Mechanistic Study of Oscillations and Bistability in the Cu(II)-Catalyzed Reaction between H$_2$O$_2$ and KSCN$^1$

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Abstract: The CuSO$_4$-catalyzed reaction of hydrogen peroxide with thiocyanate ion is the first example of a homogeneous, liquid phase, halogen-free system that oscillates under batch conditions. A detailed mechanism is proposed consisting of 30 reactions and 26 variables. The mechanism is constructed from two nonautocatalytic mechanisms for the subsystems alkaline H$_2$O$_2$-CuSO$_4$ and H$_2$O$_2$-KSCN, coupled through various intermediates to construct a feedback network, which leads to oscillatory behavior in both batch and flow configurations. The integrated mechanism simulates very well the experimentally observed oscillations in absorbance and O$_2$ evolution and two of the three kinds of bistability in a continuously stirred tank reactor. Two alternative mechanisms are also considered, providing insight into the general properties of oscillatory mechanisms.

Since the systematic design of homogeneous liquid-phase chemical oscillators began$^2$ a decade ago, reaction families based on oxyhalogen species have dominated the field. The advantage of using halogen or oxyhalogen species in constructing chemical oscillators lies in their fast reaction rates and multiple oxidation states. Only recently has progress been made in finding halogen-free chemical oscillators, providing further evidence of the generality of nonmonotonic behavior, which had long been denied or ignored by many chemists. Although they are fewer in number than the halogen-based systems, the known halogen-free (or non-halogen-based) chemical oscillators already show a wide range of behavior, opening up further opportunities for systematic design. Important examples include the oxidation of benzaldehyde by oxygen in glacial acetic acid with a CoBr$_2$ catalyst,$^3$ the oxidation of methylene blue by oxygen in strongly alkaline medium in the presence of sulfite and sulfide,$^4$ and two permanganate-reductant oscillators.$^5$ A group of oscillators discovered by Orbán and Epstein involves the hydrogen peroxide oxidation of sulfate,$^6$ thiosulfate,$^7$ (catalyzed by CuSO$_4$) and thiocyanate$^8$ (catalyzed by CuSO$_4$). Despite the apparent similarity of their constituents, these systems are mechanistically quite different. The H$_2$O$_2$-KSCN-CuSO$_4$ system oscillates only above pH 9, and its pH is essentially constant during the oscillation in color and Pt potential.$^8$ The other two systems, in contrast, are driven by pH changes of several units.$^6,7$ Another special feature of the H$_2$O$_2$-KSCN-CuSO$_4$ system is the slowly damped oscillation under batch conditions. Such batch oscillations are quite rare, even among the much larger group of halogen-based chemical oscillators.

Mechanisms for oscillatory chemical systems have been pursued almost as soon as chemists finally recognized the possibility of oscillation in a homogeneous medium. Understanding why and how such complicated behavior arises in terms of chemical species and the interactions among them is a fascinating subject in itself. In addition, this understanding facilitates the further design of new chemical oscillators. A successful mechanistic study also contributes to knowledge of the general chemistry and kinetics of the chemical species that are involved. A good example is the

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The mechanism presented here simulates nearly all the dynamic behavior of the alkaline H$_2$O$_2$-KSCN-CuSO$_4$ system observed experimentally, including slowly damped oscillation in color and oxygen evolution accompanied by a monotonic pH change under closed conditions, sustained oscillation in flow, and bistability between the two steady states and between one steady state and the oscillatory state.

Our mechanism is derived from careful mechanistic studies for the two subsystems: the oxidation of potassium thiocyanate by hydrogen peroxide and the decomposition of hydrogen peroxide catalyzed by CuSO$_4$ in strongly alkaline media. These studies were able to account for the stoichiometry and the overall kinetics of the two separate subsystems. However, simply putting together the reactions in these two mechanisms and taking into account complex formation between copper and thiocyanate ions does not lead to a mechanism capable of oscillatory behavior for any set of rate constants. It became apparent that more intermediate species need to be invoked to construct sufficient feedback cycles to permit oscillation.

