of HOI and $HIO_2$ to generate $I^-$; however, the rate law and stoichiometry of the overall sequence would remain the same. Similarly, reactions 5-10 could be important in the further reduction of $HIO_2$ in process D. Again, two pathways would result without affecting the rate law and stoichiometry. We note that Bünau and Eigen[33] did not find evidence for a pathway involving HOI in process B, suggesting that the sequence 14-15 is not dominant.

Reactions 16-18 for the buffer system are reversible elementary steps for dissociation of the respective weak acids.

## Conclusion

The oscillatory Landolt reaction is an important new addition to the growing list of oscillatory chemical systems.[17] Because the reaction can be described in terms of experimentally accessible component processes, an empirical characterization of the dynamical behavior is possible. The major qualitative features of the system are well-described by the empirical rate law model developed here. Quantitative agreement between calculation and experiment must await further refinement of the model and a better characterization of the experimental behavior. A detailed mechanism for the reaction has been developed by combining previously proposed schemes for the individual component processes.

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# A Mechanism for Dynamical Behavior in the Landolt Reaction with Ferrocyanide[1]

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**Abstract:** A mechanism consisting of 13 elementary steps is proposed for the reaction of iodate, sulfite, and ferrocyanide. Computer simulations with the mechanism give excellent agreement with experimental observations of the batch behavior of both the component Landolt (iodate-sulfite) and the full system and with the bistability and oscillation found with the full system in a stirred tank reactor.

One of the most remarkable outcomes of the study of chemical oscillation has been the ability of chemists to construct, given data on the time variation of the concentration of one or two species, complex mechanisms involving a dozen or more elementary steps whose predictions yield excellent agreement with a wide variety of observed dynamical behavior. The best known example of such an achievement is the Field-Körös-Noyes mechanism[2] for the Belousov-Zhabotinskii reaction. Other oscillating reactions for which mechanisms in substantial agreement with experiment are available include the Bray-Liebhafsky,[3] chlorite-iodide,[4] and bromate-iodide[5] reactions.

Edblom, Orbân, and Epstein (EOE)[6] recently found that the reaction of iodate, sulfite, and ferrocyanide exhibits both bistable and oscillatory behavior in an open system. This modified Landolt reaction[7] appears tailor-made for mechanistic studies, since it allows for measurement of an unprecedented number of species concentrations. Ion-selective and pH electrodes can be used to monitor $[H^+]$ and $[I^-]$. The iodine concentration can be measured spectrophotometrically, and both ferro- and ferricyanide ions absorb in the visible. The very high extinction coefficients of the latter species have hampered quantitative studies of their behavior to date, but considerable qualitative information has been obtained.

We present here a mechanism for the Landolt reaction with ferrocyanide. The basic outlines of the mechanism were suggested by EOE in their experimental study of this system. Here we expand those ideas into a detailed mechanism consisting of 13 elementary steps. When this study was nearly complete, we became aware of an independent investigation by Gâspâr and Showalter.[8] Their mechanism, though it focuses primarly on a set of empirical rate laws rather than on the component elementary steps, resembles the present one in all major respects. The striking similarity between two mechanisms arrived at independently and by different routes recalls a similar occurrence in the development of a mechanism for the Briggs-Rauscher oscillating reaction[9,10] and lends support to the mechanisms proposed.

## Experimental Background

The experimental data to be considered are those obtained by EOE.[6] In summary, the simple Landolt (iodate-sulfite) reaction behaves as a clock reaction in a closed (batch) system,[11] showing a rapid drop in pH and a sharp rise in redox potential followed by a slower increase in pH accompanied by a constant redox potential and the production of $I_2$. In a stirred tank reactor (CSTR), the Landolt reaction exhibits bistability between a high pH, low redox potential, low $I_2$ steady state stable at high flow rates and a low pH, high potential, high $I_2$ state stable at low flow rates. No oscillations were observed in this reaction at any temperature.

The mixed system obtained by adding ferrocyanide to the components of the Landolt reaction behaves rather differently. The batch behavior is changed only slightly, in that the brown iodine color that persists after the sharp pH change in the Landolt reaction appears only transiently in the mixed system. The differences in the CSTR are more significant. At 20 °C, the mixed system is bistable over a considerably narrower range of flow rates than the Landolt reaction and the difference in redox potential between the two steady states is only about 100 mV compared

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[†] Brandeis University.

