

cell were ratioed to produce a percent transmittance spectrum. A resolution of 0.5 wavenumbers was obtained.

The single photon absorption cross section at a given frequency is defined as $\sigma_{0,1} = \ln(T/T_0)/(NL)$, where T is the percent transmittance at some frequency the sample does not absorb and T_0 is % transmittance at a given frequency. N is the number density (number of molecules per cubic centimeter at a given pressure and temperature) and L is the path length of the cell in centimeters. The resulting units of $\sigma_{0,1}$ are centimeters squared.

Multiphoton absorption cross sections were determined both by calorimetric and photoacoustic methods for (*E*)- and (*Z*)-crotononitriles (0.01–0.25 torr). Calorimetric determination of absorbed energy employed a Sciencetech calorimeter placed at the exit window of a 43-cm path length Pyrex cell fitted with NaCl windows. Measurements of attenuation of transmitted laser beam intensity were performed over a fluence range of 1–5 J/cm². Photoacoustic determination of absorbed energy was made with an electret microphone (Knowles Electronics, Inc., Model BT-1759) positioned at the center of a 23-cm path length brass photoacoustic cell fitted with BaF₂ windows. Background signals due to window heating were isolated from the volume observed by the microphone by cylindrical constrictions placed at either end of the cell 5 cm from the windows. Signals were fed directly into an oscilloscope. The peak-to-peak amplitude of the first acoustic wave following the laser pulse was measured.

The multiphoton absorption cross section at a given frequency is defined as $\sigma_n = E/(N\Phi)$, where E is the energy absorbed per torr of gas

molecules (J/torr) in the cell volume. N' is the number of molecules per torr in the cell volume at a given temperature and Φ is the laser fluence (J/cm²). The average number of photons absorbed (N) are calculated from E . The resulting units of σ_n are centimeters squared.

Product Analysis. Irradiated samples were analyzed by transferring the entire contents of the irradiation cell to a Varian 3700 FID gas chromatograph equipped with a gas sampling valve, interfaced to a Hewlett-Packard 3380 reporting integrator. The GC was operated at room temperature with all columns except for FFAP, which was heated to 80 °C. Products were characterized by GC/mass spectrometry with comparisons made to authentic samples of isomers and selected fragmentation products using a Hewlett-Packard 5985 mass spectrometer. Mass balances of >90% were obtained for all reported data.

(*E*)- and (*Z*)-1,3-pentadienes, -1,4-pentadienes, and -cyclopentadienes were analyzed by using a 12 ft × 19 in. column of 20% dimethylsulfolane on Chromosorb P. (*E*)- and (*Z*)-2-butenes were analyzed by using a 20 ft × 1/8 in. column of 20% propylene carbonate on Chromosorb P. (*E*)- and (*Z*)-2-pentenes and *cis*-2-hexene were analyzed by using a 20 ft × 1/8 in. column of 20% 3,3'-oxydipropionitrile on Chromosorb P. Methyl and ethyl crotonates and (*E*)- and (*Z*)-crotonitriles were analyzed by using a 10 ft × 1/8 in. 5% FFAP column on Chromosorb G.

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A New Iodate Oscillator: The Landolt Reaction with Ferrocyanide in a CSTR¹

Elizabeth C. Edblom,[†] Miklós Orbán,[‡] and Irving R. Epstein*[†]

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254, and Institute of Inorganic and Analytical Chemistry, L. Eötvös University, H-1443 Budapest, Hungary. Received November 8, 1985

Abstract: At a temperature of 30 °C or higher, the reaction of sulfite, iodate, and ferrocyanide exhibits sustained oscillation in a CSTR. The system may be thought of as a $\text{Fe}(\text{CN})_6^{4-}$ perturbation of the bistable Landolt (SO_3^{2-} – IO_3^-) reaction in which the ferrocyanide serves to consume the I_2 produced in the reduction of iodate, thereby “resetting the clock”. The reaction may be monitored with pH, redox or iodide-selective electrodes, or spectrophotometric measurement of iodine, ferrocyanide, or ferricyanide.