As detailed below, the intermediates we propose are cyanosulfite, OOS(O)CN, and peroxocyanosulfite, OOS(O)CN, ions as well as the hypothiocyanite ion, OSCN, and the peroxo-hypothiocyanate ion, OOSCN, used in Wilson and Harris's mechanism for the oxidation of SCN$^-$ by H$_2$O$_2$. We discuss in the last section other sets of intermediates that can give rise to oscillatory behavior. The mechanism chosen appears most reasonable in terms of the plausibility of the intermediates, the elementary reactions, and the rate constants. It also gives better agreement with the experiments in the shape and frequencies of oscillation, as well as multistable behavior under flow conditions. Nevertheless, as we shall describe, the present mechanism is far from giving complete agreement with all aspects of the system's dynamical behavior.

**Experimental Background**

Under basic conditions, the two subsystems H$_2$O$_2$-KSCN$^-$ and H$_2$O$_2$-CuSO$_4$ were shown to behave monotonically and did not show evidence of strong autocatalysis. The oxidation of KSCN by H$_2$O$_2$ in alkaline solution is very slow. The final products are sulfate, bicarbonate, and ammonium ions. The reaction pathway is thought to involve oxygen transfer from hydrogen peroxide to thiocyanate followed by bond cleavage between the sulfur and the cyanide and finally between the carbon and the nitrogen. There is weak acid catalysis at low pH, producing a small amount of HCN.

The decomposition of hydrogen peroxide to oxygen and water catalyzed by cupric ion is much faster in strongly alkaline than in acidic media. The formation of a yellow superoxide-cuprous complex, H$_2$O$_2$-Cu(I), which exists only at pH > 9, plays a crucial role in determining the pathway of copper catalysis under different pH conditions.

When the three components of the present system are mixed in batch (no material fluxes), as done by Orbtin, the rate of oxidation of KSCN by H$_2$O$_2$ increases moderately, but the decomposition of H$_2$O$_2$ is largely hindered. At a sufficiently high initial pH with appropriate reagent concentrations, a most surprising phenomenon is observed: oxygen evolution, the appearance and disappearance of a yellow color and increases and decreases in the potential of a Pt electrode take place periodically, while the pH decreases slowly and monotonically. The oscillation ceases when the pH falls below 9, where the yellow peroxy-cuprous complex is no longer able to form. The experimental batch oscillations are shown in Figure 1.

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The Cu(II)-catalyzed reaction between continuously stirred tank reactor (CSTR), Figure 1, conditions two steady states are found in the CSTR: SSI at high (8-10) pH and in alkaline medium. Decomposition of hydrogen peroxide were studied by Luo et al.\(^2\) fast equilibria and five kinetic steps in the pH range 11-12: see Cu\(^{2+}\) Cu\(^{2+}\) Cu\(^{0H}\)f Cu\(^{(1)}\) complex (H\(_{02}\)-Cu\(^{(1)}\) represents both H\(_{02}\)Cu(OH)\(_2\) and O\(_{2}\)Cu(OH)\(_2\)\(^{-}\)) was identified as the key species in the reaction in strongly alkaline medium. Its apparent formation constant, \(K_3\), is highly pH dependent (eq 11). Other equilibria of copper(II) and superoxide radical is rate determining. Only lower bounds and the ratio of the rate constants for copper(II) reoxidation by dioxygen and hydrogen peroxide (\(k_3\) and \(k_4\)) were estimated; the overall kinetic behavior is not sensitive to the actual values of these rate constants. The superoxide radical serves as a precursor for molecular oxygen formation rather than an active intermediate or a catalyst.

**Cu(II)-KSCN-CuSO\(_4\) Subsystem.** Wilson and Harris\(^6\) investigated the stoichiometry of the reaction in both alkaline and acidic conditions. In alkaline medium they found

\[
4\text{H}_2\text{O}_2 + \text{SCN}^- \rightarrow \text{HSO}_4^- + \text{HOCN} + 3\text{H}_2\text{O}
\]

(12)

HOCN + 2H\(_2\)O \rightarrow NH\(_4\)\(^+\) + HCO\(_3\)\(^-\)

(13)

while in acidic media

\[
3\text{H}_2\text{O}_2 + \text{SCN}^- \rightarrow \text{HSO}_4^- + \text{HCN} + 2\text{H}_2\text{O}
\]

(14)

They suggested a stepwise mechanism (eq 15-21) for the reaction.

\[
\text{SCN}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HOSCN} + \text{OH}^- \quad (\text{pH} > 4)
\]

(15)

