.3, respectively.

In summary:

$$Cu^{2+} + n \, SCN^- \rightleftharpoons [Cu^{II}(SCN)_n]^{(n-2)-} \qquad n = 1, 2, 3, 4$$

and

$$Cu^+ + n \, SCN^- \rightleftharpoons [Cu^{I}(SCN)_n]^{(n-1)-} \qquad n = 3, 4, 5, 6$$

It can be seen from the values of pK_d, that the Cu(I) complexes are more stable than those of Cu(II). The cuprous ions are thus stabilized by complexation.

Precipitation. The OH^- ion induces precipitation of the hydroxide, $Cu(OH)_2$, if its solubility product is exceeded:

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2 OH^- \qquad K_s = 2.5 \times 10^{-19} \text{ at } 25 °C$$

In highly basic medium, there is a competition between precipitation and complexation with the formation of soluble complexes $[Cu^{II}(OH)_3]^-$ and $[Cu^{II}(OH)_4]^{2-}$.

Brönsted Acidity. The Cu^{2+} ion ($[Cu(H_2O)_6]^{2+}$ in aqueous solution) is also a Brönsted acid:

$$[Cu(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Cu^{II}(H_2O)_5(OH)]^+ + H_3O^+ \qquad K_a=10^{-7}$$
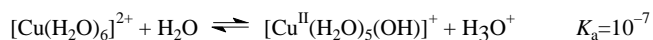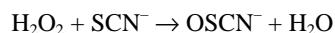
Thiocyanate Ion, SCN⁻. *Lewis Basicity.* Thiocyanate is an ambidentate Lewis base, which reacts with a Lewis acid either on the sulfur or nitrogen atom. For the copper complex, SCN⁻ binds on the sulfur atom.

Brönsted Basicity. The SCN⁻ ion is a conjugate base of the acid HSCN. Because this is a strong acid ($pK_a = -1$), it is entirely dissociated in water; thus, its conjugate base is very weak:

$$HSCN + H_2O \rightarrow SCN^- + H_3O^+$$
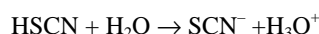
Reducing Properties. The hypothiocyanate ion (OSCN⁻) is an oxidizing agent derived from SCN⁻; it is generally obtained by the action of H_2O_2 (H_2O_2/H_2O system).

$$H_2O_2 + SCN^- \rightarrow OSCN^- + H_2O$$

With excess H_2O_2, the peroxohypothiocyanate ion (OOSCN⁻) may also be formed:

$$H_2O_2 + OSCN^- \rightarrow OOSCN^- + H_2O$$
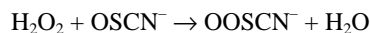
Higher oxidized derivatives of SCN⁻ are generally not mentioned in chemistry textbooks.

Hydroxide Ion, OH⁻. *Brönsted Basicity.* The base OH⁻ is the strongest Brönsted base that exists in aqueous solution and corresponds to the H_2O/OH^- system with a pK_a of 14.

Oxidation–Reduction. Due to its basicity, OH⁻ increases the pH and alters the properties of pH-dependent redox systems; we consider here the apparent standard potentials. At a pH of 9, the apparent standard potential of the H_2O_2/H_2O system, E'°, is $1.78 – 0.06 \times pH = 1.24$ V and that of O_2/H_2O_2 is $0.68 – 0.06 \times pH = 0.14$ V. It can be seen that in basic medium the reducing properties of H_2O_2 are enhanced.

Possible Reactions in A Mixture of the Above Four Entities. In view of the principal properties of the four starting compounds, the initial reaction mixture will be basic in both the Brönsted (OH⁻ ions) and the Lewis sense (SCN⁻ and OH⁻ ligands). Under the experimental concentrations, the presence of the sole acid (Cu^{2+}) is negligible. The following reactions are likely to occur:

- precipitation of $Cu^{II}(OH)_2$,
- complexation of Cu(II) by SCN⁻,
- dismutation of H_2O_2 catalyzed by Cu(II) in basic medium with liberation of O_2,
- oxidation of SCN⁻ by H_2O_2 [8, 9],
- (and possibly) reduction by H_2O_2 of the complexes of Cu(II) into a complex of Cu(I) [10].