Iodate-based reactions were the first chemical oscillators to be discovered, yet this group has remained much smaller in number than either the bromate- or chlorite-based oscillators.² Iodate oscillators characterized to date include the Bray (hydrogen peroxide–iodate) reaction,³ the Briggs–Rauscher (hydrogen peroxide–manganous–malonic acid–iodate) system,⁴ and their variants.^{5,6} In addition, a number of systems containing chlorite, iodate, and a reductant exhibit oscillation, though these have been classified as chlorite oscillators.⁷ Oscillations have been reported⁸ in the arsenite–iodate reaction, but these claims have been challenged,⁹ and our own experiments confirm that the system is bistable, i.e., it exhibits two different stable stationary states under the same set of experimental conditions, but it is not oscillatory. Beck et al.¹⁰ have reported “oligo-oscillations” in systems consisting of iodate, sulfite, and various reducing agents.

Many of the recently discovered oscillators have been found with use of a systematic search procedure¹¹ based upon the cross-shaped phase diagram model of Boissonade and De Kepper.¹² In this approach, one begins with an autocatalytic reaction and adds to it an appropriate feedback species in a continuous flow stirred tank reactor (CSTR). The Landolt-type reactions,¹³ which

are autocatalytic oxidations of suitable substrates by iodate, constitute a promising starting point from which to design new iodate-based oscillators. We report here the discovery of a new

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[†] Brandeis University.

[‡] L. Eötvös University.

iodate oscillator which may be viewed either as a ferrocyanide perturbation of the classic iodate-sulfite Landolt reaction or as a combination of two (IO_3^- - SO_3^{2-} and IO_3^- - $\text{Fe}(\text{CN})_6^{4-}$) Landolt-type reactions.

Experimental Section

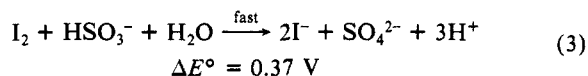
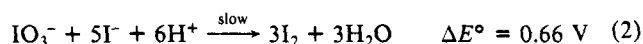
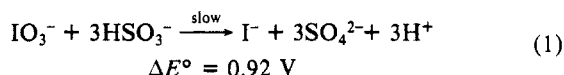
The flow experiments were carried out in a thermally regulated CSTR.¹⁴ The temperature was maintained constant to within $\pm 0.1^\circ\text{C}$ during each experiment. The four inlet solutions were pumped into the reactor by a Sage 375A peristaltic pump. Flow experiments were carried out, keeping the reservoir concentrations fixed and varying the input pumping rate. In order to reveal any hysteresis behavior this pumping rate was varied in both directions.¹⁵ At each setting sufficient time was allotted for the system to reach a stationary steady state or oscillatory state. Batch experiments were monitored with the same probes as the flow experiments. Both batch and flow experiments were run at 20, 30, and 40°C .

Iodate, sulfite, and ferrocyanide stock solutions were prepared with distilled water, which was passed through an ion exchange column filled with oxycellulose to remove trace metal impurities, and analytical grade KIO_3 , Na_2SO_3 , and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, produced by Fisher Co. (USA) and Reanal (Hungary).

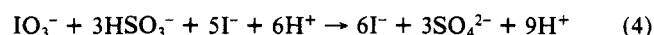
Concentrations of the sulfite and ferrocyanide solutions were checked by using iodometric and $\text{Ce}(\text{SO}_4)_2$ titrations, respectively. A platinum redox electrode and a $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4$ reference electrode were used to follow the reaction potentiometrically. The pH was followed with a combined glass electrode. Some measurements were also made with an Orion iodide-specific electrode.

Results

The IO_3^- - SO_3^{2-} (Landolt) System. Batch. Under batch conditions with iodate in excess the sulfite-iodate reaction shows a sharp increase in potential (≈ 400 mV) and a rapid decrease in pH (7.9-3.75) several minutes after the reaction is initiated (Figure 1). When the plateau in potential is reached, the pH begins to increase slowly and iodine appears. An identical pH vs. time curve has been reported by Sorum et al.¹⁶ The treatment of reactions 1-3 by Eggert and Scharnow¹⁷ nicely explains these observations.



Both reaction 1 and reaction 2, the Dushman reaction,¹⁸ are slower than reaction 3. Step 1 is the dominant process from the point of IO_3^- addition until point I in Figure 1. As more I^- is produced steps 2 and 3 come into play. The reaction begins to speed up due to the autocatalytic production of I^- and H^+ , reaction 4 ((4) = (2) + 3 \times (3)). The pH drops due to the production of H^+



ions in the fastest process, (3), and the potential increases corresponding to consumption of HSO_3^- and formation of I^- . The reaction proceeds with all three steps participating until point II, where all the HSO_3^- has been consumed. A color change from clear and colorless to deep brown takes place in the solution here, indicating the formation of I_2 . After point II only process 2 can continue. Now acid is consumed and the pH rises again to a steady value. Likewise, the potential also increases to a constant value as the IO_3^- reacts with the I^- to form I_2 .