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**Scheme I.** Overall Processes in the Iodate-Sulfite-Ferrocyanide-System

$$IO_3^- + 3HSO_3^- \xrightarrow{\text{slow}} I^- + 3SO_4^{2-} + 3H^+ \tag{A}$$

$$IO_3^- + 5I^- + 6H^+ \xrightarrow{\text{slow}} 3I_2 + 3H_2O \tag{B}$$

$$I_2 + HSO_3^- + H_2O \xrightarrow{\text{fast}} 2I^- + SO_4^{2-} + 3H^+ \tag{C}$$

$$IO_3^- + 3HSO_3^- + 5I^- + 6H^+ \rightarrow 6I^- + 3SO_3^{2-} + 9H^+ \tag{D}$$

$$IO_3^- + 6Fe(CN)_6^{4-} + 6H^+ \rightarrow I^- + 6Fe(CN)_6^{3-} + 3H_2O \tag{E}$$

$$I_2 + 2Fe(CN)_6^{4-} \rightarrow 2I^- + 2Fe(CN)_6^{3-} \tag{F}$$

$$2Fe(CN)_6^{3-} + SO_3^{2-} + H_2O \rightarrow 2Fe(CN)_6^{4-} + SO_4^{2-} + 2H^+ \tag{G}$$

**Scheme II.** Reaction Mechanism and Rate Constants

| | | |
|---|---|---|
| $IO_3^- + HSO_3^- \rightarrow SO_4^{2-} + HIO_2$ | $k_1 = 2.95 \times 10^{-1}\ M^{-1}\ s^{-1}$ | (1) |
| $HIO_2 + I^- + H^+ \rightarrow 2HOI$ | $k_2 = 2.0 \times 10^{10}\ M^{-2}\ s^{-1}$ | (2) |
| $HIO_2 + HOI \rightarrow IO_3^- + I^- + 2H^+$ | $k_3 = 1.0 \times 10^{5}\ M^{-1}\ s^{-1}$ | (3) |
| $IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI$ | $k_4 = 3.0 \times 10^{5}\ M^{-3}\ s^{-1}$ | (4) |
| $HOI + I^- + H^+ \rightarrow I_2 + H_2O$ | $k_5 = 3.0 \times 10^{12}\ M^{-2}\ s^{-1}$ | (5) |
| $I_2 + H_2O \rightarrow HOI + I^- + H^+$ | $k_6 = 2.2\ s^{-1}$ | (6) |
| $I_2 + HSO_3^- + H_2O \rightarrow 2I^- + SO_4^{2-} + 3H^+$ | $k_7 = 1.0 \times 10^{6}\ M^{-1}\ s^{-1}$ | (7) |
| $SO_3^{2-} + H^+ \rightarrow HSO_3^-$ | $k_8 = 5.0 \times 10^{10}\ M^{-1}\ s^{-1}$ | (8) |
| $HSO_3^- \rightarrow SO_3^{2-} + H^+$ | $k_9 = 3.0 \times 10^{3}\ s^{-1}$ | (9) |
| $I_2 + Fe(CN)_6^{4-} \rightarrow I_2^- + Fe(CN)_6^{3-}$ | $k_{10} = 1.3 \times 10^{3}\ M^{-1}\ s^{-1}$ | (10) |
| $I_2^- + Fe(CN)_6^{3-} \rightarrow I_2 + Fe(CN)_6^{4-}$ | $k_{11} = 2.0 \times 10^{8}\ M^{-1}\ s^{-1}$ | (11) |
| $Fe(CN)_6^{4-} + I_2^- \rightarrow Fe(CN)_6^{3-} + 2I^-$ | $k_{12} = 1.0 \times 10^{8}\ M^{-1}\ s^{-1}$ | (12) |
| $Fe(CN)_6^{3-} + 2I^- \rightarrow Fe(CN)_6^{4-} + I_2^-$ | $k_{13} = 1.3 \times 10^{-3}\ M^{-2}\ s^{-1}$ | (13) |

to a 200-mV difference in the Landolt system. At 30 °C and above, large-amplitude oscillations appear in the mixed system and the phase diagram shows the characteristic cross-shape[12] found in many bistable and oscillatory chemical systems.[13]

## Simulations

We simulate the data at 40 °C, since at that temperature the oscillatory region is quite broad and the oscillations are most reproducible. Problems of obtaining rate constants at 40 °C are discussed below. The computational study was structured in much the same way as the experimental work. That is, we began by investigating the pure Landolt system in both batch and flow configurations. When satisfactory results were obtained, a flow of $Fe(CN)_6^{4-}$ and appropriate reactions of that species and of $Fe(CN)_6^{3-}$ were introduced.