Because these processes always evolve collectively, the oscillating behavior cannot be interpreted by taking only the individual chemical properties of the starting compounds into
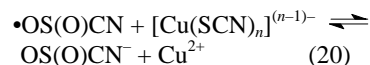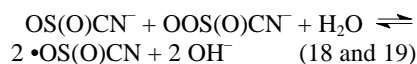
account. A so-called systemic study is required, which takes into account the overall kinetic network of the reaction mechanism.

Systemic Study of the Oscillating Reaction

The reaction mechanism proposed to account for this oscillating reaction is shown in Scheme I.

It is comprised of a 30-step kinetic scheme involving a total of 26 species. It postulates the involvement of a variety of molecular, radical, and ionic intermediates. Although it appears complicated, we will show that the presence of several coupled processes such as autocatalysis, inhibition, and regeneration can give rise to an oscillating chemical system. The steps that govern the oscillatory behavior can be readily identified in this kinetic scheme [11].

Identification of an Autocatalytic Process and the Corresponding Autocatalyst. Consider first the following steps:

$$OS(O)CN^- + OOS(O)CN^- + H_2O \rightleftharpoons$$
$$2 \bullet OS(O)CN + 2\ OH^- \qquad (18\ and\ 19)$$

$$\bullet OS(O)CN + [Cu(SCN)_n]^{(n-1)-} \rightleftharpoons$$
$$OS(O)CN^- + Cu^{2+} \qquad (20)$$

Step (18) is a process of mediamutation represented by the action of cyanosulfite anion $OS(O)CN^-$ on a peroxocyanosulfite anion $OOS(O)CN^-$. This leads to the formation of two cyanosulfite radicals $\bullet OS(O)CN$. The oxidation of thiocyanate by hydrogen peroxide in steps 5–9 fuels this step. The equilibrium in 18, 19 is coupled with the irreversible step 20 during which the radical is reduced to the cyanosulfite anion $OS(O)CN^-$. The following autocatalytic process emerges from a combination of step 18 and two steps 20:

$$1\ OS(O)CN^- + ... \rightleftharpoons 2\ OS(O)CN^- + ...$$

in which the cyanosulfite anion $OS(O)CN^-$ acts as an autocatalyst. The overall process speeds up as more and more cyanosulfite ions accumulate.

Inhibition of the Autocatalyst. There are two inhibition processes of the autocatalyst. A first inhibitory process is represented by step 21 in which the autocatalytic species (cyanosulfite anion) is used up:

$$OS(O)CN^- + HO_2\bullet \rightleftharpoons SO_3\bullet^- + HOCN \qquad (21)$$
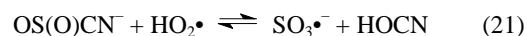
A sulfite radical–anion $SO_3\bullet^-$ is also formed during this step. Then, $SO_3\bullet^-$ reacts with a thiocyanatocopper(I) complex which is transformed into Cu^{2+} (step 22).

$$SO_3\bullet^- + [Cu(SCN)]^{(n-1)-} \rightleftharpoons SO_3^{2-} + Cu^{2+} + n\ SCN^- \qquad (22)$$
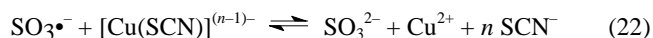
This step corresponds to the second inhibitory process as it competes with the autocatalytic step (20) for the consumption of thiocyanatocopper(I) complex.

Regeneration. Regeneration is the reformation of the thiocyanatocopper(I) complex $[Cu^I(SCN)_n]^{(n-1)-}$ from Cu^{2+}.

Scheme I: Complete Reaction Mechanism

$H_2O_2 + Cu^{2+} + OH^- \rightleftharpoons [HO_2 \cdot Cu^I]^+ + H_2O$ (1) $k_1 = 1.0 \times 10^5$ $M^{-2}s^{-1}$

    (2) $k_2 = 0.3$ $M^{-1}s^{-1}$

$[HO_2 \cdot Cu^I]^+ + n\ SCN^- \rightarrow [Cu^I(SCN)_n]^{(n-1)-} + HO_2\cdot$ (3) $k_3 = 1 \times 10^{-2}$ s^{-1}

$2\ HO_2\cdot \rightarrow H_2O_2 + O_2$ (4) $k_4 = 20$ $M^{-1}s^{-1}$

$H_2O_2 + SCN^- \rightarrow OSCN^- + H_2O$ (5) $k_5 = 7.5 \times 10^{-4}$ $M^{-1}s^{-1}$