Flow. In flow conditions the Landolt system exhibits bistability. At high flow rates the system remains in a steady state (SSI) characterized by high pH, low potential, and very low, if any, concentration of I_2 . Visually the solution is clear and colorless.

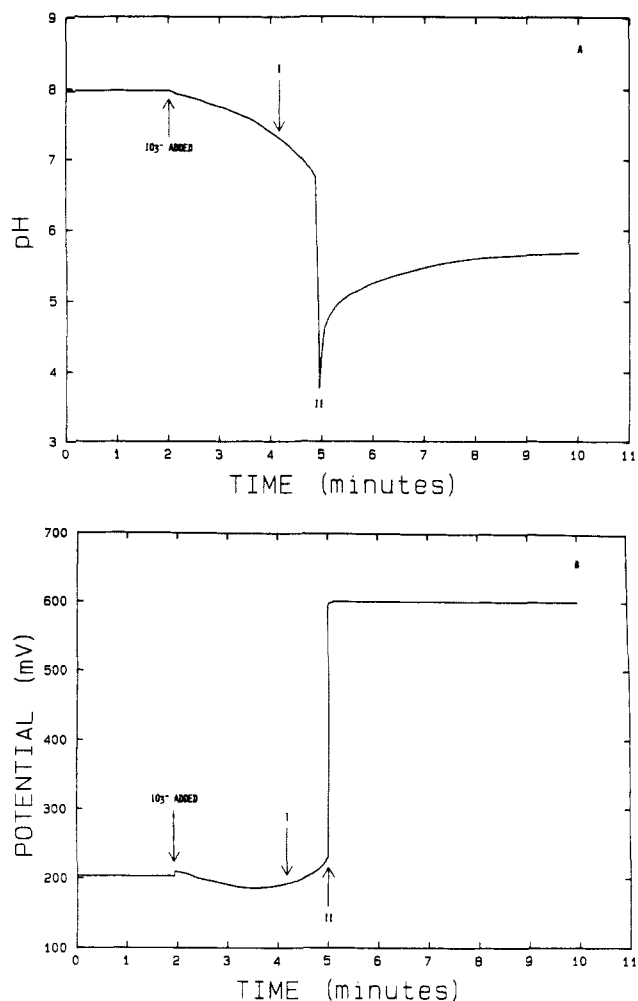
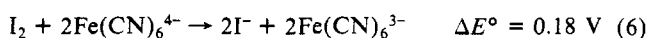
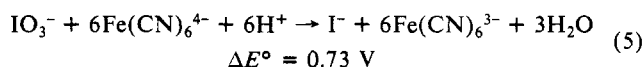


Figure 1. Batch responses of (A) pH and (B) Pt electrodes in the iodate-sulfite system. Initial conditions: $[\text{IO}_3^-] = 0.0715 \text{ M}$, $[\text{SO}_3^{2-}] = 0.0865 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.00506 \text{ M}$, $T = 30^\circ\text{C}$.

Steady state SSII, on the other hand, shows a lower pH, a higher potential, and a brown color, indicating a high concentration of iodine. Figure 2A shows the hysteresis observed as the flow rate is varied. Once SSII was reached it was impossible to return the system to SSI even by going to the highest flow rate accessible with our pump. The SSI-SSII transition can be accomplished, however, by appropriate chemical perturbation to consume the I_2 (e.g., injection of additional sulfite).

The Mixed System. The presence of bistability often indicates the possibility of oscillation.^{11,12} With that ultimate goal in mind several different compounds or "feedback species" were added to the Landolt system. Potassium iodide, malonic acid, acetone, phenol, and potassium ferrocyanide were all tried in the hope of perturbing the system into oscillation. Only the ferrocyanide had any measurable effect on the system (Figure 2B). The other four compounds not only failed to induce oscillation but they also left the region of bistability unchanged.

The introduction of ferrocyanide results in the presence of two Landolt-type systems. The $\text{Fe}(\text{CN})_6^{4-}$ ion can replace the HSO_3^- ion to react with the IO_3^- in a Landolt-type reaction.¹⁷ The role of the iodine species is the same in both systems. However, the ferrocyanide-iodate reaction takes place at a much slower rate, i.e., reactions 5 and 6 are considerably less rapid than their sulfite counterparts (1) and (3).