As in the experiments, the initial reactants in the batch system or the input feed to the CSTR consisted[14] of $IO_3^-$, $SO_3^{2-}$, $H^+$, and $Fe(CN)_6^{4-}$. All input concentrations and flow rates were identical with those used in the experiments. A constant $1 \times 10^{-6}$ M input of $I^-$ was also included both to provide a means of initiating the reaction and to account for iodide impurities in the iodate stock solutions.

The set of differential equations was integrated numerically with use of ROW4S,[15] an extended ordinary differential equation solver suitable both for stiff systems and for sensitivity analysis calculations.[16]

## Constructing the Mechanism

**Choice of Reactions.** The basic structure of our mechanism derives from the seven overall reactions proposed by EOE[6] and summarized in Scheme I. Starting from these stoichiometric processes, we then chose a set of elementary steps consistent with both the stoichiometries and the available kinetics and thermodynamic data. The resulting mechanism is given in Scheme II.

Our mechanism contains little if any new chemistry. Only reaction 1 has not been proposed previously, and it gives rise to well-known products. Steps 2–6 were used by De Kepper and Epstein[10] in their simulation of oscillation and bistability in the Briggs–Rauscher reaction. Reaction 7 probably takes place via the intermediate $HSO_3I$[17], but under our conditions this possibility is kinetically indistinguishable from the reaction given. Reactions 8 and 9 represent the sulfite–bisulfite equilibrium. Steps 10–13 were taken from a study of Reynolds[18] in which he showed that the only iodine species that oxidizes ferrocyanide to ferricyanide in appreciable amounts is $I_2$.

Since the sulfite introduced exists primarily as $HSO_3^-$ at the pH's of interest in this study,[19] we have written eq 1 and 7 in terms of bisulfite. One could, of course, elaborate the mechanism by including the corresponding reactions with sulfite, but we feel that little would be gained to compensate for the introduction of two additional disposable parameters. Similarly, we include only $I_2$ in our mechanism, omitting explicit consideration of $I_3^-$, even though appreciable amounts of the latter species are surely present. Reaction G of Table I is not taken into account in mechanism. EOE suggested this reaction as a possible source of a time lag that would facilitate oscillation. It was included in our initial calculations, but we found that, with rate constants ranging from $10^{-3}$ to $10^1\ M^{-2}\ s^{-1}$, it had no significant effect on the calculated behavior. It was therefore dropped from the mechanism.

**Rate Constants.** Having selected reactions 1–13 for our mechanism, we proceeded to choose values for the corresponding rate constants. Wherever possible, data from the literature were used, taking into account that the experiments to be simulated were performed at 40 °C. When experimental values were not available, rate constants were estimated by fitting the EOE experiments to our simulations. We discuss each reaction briefly below.

**Reaction 1.** The rate of the bisulfite–iodate reaction is the major determinant of the induction period in both the batch and flow simulations. For this reason, even though no value of $k_1$ was found in the literature, it was relatively easy to obtain a rate constant of $2.95 \times 10^{-1}\ M^{-1}\ s^{-1}$ by comparing our simulated and experimental results.

**Reaction 2.** Our value is taken from the Briggs–Rauscher study of De Kepper and Epstein,[10] who estimated $k_2 = 2.0 \times 10^{10}\ M^{-2}\ s^{-1}$ by comparison with the analogous reactions of bromine-containing species. Including the reverse of reaction 2 had no effect on the simulations.