$H_2O_2 + OSCN^- \rightarrow OOSCN^- + H_2O$ (6) $k_6 = 3.0 \times 10^{-1}$ $M^{-1}s^{-1}$

$2\ OOSCN^- \rightarrow OOS(O)CN^- + OSCN^-$ (7) $k_7 = 5.0 \times 10^2$ $M^{-1}s^{-1}$

$OOSCN^- + OOS(O)CN^- + OH^- \rightarrow OSCN^- + SO_4^{2-} + HOCN$ (8) $k_8 = 1.0 \times 10^3$ $M^{-1}s^{-1}$

$2\ OOS(O)CN^- + OH^- \rightarrow OS(O)CN^- + SO_4^{2-} + HOCN$ (9) $k_9 = 1.0$ M^{-1} s^{-1}

$HOCN + 2\ H_2O \rightarrow HCO_3^- + NH_4^+$ (10) $k_{10} = 1.0 \times 10^{-1}$ s^{-1}

$OCN^- + 2\ H_2O \rightarrow HCO_3^- + NH_3$ (11) $k_{11} = 1.0 \times 10^{-3}$ s^{-1}

$OCN^- + H_2O \rightleftharpoons HOCN + OH^-$ (12) $k_{12} = 5.0 \times 10^{-2}$ s^{-1}

    (13) $k_{13} = 1.0 \times 10^9$ $M^{-1}s^{-1}$

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ (14) $k_{14} = 2.51 \times 10^{-1}s^{-1}$

    (15) $k_{15} = 1.0 \times 10^9$ $M^{-1}s^{-1}$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (16) $k_{16} = 1.62 \times 10^6$ s^{-1}

    (17) $k_{17} = 1.0 \times 10^9$ $M^{-1}s^{-1}$

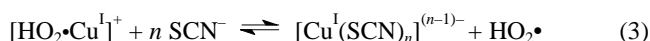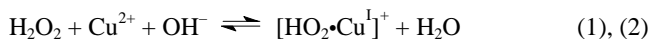$OS(O)CN^- + OOS(O)CN^- + H_2O \rightleftharpoons 2\ OS(O)CN\cdot + 2\ OH^-$ (18) $k_{18} = 3.0 \times 10^3$ $M^{-1}s^{-1}$

    (19) $k_{19} = 2.0 \times 10^6$ $M^{-1}s^{-1}$

$OS(O)CN\cdot + [Cu^I(SCN)_n]^{(n-1)-} \rightarrow OS(O)CN^- + Cu^{2+} + n\ SCN^-$ (20) $k_{20} = 1.0 \times 10^5$ $M^{-1}s^{-1}$

$OS(O)CN^- + HO_2\cdot \rightarrow SO_3\cdot^- + HOCN$ (21) $k_{21} = 2.0 \times 10^3$ $M^{-1}s^{-1}$

$SO_3\cdot^- + [Cu^I(SCN)_n]^{(n-1)-} \rightarrow SO_3^{2-} + Cu^{2+} + n\ SCN^-$ (22) $k_{22} = 1.5 \times 10^5$ $M^{-1}s^{-1}$

$2\ SO_3\cdot^- + 2\ OH^- \rightarrow SO_4^{2-} + SO_3^{2-} + H_2O$ (23) $k_{23} = 1.0 \times 10^8$ $M^{-1}s^{-1}$

$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O$ (24) $k_{24} = 2.0 \times 10^{-1}$ M^{-1} s^{-1}

$OOSCN^- + H_2O \rightarrow SO_3^{2-} + HCN + H^+$ (25) $k_{25} = 1.0 \times 10^6$ $M^{-1}s^{-1}$

$Cu^{2+} + 2\ HCN \rightarrow Cu^{II}(CN)_2 + 2\ H^+$ (26) $k_{26} = 1.0 \times 10^9$ $M^{-2}s^{-1}$

$2\ Cu^{II}(CN)_2 \rightarrow 2\ Cu^I(CN) + (CN)_2$ (27) $k_{27} = 5.0 \times 10^6$ $M^{-1}s^{-1}$

$H_2O_2 + (CN)_2 \rightarrow 2\ HOCN$ (28) $k_{28} = 1.0 \times 10^3$ $M^{-1}s^{-1}$