HOSCN + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_3 + \text{HOCN} \quad (\text{pH} > 4)

(16)

\[
\text{H}_2\text{SO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}
\]

(17)

HOCN + 2H\(_2\)O \rightarrow HCO\(_3\)\(^-\) + NH\(_4\)\(^+\)

(18)

H\(^+\) + SCN\(^-\) + \text{H}_2\text{O}_2 \rightarrow \text{HOSCN} + \text{H}_2\text{O} \quad (\text{pH} < 4)

(19)

\[
\text{H}_2\text{O}_2^+ + \text{HOSCN} \rightarrow \text{H}_2\text{SO}_4 + \text{HCN} + \text{H}^+ \quad (\text{pH} < 4)
\]

(20)

\[
\text{H}_2\text{O}_2^+ + \text{HOSCN} \rightarrow \text{H}_2\text{SO}_4 + \text{HCN} + \text{H}^+ \quad (\text{pH} < 4)
\]

(21)

Hypothiocyanous acid or hydroxothiocyanate, HOSCN, and peroxothiocynonic acid, HOOSCN, are postulated as short-lived intermediates. Sulfite oxidation by hydrogen peroxide is fast enough\(^1\) that the sulfite concentration remains very low. The measured rates of disappearance of H\(_2\)O\(_2\) or SCN\(^-\) were assigned as the rates of the assumed rate-determining steps, (13) and (20): \(k_3 = 4.0 \times 10^6 \exp(-15500/RT) \text{ M}^{-1} \text{ s}^{-1}\), \(k_{20} = 1.75 \times 10^8 \exp(-11000/RT) \text{ M}^{-2} \text{ s}^{-1}\), \(R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}\) in the temperature range 20-50 °C. Other rate constants were left undetermined, except \(k_4\) which can be estimated to some extent from literature values.

This reaction is of much interest in biochemistry and has been studied under enzyme catalysis.\(^1\) The relatively stable hypothiocyanate ion, OSCN\(^-\), was found to oxidize sulfhydryl compounds to disulfide compounds and to regenerate thiocyanate.\(^1\)

**OSC.N\(^-\) + 2RSH \rightarrow SCN\(^-\) + RSSR + H\(_2\)O (22)**

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(14) Oram, J. D.; Reiter, B. Biochem. J. 1966, 100, 382.
More structurally distinguished intermediates, HOS(O)CN and
HOS(O)2CN, were proposed,17 though neither was detected di-
rectly. They were shown indirectly, however, to be short-lived
in water.17

H2O2-KSCN-CuSO4 System. The mechanism for the oscil-
latory H2O2-KSCN-CuSO4 system presented here is composed
of 30 kinetic reactions using 26 independent variables. These
reactions are more easily grasped in groups, each containing
specifics to one part of the overall reaction.

Many of the reactions in the first two groups are adopted from
the mechanisms for the two subsystems. However, much alteration
is necessary to keep the mechanism as simple as possible, to make
it applicable over a much larger pH range, and to provide the
essential intermediates for the oscillatory network. The third group
is the centerpiece of the mechanism. It contains the machinery
of the oscillation: the positive and negative feedback loops.
These four reactions are chosen both to represent the major
effects of the copper-catalyzed alkaline H2O2 decomposition in
the mixed reaction and to provide two essential intermediates,
HOS- and Cu[SCN]n̄n̄ for the core part of the oscillation. The
use of braces will be explained in the section on numerical simu-
lation.
The stability constant for the copper(II)-thiocyanate complex
is at least 10 orders of magnitude less than that for H2O2-Cu(I).17,18
The former complex is therefore omitted from the mechanism.
On the other hand, the Cu(I) complex, Cu(SCN)n-, is extremely
stable, with $K > 10^{11}$ M$^{-2}$ (ref 18) for n = 2, and no other
copper(I) complex can compete under these conditions. On
the basis of the fact that SCN$^-$ causes the yellow color of the solution
to fade and retards the evolution of O2, we postulate that SCN$^-$
strongly complexes Cu$^+$ after it is formed from the decomposi-
tion of H2O2-Cu(I), preventing the copper from immediate reoxidation
by O2 or H2O2 (eq 7 and 8). Sharp increase in color and O2
evolution that occur in the oscillation cycle then result from auto-
catalytic reactions among the active intermediates to be
described in group 3. The lack of color of the high-flow
steady-state SSI in the CSTR supports this interpretation. Taking
these assumptions still further, the mechanism is greatly simplified
by assigning all Cu$^+$ as Cu(SCN)n-, by neglecting the complexa-
tion equilibrium, and by disregarding the oxidation of the Cu$^+$
complex by O2 or H2O2.
The values of all rate constants are listed in Table II. The
rate constant $k_{M1}$ is taken as 1.0 $\times$ 10$^{12}$ M$^{-2}$ s$^{-1}$ on the basis of
the observation of fast complex formation.17 The ratio $k_{M1}/K_{app}$
is used to calculate $k_{M2}$ with eq 11, which is updated with a new
value of [OH$^-$] at each call to the numerical integration program.
Rate constant $k_{M1}$ is roughly the average of $k_a$ and $k_b$, and $k_{M4}$
is chosen to be equal to $k_{10}$ at a pH between 11 and 12.