**Reactions 3 and 4.** These steps were also included in the Briggs–Rauscher simulations.[10] However, the values used in that study, $k_3 \approx 0$ and $k_4 = 1.43 \times 10^3\ M^{-3}\ s^{-1}$, were deduced from work by Furuichi and Liebhafsky[20] done at extremely low ($10^{-9}$ M) iodide concentrations and at 25 °C. In the present system, $[I^-]$ is typically about $10^{-2}$ M. At higher iodide concentration, iodic acid reacts in a complex fashion.[20] Even at low iodide concentrations, the rate of reaction increases approximately 20-fold between 25 and 50 °C.[20] We find that, in contrast to the situation in the Briggs–Rauscher reaction, neglect of the "reverse Dushman"[21] reaction 3 radically alters the behavior of the system. Allowing for both the elevated temperature and the high $[I^-]$ levels, we propose the rate constants given in Scheme II.

**Reactions 5 and 6.** We use the values measured by Eigen and Kustin[22] at 20 °C by a temperature-jump technique and employed in several other mechanistic studies.[9,10,23] No attempt was made to correct $k_5$ and $k_6$ for the effects of the increased temperature.

**Reaction 7.** This reaction is too rapid to be followed by conventional techniques; the brown iodine color disappears instantaneously on addition of sulfite. A value of $k_7 = 1.0 \times 10^6\ M^{-1}\ s^{-1}$ gave the best fit to our data. This value is significantly lower

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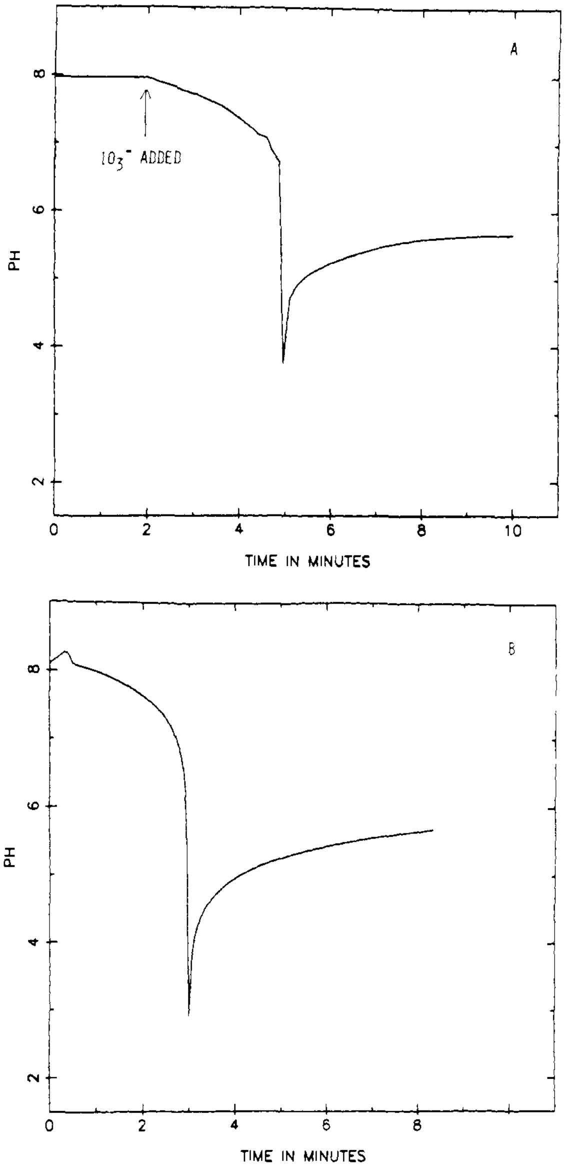

**Figure 1.** Experimental (A) and calculated (B) pH responses re Landolt system. Initial concentrations: $[IO_3^-] = 0.0715$ M = 0.0865 M, $[H_2SO_4] = 0.00506$ M.

than the $2.3 \times 10^9$ $M^{-1}$ $s^{-1}$ obtained by von Bünau and Eigen[17] for reaction 7 by a stopped-flow technique at 22 °C and unit ionic strength. It is somewhat closer to the value of $2.2 \times 10^7$ $M^{-1}$ $s^{-1}$ that those authors found for the reaction between $HSO_3^-$ and $I_3^-$. Under our conditions, most of the iodine is actually present at triiodide. While one might argue that ionic strength corrections would further reduce the von Bünau–Eigen value for the bisulfite–triiodide rate constant, furture refinements of the mechanism should probably aim at adjusting our value of $k_7$ upward while making compensating changes in other rate constants.