$H_2O_2 + Cu^I(CN) + H_2O \rightarrow Cu^{2+} + 2\ OH^- + OH\cdot + HCN$ (29) $k_{29} = 3.0 \times 10^1$ $M^{-1}s^{-1}$

$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O$ (30) $k_{30} = 2.0 \times 10^9$ $M^{-1}s^{-1}$

This involves the equilibrium (1, 2 in Scheme I) where Cu^{2+} is first transformed into the yellow complex $[HO_2 \cdot Cu^I]^+$ ($\lambda_{max} = 400$ nm), and then into the thiocyanatocopper(I) complex by step 3.

$$H_2O_2 + Cu^{2+} + OH^- \rightleftharpoons [HO_2 \cdot Cu^I]^+ + H_2O \qquad (1), (2)$$

$$[HO_2 \cdot Cu^I]^+ + n\ SCN^- \rightleftharpoons [Cu^I(SCN)_n]^{(n-1)-} + HO_2\cdot \qquad (3)$$

The overall result is the transformation of a Cu^{2+} species into $[Cu^I(SCN)_n]^{(n-1)-}$.
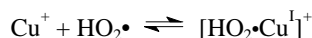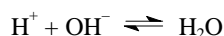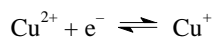
Qualitative Account of an Oscillation. All the steps discussed above are coupled together and occur simultaneously. At the onset of the autocatalytic step (step 18 + twice step 20), the concentration of cyanosulfite ion $OS(O)CN^-$ rises rapidly. Its rise, however, is limited by step 21 and subsequently by step 22 where a sulfite radical–anion

$SO_3\cdot^-$ then reacts with a thiocyanatocopper(I) complex, which is transformed into Cu^{2+} (step 22). As the thiocyanatocopper(I) complex is required for step 20 of the autocatalytic process, the effect of steps 21 and 22 is to reduce the concentration of the autocatalyst, that is, to inhibit the autocatalytic process. Cupric ion (Cu^{2+}) from step 22 is transformed into $[Cu^I(SCN)_n]^{(n-1)-}$ by steps 1, 2, and 3. The overall effect is to restart the autocatalytic process by step 20. As a consequence of these coupled processes, the concentrations of all the intermediate species are oscillating. The concentration of the yellow $[HO_2Cu^I]^+$ is monitored by UV–vis spectrophotometry at 400 nm while the global oxidation–reduction potential is recorded by potentiometry.
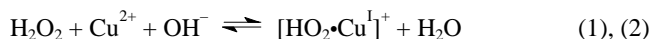
Discussion

Examination of all the steps involved in the reaction mechanism indicates that systematic analysis of the individual

equilibrium properties of the starting compounds is not sufficient. For instance, the reversible steps 18 and 19 include other oxidized derivatives of thiocyanate, such as the peroxocyanosulfite $OOS(O)CN^-$ anion and the cyanosulfite radical $OS(O)CN•$. These species are not generally considered in the analysis of the chemistry of the H_2O_2/SCN^- system. Furthermore, step 20 requires the presence of the thiocyanatocopper(I) ion $[Cu^I(SCN)_n]^{(n-1)-}$. This anion is formed in steps 1, 2, and 3, which involve the single electron redox system $H_2O_2/HO_2•$, which is not generally considered in elementary chemistry courses. Thus, reversible steps 1 and 2 can be expressed more accurately as follows:

$$H_2O_2 \rightleftharpoons HO_2• + H^+ + e^-$$

$$Cu^{2+} + e^- \rightleftharpoons Cu^+$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$Cu^+ + HO_2• \rightleftharpoons [HO_2•Cu^I]^+$$

giving:

$$H_2O_2 + Cu^{2+} + OH^- \rightleftharpoons [HO_2•Cu^I]^+ + H_2O \qquad (1), (2)$$

$[HO_2•Cu^I]^+$ binds several SCN^- anions to produce the thiocyanatocopper(I) complex in step 3.

In addition, certain species arise, which could not have been predicted from simple consideration of the properties of the starting compounds. Such species include hydrocyanic acid HCN in step 25 and cyanogen $(CN)_2$ in step 27. By showing how toxic species may be formed from nontoxic starting compounds, such systems can give students valuable insights into problems that may be encountered with complex reaction systems in industrial processes (unwanted by-products), pharmaceutical chemistry (side effects and drug interactions) and environmental science (fate of pollutants). Moreover, the presence of nonlinear couplings in such mechanisms sensitizes students to more general questions related to population dynamics or to enzyme regulation [12].