| Table II. Rate Constants in the Mechanism for
H2O2-KSCN-Cu(II) |
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*For expression for $K_{app}$, see text. Calculated from the equilibrium
constants in ref 18.

The use of brackets for some of the OH$^-$ will be explained in the
section on numerical simulation.

This group of reactions provides a complete route for the ox-
idation of SCN$^-$ to the final products. It is derived from Wilson
and Harris's work10 but augments their mechanism by including
more intermediates. The reason for this addition is to provide
sufficient degrees of freedom for the next group of reactions to
construct a plausible feedback loop that generates oscillatory
behavior even under batch conditions when copper ion is included.
The first step of thiocyanate oxidation to hypothiocyanite ion,
(M5), is still the rate-determining step of this part of the reaction.
The equilibrium constant for the deprotonation of HOSCN is not
known. On the basis of the similarity of SCN$^-$ to halide, and for
convenience, we choose to use the anion forms for all the oxidized
thiocyanate intermediates. The rate constant for this reaction is
taken to be very close to the non-acid-catalyzed overall reaction
rate measured by Wilson and Harris.10

The second step, (M6), is considered to resemble a ligand-
exchange reaction, in which HOO$^-$ replaces OH$^-$. This reaction
should therefore be faster than (M5), which requires O-O bond
breaking. The "OOSCN ion is then explicitly defined as a per-
obxyhypothiocyanite ion. It differs from "OS(O)OCN, which we
refer to as a cyanosulfite ion, in which the oxygen in parentheses
is double bonded to the sulfur.

Reactions M7, M8, and M9 take account of two empirical
observations: (1) oxygen transfers between sulfur species are

usually rapid; (2) the higher the oxidation state of a sulfur species, the higher its affinity for additional oxygens. Again, in OOS- (O)CN, peroxycyanosulfite ion, the sulfur is singly bonded to peroxide and doubly bonded to oxygen. The rate constants for these proposed reactions, listed in Table II, were estimated on the basis of the above rules and then refined by fitting the simulations to the oscillation experiments.

The three fast equilibria are necessary because the species involved are present in high concentrations during some stage of the reaction and because the relevant pKa's lie between the pH's of the two steady states. In the absence of experimental data, the rate constant for the bimolecular direction of each equilibrium has been taken at or near the diffusion limit, and that of the monomolecular direction estimated from the individual equilibrium constant.18

The hydrolysis of OCN is known to be very slow in basic media and to show acid catalysis.13 However, no quantitative measurement has been done on this reaction in conditions close to those of the oscillation. The values of $k_{M10}$ and $k_{M11}$ used in the calculations are crude estimates.

3. Feedback networks:

- $\text{OS(O)CN} + \text{OOS(O)CN} + \text{H}_2\text{O} \rightarrow 2\text{OOS(O)CN} + [2\text{OH}^-]$ $k_{M18}$, $k_{M19}$ (M18, M19)
- $\text{OS(O)CN} + \text{Cu}^{+}[\text{SCN}]^- \rightarrow \text{OS}^+\text{CN} + \text{Cu}^{2+} + [n\text{SCN}^-]$ $k_{M20}$ (M20)
- $\text{OS(O)CN} + \text{H}_2\text{O}_2 \rightarrow \text{SO}_3^- + \text{HOCN}$ $k_{M21}$ (M21)
- $\text{SO}_3^- + \text{Cu}^{+}[\text{SCN}]^- \rightarrow \text{SO}_3^- + \text{Cu}^{2+} + [n\text{SCN}^-]$ $k_{M22}$ (M22)
- $2\text{SO}_3^- + [2\text{OH}^-] \rightarrow \text{SO}_4^{2-} + \text{SO}_3^- + \text{H}_2\text{O}$ $k_{M23}$ (M23)
- $\text{H}_2\text{O}_2 + \text{SO}_3^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$ $k_{M24}$ (M24)