**Reactions 8 and 9.** The $pK_a$ of $HSO_3^-$ is 7.2.[24] Since the sulfite is fed in as $SO_3^{2-}$, the sulfite–bisulfite equilibrium must be taken into account. We estimate $k_8$ as approximately the diffusion-controlled value; $k_9$ is then obtained from the $pK_a$. The results are sensitive only to the equilibrium constant $k_8/k_9$ and not to the individual values.

**Reactions 10–13.** Our rate constants for the four reactions involving ferro- and ferricyanide are derived from the work of Reynolds.[18] Values for $k_{10}$ and $k_{13}$ are taken directly from that work. Reynolds calculates the ratio $k_{11}/k_{12}$ to be approximately 2. Since these electron-transfer reactions should be significantly faster than reaction 7, we choose values of $2.0 \times 10^8$ and $1.0 \times 10^8$ $M^{-1}$ $s^{-1}$ for $k_{11}$ and $k_{12}$, respectively. These rate constants best reproduce the $I_2$ production and consumption that occur just after the pH minimum in the oscillating system. Without these reactions, the mechanism failed to yield oscillation.

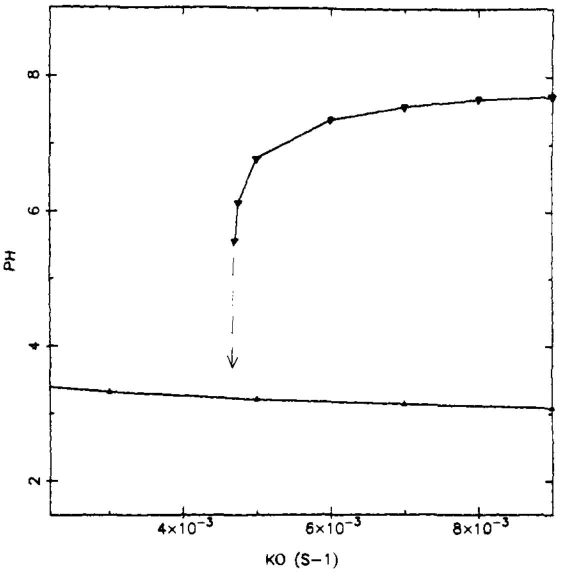

**Figure 2.** Calculated hysteresis loop for the pure Landolt system. Input concentrations: $[IO_3^-]_0 = 0.0715$ M, $[SO_3^{2-}]_0 = 0.0865$ M, $[H_2SO_4]_0 = 0.00506$ M, $[I^-]_0 = 1.0 \times 10^{-6}$ M.

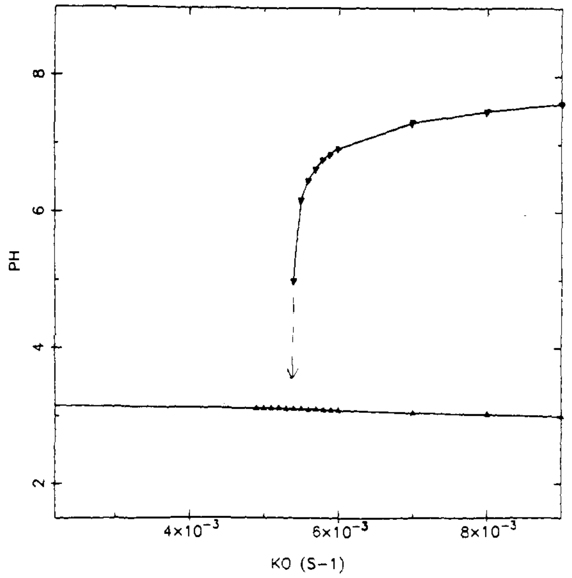

**Figure 3.** Calculated hysteresis loop for the mixed system. Input concentrations: $[IO_3^-]_0 = 0.075$ M, $[SO_3^{2-}]_0 = 0.0893$ M, $[H_2SO_4]_0 = 0.0045$ M, $[Fe(CN)_6^{4-}]_0 = 0.010$ M, $[I^-]_0 = 1.0 \times 10^{-6}$ M.