The systemic analysis described above shows that a coupling of non-linear processes such as autocatalysis, inhibition, and regeneration could give rise to chemical oscillations. The comprehension of such mechanisms can help in the discovery of new oscillating reactions. Another approach would be to study reaction mixtures that are comparable to the one described here, but in which one of the starting compounds is replaced by one of similar chemical reactivity. Some examples are: replacing Cu(II) by Mn(II), SCN^- by $S_2O_3^{2-}$, and H_2O_2 by peracetic acid. In all cases, oscillating reactions have been observed [13, 14]; however, the various constraints (initial concentrations, experimental conditions) must be optimized and the responses of the system (frequency and duration of oscillations) will also be affected. In these cases, the overall kinetic schemes and the orders of magnitude of the rate constants are not likely to be very different from those of the system described here. On the other hand, replacing Cu(II) by other metal cations (Ag(I), Hg(II), Fe(II), Fe(III), Co(II)) or H_2O_2 by persulfate $S_2O_8^{2-}$ abolishes the oscillatory behavior. Despite the similarity in chemical properties, replacing a starting compound can significantly alter the mechanism (processes, rate constants etc.), which is no longer compatible with oscillation. As a final comment to help explain the absence of oscillations in some situations, all the reaction steps shown in Scheme I would appear to be required and the numerical value of the corresponding rate constant is rather critical.

Conclusion

In this paper, we have attempted to show that teaching of chemical reactivity should not be restricted to a systematic analysis of the properties of individual compounds in situations of thermodynamic equilibrium. Although chemical equilibrium is the bedrock of chemistry, the complexity of many chemical systems can only be comprehended by study of non-equilibrium situations. Such situations can be approached by a systemic study that considers the possible couplings between the reaction steps. The systemic and systematic approaches can be seen to be complementary. The systemic analysis can help provide a better understanding of individual chemical reactivities [15] while a systematic study can establish the relevant reaction mechanism and kinetic schemes. By teaching the two approaches at the same time, students may obtain an overall grasp of both equilibrium and nonequilibrium chemical systems. The proposed oscillating reaction constitutes a pedagogic example to illustrate these two approaches.

References

1. 1. Pilling, M. J.; Seakins, P. W. *Reaction Kinetics*; Oxford University Press: New York, 1995.

2. 2. Kondepudi, D.; Prigogine, I. *Modern Thermodynamics, From Heat Engines to Dissipative Structures*; Wiley: New York, 1998.

3. 3. Epstein, I. R.; Pojman, J. A. *An Introduction to Nonlinear Chemical Dynamics*; Oxford University Press: New York, 1998.

4. 4. Rosenthal, J. *J. Chem. Educ.* **1991**, *68*(9) 794.

5. 5. Benini, O.; Cervelatti, R.; Fetto, P. *J. Chem. Educ.* **1996**, *73*(9), 865.

6. 6. Orban, M. *J. Am. Chem. Soc.* **1986**, *108*, 6893.

7. 7. Luo, Y.; Orban, M.; Kustin, K.; Epstein I. R. *J. Am. Chem. Soc.* **1989**, *111*, 4541.

8. 8. Wilson, I. R.; Harris, G. M. *J. Am. Chem. Soc.* **1960**, *82*, 4515.

9. 9. Wilson, I. R.; Harris, G. M. *J. Am. Chem. Soc.* **1961**, *83*, 286.

10. 10. Luo, Y.; Kustin, K.; Epstein, I.R. *Inorg. Chem.* **1988**, *27*, 2489.

11. 11. Luo, Y.; Epstein, I. R. *Adv. Chem. Phys.* 1990; *LXXIX*, 269.

12. 12. Murray, J. D. *Mathematical Biology*; Springer-Verlag: New York, 1990, pp 9460–9466.

13. 13. Strizhak, P. E.; Pojman, J. A. *Chaos* **1996**, *6*, 461.

14. 14. Gao, Q.; Xue, W.; Lin, J.; Zang, Y.; Zhao, X. *Chin. Sci. Bull.* **1996**, *41*, 1959.

15. 15. Pojman, J. A.; Craven, R.; Leard, D. C. *J. Chem. Educ.* **1994**, *71*, 84.