Only intermediates and Cu(II), but no input reagents, appear on the right-hand side of this group of reactions—a fact that ensures that if the mechanism can oscillate under flow conditions, it is likely to oscillate in batch as well. This feature also explains why even though neither of the subsystems is autocatalytic, the system oscillates when they are mixed.

The autocatalysis, a positive feedback loop in this case, is accomplished by the sequence (M18, M19) + 2(M20), involving two intermediates from the second group. "OS(O)CN" and "OOS(O)CN," and one from the first group, the Cu"-thiocyanate complex. Intermediate "OS(O)CN" is produced very slowly in the reaction M9, and it initially has a very low concentration. It is generated autocatalytically through the formation and reduction of the radical "OS(O)CN," when the concentrations of "OS(O)CN" and Cu"[SCN]" become high enough to make this pathway significant. The Cu" is simultaneously oxidized to Cu"", and the fast equilibrium, (M1) and (M2), produces the yellow superoxy complex almost immediately if the system is in the appropriate pH range. The sharp increase in color stops when most of the Cu" has been consumed.

To bring the system back to the state it was in prior to the autocatalysis, so that the above process can start again, a negative feedback, i.e., a process that is activated as a result of the positive feedback but that functions in the opposite direction, is required. In the present mechanism, the negative feedback pathway is composed of three reactions, (M21), (M22), and (M23)). Keeping in mind that the formation and the decomposition of the HO2-Cu(I) complex are both rapid, we know that HO2° builds up as sharply as the absorbance, but with a very brief delay. With an appropriate $k_{M22}$, the autocatalytic species, "OS(O)CN," is consumed by HO2° when both species reach sufficient levels, and the first turning point of the oscillation occurs. However, the monomolecular decomposition (M3) produces Cu"+[SCN]" simultaneously with HO2°. The former species can reinitiate the positive feedback pathway, and since the process is autocatalytic the system would be prevented from returning to the original state. Step M22 ensures that [Cu"+[SCN]" ] is maintained at a low level until SO3"- is exhausted, i.e., when "OS(O)CN" is consumed. This phase-shift control step is as crucial as the direct competition for the autocatalytic species between the positive and negative feedback processes. The disproportionation of the SO3"- radical (M23) is included for completeness, though it does not play an essential role.

Not surprisingly, none of the rate constants in this group, except $k_{M24}$, can be found in the literature. The values listed in Table II have all been fitted to give the best agreement with the oscillation experiments. They are certainly subject to further improvement as discussed below. Reaction M24 is fast enough12 to keep [SO3"-] well below the concentrations of the major products, so that inclusion of its equilibrium with HSO3" is not expected to make a significant difference, even though the pH is 7.2.19

4. Acid-producing reactions (low-pH steady state):

- $\text{OS(O)CN} + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{SO}_3^- + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ $k_{M25}$ (M25)
- $\text{Cu}^{2+} + 2\text{H}_2\text{O}_2 \rightarrow \text{Cu(OH)}_2 + 2\text{H}_2\text{O}$ $k_{M26}$ (M26)
- 2Cu(OH)2 → 2Cu(OH) + (CN)2 $k_{M27}$ (M27)
- $\text{H}_2\text{O}_2 + (\text{CN})_2 \rightarrow 2\text{HOCN}$ $k_{M28}$ (M28)
- $\text{H}_2\text{O}_2 + \text{Cu}^{2+} + \text{OH}^- \rightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O}$ $k_{M29}$ (M29)
- $\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ $k_{M30}$ (M30)

This group of reactions comes into play when the pH is ≤ 7 to bring the system to the lower pH of steady state II when the flow rate is sufficiently low. It does not have any effect on either oscillatory state or the high-pH steady state I.