## Results

**The $IO_3^-$–$SO_3^{2-}$ (Landolt) System.** The batch and flow behavior of the Landolt system were simulated with a mechanism consisting of reactions 1–9 of Scheme II. Appropriate combinations of these elementary steps give the overall stoichiometric processes A–D in Scheme I.

Figure 1 shows the experimental and calculated batch behavior. In both cases the pH drops from about 8 to 3 roughly 3 min after iodate is added to the sulfite and acid. The pH then gradually increases to about 5.5. In the experiment, the solution turns brown at the pH minimum, indicating the presence of $I_2$. The simulations show a corresponding increase in $[I_2]$ from $10^{-8}$ to $10^{-3}$ M.

In flow, the Landolt system exhibits bistability, but not oscillation. Figure 2 shows an example of this behavior. Experimentally, the transition from the flow to the thermodynamic

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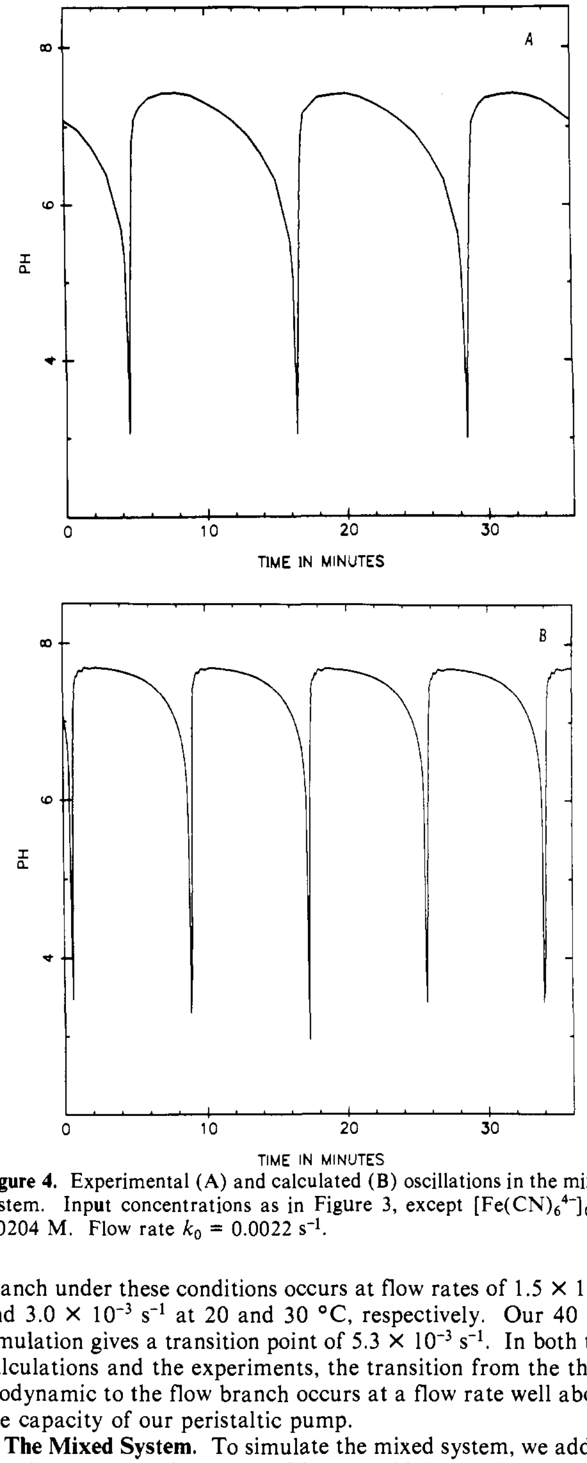

**Figure 4.** Experimental (A) and calculated (B) oscillations in the mixed system. Input concentrations as in Figure 3, except $[Fe(CN)_6^{4-}]_0$ = 0.0204 M. Flow rate $k_0$ = 0.0022 $s^{-1}$.

branch under these conditions occurs at flow rates of 1.5 × $10^{-3}$ and 3.0 × $10^{-3}$ $s^{-1}$ at 20 and 30 °C, respectively. Our 40 °C simulation gives a transition point of 5.3 × $10^{-3}$ $s^{-1}$. In both the calculations and the experiments, the transition from the thermodynamic to the flow branch occurs at a flow rate well above the capacity of our peristaltic pump.