The first reaction is taken directly from Wilson and Harris' mechanism,10 with the rate constant fitted to the oscillation experiment. Another acid-catalyzed reaction in that mechanism, eq 20, is not included here, since it becomes comparable to the non-acid-catalyzed reaction, (M5), only as the pH approaches 1.10

Reactions M26 and M27 involving copper ion catalysis correspond to the familiar analytical reaction in which Cu"+ is reduced by HCN to a very stable complex, Cu(CN), with accompanying production of (CN)2.20 Steps M29 and M30 are analogous to reactions in the mechanism for the H2O2-Cu+ reaction. We now take into consideration the oxidation of the copper(1) complex by H2O2, because H2O2 is a good oxidant in acidic medium, though it behaves as a reductant in strong alkaline media. For simplicity, competition between the thiocyanate and cyanide complexes of copper(I) is not taken into account, even though the complexes have stability constants of similar magnitude.18 All rate constants in this group, except the diffusion-controlled $k_{M30}$, are fitted numbers.

Numerical Simulation and Results

All reactions and intermediates, 26 in total, that appear on the left-hand side of eq M1-M30, except H+, are taken as independent variables. We replace [H+] by 10^{-14}/[OH^-] in the rate law for reaction M25. The H+ production in (M25) and (M26) is taken into account stoichiometrically by subtracting one OH- for every H+ produced. With the exception of (M1) and (M26), all reactions have unimolecular or bimolecular kinetics. The OH- in brackets in (M8), (M9), (M19), and (M23) are taken into account in the stoichiometry but do not enter into the rate laws of these reactions. The underlying assumption is that these reactions are not elementary steps and that fast protonation or deprotonation follows the rate-determining bimolecular step to yield the indicated products. A similar assumption is made in

Figure 5. Calculated batch oscillations in (a) [HO₂⁻⁻Cu(I)] and (b) \( d[O_2]/dt \) and monotonic pH curve (c) during the same time interval. Initial conditions: \([H_2O_2]_0 = 0.25 \) M, \([KSCN]_0 = 0.025 \) M, \([NaOH]_0 = 0.025 \) M, \([CuSO_4]_0 = 7.5 \times 10^{-3} \) M.

the case of SCN⁻ bound to copper ion. However, for simplicity, the SCN⁻'s in braces in (M3), (M20), and (M22) are not even included in the stoichiometry. They are dummy symbols here to show the sense of the chemistry.

The resulting set of 26 differential equations was integrated numerically with the Gear package.²² The calculated [HO₂⁻⁻Cu(I)] may be compared with the experimental absorbance. The calculated rate of \( O_2 \) production, \( d[O_2]/dt \), should correspond, at least qualitatively, to the \( O_2 \) evolution (in terms of current) measured with the mass spectrometer.⁸

**Batch Oscillation.** With considerable computational effort in matching so many free parameters (rate constants), we have been able to simulate the damped oscillation seen in a closed system (zero flow rate) with the mechanism (M1)-(M30) and the rate constants listed in Table II with initial conditions identical with those of the experiments (Figure 1). The calculated oscillations in [HO₂⁻⁻Cu(I)] and \( d[O_2]/dt \) are illustrated in Figure 5. The period agrees with the experiment to within a factor of 2. The shape of the \( d[O_2]/dt \) oscillation resembles that of the experimental \( O_2 \) evolution (Figure 1d). The magnitude of the [HO₂⁻⁻Cu(I)] oscillation is consistent with the measured absorbance change, according to the estimated extinction coefficient of the HO₂⁻⁻Cu(I) complex.¹¹ In agreement with the experimental findings, \([OH^-]\) shows a slow monotonic change over the course of the oscillation, which terminates when the pH approaches 9 (see Figure 1).

**Oscillation and Bistability in Flow.** The mechanism gives oscillation when the flow is turned on, as shown in Figure 6. However, as we see by comparing the upper part of Figure 4 with the calculated bistability between the oscillatory state and SSI in Figure 7, the calculated oscillatory state is not as robust to changes in flow rate as its experimental counterpart.

Owing to the reactions in group 4 of the mechanism, the low-pH SSII appears at input concentrations and flow rates close to those

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of the experiments. Figure 8 depicts the calculated SS-I-SSII hysteresis, which is qualitatively similar to the lower part of Figure 4. However, the search for bistability between the oscillatory state and SS-II has proved unsuccessful to date. A complete phase diagram resembling Figure 4 has not been constructed because of the prohibitive amount of computing time that would be required for such a large system.

Discussion

The proposed mechanism for the oscillatory $\text{H}_2\text{O}_2$-$\text{KSCN}$-$\text{CuSO}_4$ system, (M1)-(M30), has shown great success in simulating the observed oscillations in both batch and flow conditions. Despite the large number of steps and the difficulty of fitting 80% of the rate constants, the calculated results account well for most of the major dynamical features, including the period, magnitude, and the shape of the oscillation, as well as the multistable behavior.

Not surprisingly, some significant discrepancies remain between the results of our simulations and the experiments. For the batch behavior, only the effects of varying $[\text{OH}^-]$ are accurately reproduced by the simulations: at higher $[\text{OH}^-]$, the total number of oscillations increases while the period remains constant. When the other initial concentrations are varied, the effects are smaller than or even occasionally in the direction opposite to those of the experiments. The lower pH of the calculated SS-II is 5.5, about one unit above that in the actual chemical system. As noted in the previous section, the range in $k_0$ of bistability between SS-I and oscillation is much smaller than found experimentally, and we have been unable to reproduce the bistability between SS-II and the oscillatory state.

One possible origin of these deficiencies is that the feedback scheme in the oscillation core is too simple, insufficient to maintain the oscillation at higher flow rates. Adding more reactions and more intermediates may help to increase the nonlinearity. However, without any evidence as to what species should be introduced, we hesitate to complicate further a mechanism that already contains 26 independent species. Other potential sources of discrepancy are the oversimplification of complex and protonation equilibria and inadequacies in our fitting of the unknown rate constants, perhaps as a result of cross correlations among them.

We emphasize that in a mechanism of this complexity the choice of intermediates, upon which the feedback loops are built, is not unique unless those intermediates have been experimentally verified or are well-known in the subsystems. What really matters, if not enough is known, is the overall structure of and competition between the feedback pathways. To illustrate this point, we give two examples of alternative oscillatory feedback networks that use completely different sets of intermediates but follow the same pattern in the positive and negative feedbacks. Both alternatives show batch and CSTR oscillations under the same conditions as the proposed mechanism.

Equations 23–25 accomplish the autocatalysis in the same manner as (M18)–(M20). Step 26 plays the same role as (M21), suppressing the autocatalysis, while (27) corresponds to (M22). Since both HOClSn and Cu$^{+}[\text{SCN}]_n$ are consumed during the autocatalysis, controlling the timing of the accumulation of either will yield the desired phase shift. Equation 28 is included for completeness. This alternative worked almost as well as our preferred mechanism in generating both batch and flow oscillations. No detailed studies of bistability in the CSTR were performed.

This scheme was rejected for several reasons: the radical-molecule adduct HOI$^{+}[\text{SCN}]^*_n$ seemed less plausible than the other postulated intermediates; oscillations ceased when a reaction between SCN$^-$ and Cu$^{+}[\text{SCN}]_n$ with a reasonable rate constant was included. Another serious drawback involves eq 26, which is crucial for the negative feedback chain. Pulse radiolysis experiments$^{22}$ show that the reaction should have a rate constant of $1.6 \times 10^9 \text{M}^{-1} \text{s}^{-1}$, which is about 5 orders of magnitude higher than the maximum value that produces oscillation, and the products should be SCN$^-$ and O$_2$ instead of an adduct, HOClSn.

2. Autocatalysis in $\text{S}_2\text{O}_5^2$:

$\text{S}_2\text{O}_5^2^- + 2\text{Cu}^{+}[\text{SCN}]_n \rightarrow \text{SO}_3^{2-} + 2\text{Cu}^{2+} (+n\text{SCN}^-) k_{29}$

$\text{SO}_3^{2-} + \text{OOS(O)CN} \rightarrow \text{S}_2\text{O}_5^2^- + \text{OCN} k_{30}$

$\text{S}_2\text{O}_5^2^- + 2\text{H}_2\text{O} \rightarrow \text{SO}_3^{2-} + 2\text{H}_2\text{O} k_{31}$

$\text{S}_2\text{O}_5^2^- + 2\text{Cu}^{+}[\text{SCN}]_n \rightarrow \text{SO}_3^{2-} + 2\text{Cu}^{2+} (+n\text{SCN}^-) k_{32}$