**The Mixed System.** To simulate the mixed system, we added reactions 10–13 and an input of ferrocyanide ion to the reactions and inputs of the Landolt system.

In batch, the experimental pH response is unchanged in going from the pure Landolt to the mixed system. The calculated pH traces also show no effect from the addition of ferrocyanide. The disappearance of the $I_2$ color after the pH drop that distinguishes the observed batch behaviors of the Landolt and mixed systems is also found in the simulations. Reactions 10–13 provide a pathway for the reduction of the $I_2$ produced in the first stage of the reaction.

Experimentally, adding $Fe(CN)_6^{4-}$ to the system in a CSTR has two primary effects: the region of bistability is narrowed, and at sufficiently high ferrocyanide input above 30 °C oscillation takes place. The simulations reproduce both of these features. Figure 3 illustrates bistability in the mixed system, while Figure 4 shows the oscillatory behavior. The calculated and experimental waveforms and amplitudes are in excellent agreement, though the calculated period is too short by about a factor of 2. The iodide concentration (not shown) undergoes small amplitude oscillations about a mean value of ~2.5 × $10^{-2}$ M in both the simulations and the experiments.

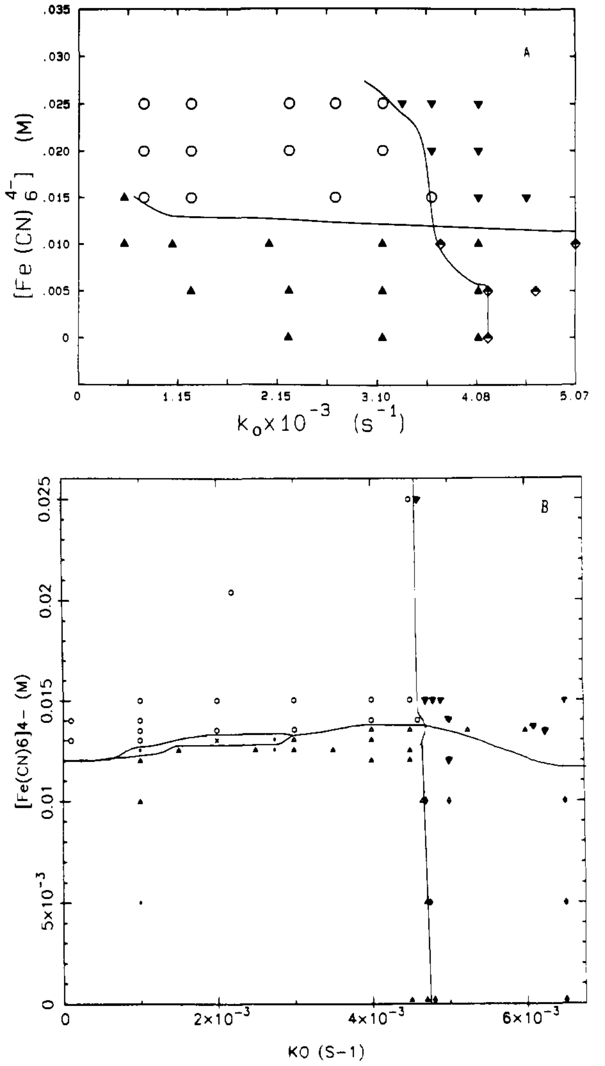

**Figure 5.** Experimental (A) and calculated (B) phase diagrams for the mixed system at 40 °C in the $k_0[Fe(CN)_6^{4-}]_0$ plane. Fixed concentrations as in Figure 3. Symbols: ▽ = SSI, △ = SSII, ◇ = bistability (SSI-SSII), ○ = oscillations, × = bistability (SSII-oscillation).

The cross-shaped phase diagram for the mixed system at 40 °C is shown in Figure 5. SSI refers to the high pH (pH ≈ 7) steady state, while SSII is the low (pH ≈ 3) state. The locations and shapes of the boundaries between regions of different dynamical behavior agree quite well. The narrow region of bistability between SSII and the oscillatory state predicted by the simulation was not seen by EOE, though its size would have made it easy to miss. Future experiments will probe whether the system really does undergo the subcritical Hopf bifurcation predicted by the simulations to yield this stationary–oscillatory bistability.