Again, the first two reactions give rise to autocatalysis in either $\text{S}_2\text{O}_5^2$ or $\text{SO}_3^{2-}$, depending on how one sums the equations. The negative feedback and the phase shift, constituted by eq 31 and 32, have nearly the same pattern as the two previous examples. A significant difference is that in eq 31 $\text{S}_2\text{O}_5^2$ is consumed by a reagent, which is always in large excess and monotonically decreasing, instead of by an autocatalytically produced intermediate. This fact causes the shape and the period of the calculated oscillations to be quite different from those in Figure 5. The period is much longer, and no more than four cycles are obtained before the oscillations die out.

Dithionite and dithionate ions are used extensively in the textile industry and in environmental research as powerful reductants. No examples have appeared in the literature in which they are reduced by a metal ion. The plausibility of eq 29 and 32 is therefore questionable. In addition, the potential for Cu$^{2+}$/$\text{Cu}^+$ in the presence of any plausible counterion should be much higher than that for $\text{S}_2\text{O}_5^2$/$\text{SO}_3^{2-}$.

Of course, the above examples do not constitute all possible alternative mechanisms that can give rise to oscillations. Specifying the number of alternatives is as vain a goal as proving the validity of a single mechanism. By calculating equations on


Conformational Analysis via NMR Isotope Shifts. Side-Chain Equilibria in N-Alkylpiperidines

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Abstract: Conformational equilibria involving the N-alkyl side chain of N-alkylpiperidines were detected via NMR isotope shifts. Introduction of a single deuterium at C1' of the side chain causes a gauche =1 gauche equilibrium to be nondegenerate and observable by the separation of signals for C2 and C6 in 13C NMR spectra at low temperature. The separation is temperature dependent, as expected for an equilibrium isotope effect. Actual $K_{eq}$ and $\Delta G^\circ_{eq}$ for the isotopically perturbed equilibrium cannot be directly calculated by the application of Saunders' equation because the equilibration process is too rapid to obtain the maximum chemical shift difference between C2 and C6 at the slow exchange limit. Nonetheless, some useful estimates of these values can be made. The observations can be accounted for by the presence of both gauche and anti conformers in the equilibrium. MM2 calculations using Allinger's parameters for amines also support the conclusion that both gauche and anti conformers are present, with the proportion of gauche conformers declining in the sequence N-ethylpiperidine > N-propylpiperidine, N-butylpiperidine > N-benzylpiperidine.

Isotope effects on NMR chemical shifts can be used to differentiate equilibrating systems from static structures. The technique is particularly well suited to detect degenerate equilibria, which have low energy barriers and are thus too rapid to be accessible by other NMR techniques. Bushweller et al. have demonstrated that some conformational equilibria occurring via C=N bond rotations in amines occur too rapidly to be detectable by ordinary dynamic NMR techniques. For example, even at the temperature of 99 K where nitrogen inversion and one C=N bond rotation process were slow on the NMR time scale, it was still not possible to determine with certainty whether the major conformer of diethylmethylamine actually had $C_2$ symmetry or simply time-averaged symmetry due to very rapid C=N bond rotations. In this paper we explore the application of the isotopic perturbation method to conformational analysis of acyclic alkyl chains of tertiary amines, with the specific example of N-alkylpiperidines. It has recently been reported that substantial conformational equilibrium isotope effects (CEIE) are associated with deuteriation adjacent to the nitrogen in cyclic amines, if. If this type of effect accompanies deuteriation of alkyl groups, it could be used to advantage in conformational analysis.

Scheme I

\[
\begin{align*}
N & \quad (8) \quad R \quad H \quad (7) \quad D \quad R \quad (3-5-1'-d) \\
+ & \quad (9) \quad \text{ClO}_4^- \quad \text{Ph} \quad (6-1'-d) \\
\text{N} & \quad \text{D} \quad \text{Pb} \quad \text{Ph}
\end{align*}
\]

\(N-(n-Alkyl)piperidines\) can be assumed to have gauche 1 and/or anti 2 conformations, defined by the alignment of alkyl substituents relative to the nitrogen lone pair. In the case of the gauche conformation, there would be two isoenergetic enantiomeric structures, 1a and 1b. Interconversion among these three possible