## Discussion

The mechanism presented here is essentially an elaboration in terms of elementary steps of the scheme proposed by EOE and summarized in Scheme I. The qualitative picture presented in ref 6 for the origin of the oscillation remains valid. The Landolt reaction, process A (or D), dominates the first phase, producing $I^-$ and $H^+$ autocatalytically. When all the sulfite is consumed, the Dushman reaction, process B, generates a large quantity of $I_2$, which is consumed by ferrocyanide in process F. Sulfite and ferrocyanide are replenished by the flow, thereby "resetting the clock". Uncertainties remain about several of the "experimental" rate constants, since they were determined at lower temperature and/or lower ionic strengths than those employed here. Nonetheless, in comparison with simulations of other systems of similar complexity, the agreement found between simulation and experiment is impressive.

The batch behavior is reproduced almost quantitatively. The ability of a mechanism to yield both bistability and oscillations of the correct amplitude and wave form *with the actual experimental parameters* is almost unprecedented in the literature of oscillating reactions. The prediction of the oscillation period, though not exact, is within a factor of 2, good agreement for this type of study. It remains to be seen whether the calculated region of bistability between stationary and oscillatory states will be found experimentally.

As pointed out elsewhere,[6,8] this reaction is an ideal one for detailed kinetic studies. The availability of a reliable mechanism should make it an even more attractive system for further investigation.

**Acknowledgment.** This work was supported by the National Science Foundation (CHE8419949) and by a U.S.-Hungarian Cooperative Grant from the NSF (INT8613532) and the Hungarian Academy of Sciences. We are grateful to Prof. Kenneth Showalter for sharing his results with us prior to publication. We thank Prof. Kenneth Kustin for a critical reading of the manuscript.

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# Mechanism of Titanocene Metallacyclobutane Cleavage and the Nature of the Reactive Intermediate

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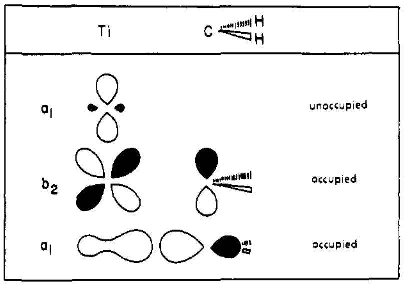
*Received December 10, 1986*

**Abstract:** The mechanism of titanocene metallacyclobutane cleavage to give a titanocene methylidene is examined in detail. The reaction of titanocene metallacyclobutanes with acetylenes or olefins displays either first- or second-order kinetics depending upon the metallacycle, its reaction temperature, and the trapping reagent. The rate-determining step for cleavage is the formation of an olefin-titanocene methylidene complex. Evidence for this complex is presented by competition experiments and kinetic studies of titanocene methylidene phosphine adducts. Deuterium isotope effect studies on an $\alpha$-$d_2$ metallacycle reveal a preference for cleavage toward placing deuterium in the liberated olefin. The studies presented allow for the rational control of the catalytic activity of titanocene metallacyclobutanes.

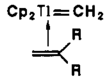
**Chart I**



Titanocene metallacyclobutanes[1] show a wide variety of reactivities with organic and inorganic reagents. Their reactions include methylene transfer to organic carbonyls,[2] formation of enolates,[2a,e,3] electron transfer from activated alkyl chlorides,[4] olefin metathesis,[5] ring-opening polymerization,[6] and complexation with metal halides.[7] All these reactions presumably occur through a reactive intermediate that exhibits behavior consistent with that of a transition-metal carbene. The intermediate has been postulated to be free titanocene methylidene[5d] A or a titanocene methylene olefin complex[5d] B. The cleavage of the metallacycle to give the reactive intermediate is the rate-determining step in all the above reactions. Controlling the rate of cleavage and understanding the nature of the reactive intermediate could lead to better catalyst design, better selectivity in organic reactions, and higher stereocontrol in polymerization.[8]

$Cp_2Ti=CH_2$

A



$Cp_2Ti=CH_2$

B

The metallacycle can be envisioned to lose olefin in a one-step process or by a slipping mechanism in which a methylidene-olefin complex forms first and then the olefin dissociates. This question has been approached theoretically by several groups. Rappé has

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