Batch. As a comparison of Figures 1 and 3 reveals, the batch behavior of these two Landolt systems is quite different. Upon

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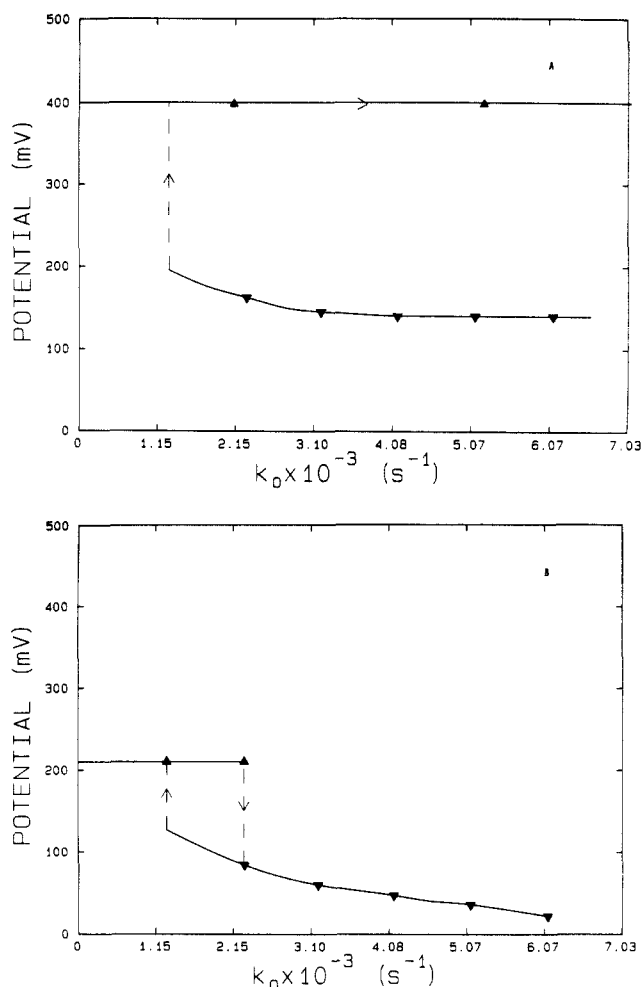


Figure 2. Hysteresis loops at 20 °C for (A) iodate-sulfite and (B) iodate-sulfite-ferrocyanide. Input concentrations: $[\text{IO}_3^-]_0 = 0.0715 \text{ M}$, $[\text{SO}_3^{2-}]_0 = 0.0865 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.00506 \text{ M}$, and (in B only) $[\text{Fe}(\text{CN})_6^{4-}]_0 = 0.0204 \text{ M}$.

iodate addition to a weakly acidic $\text{Fe}(\text{CN})_6^{4-}$ solution the pH rises gradually from 3 to 5. An instantaneous redox potential increase of about 100 mV accompanies mixing of the iodate and ferrocyanide.

The changes in the batch behavior of the mixed system (Figure 4) are far from dramatic. The pH response curves for the sulfite and the mixed reactions are nearly superimposable. Likewise, there is little new in the first portion of the Pt response curve. The noticeable difference occurs after the minimum in the pH. Without the $\text{Fe}(\text{CN})_6^{4-}$ the final state is deep brown, indicating the presence of iodine. Now the I_2 appears only for a matter of seconds. It quickly disappears and we are left with a bright yellow solution which lies about 200 mV lower in potential than the corresponding state of the sulfite system (Figures 1B and 4). Since a transient brown color is observed at the pH minimum, point III on Figure 4, I_2 must be produced and then rapidly consumed, most likely by reactions 2 and 6, respectively.

Flow. At 20 °C the system exhibits only bistable behavior (Figure 2B). However, the size of its hysteresis loop has shrunk dramatically (cf. Figure 2A) as a result of ferrocyanide addition. SSI remains the same as it was for the pure Landolt system but SSII lies approximately 200 mV lower in potential. Another difference in these two hysteresis loops is that with ferrocyanide the system does return to SSI at a flow rate accessible with our equipment.

At 30 °C and above the addition of ferrocyanide to the bistable SO_3^{2-} - IO_3^- system in the CSTR initiates periodic oscillations in both the pH and Pt potentials (Figure 5). These oscillations are strongly temperature dependent as illustrated in Figure 6. No oscillations appear at 20 °C, and it is not until 30 °C that the system is far enough from the critical point in the temperature-

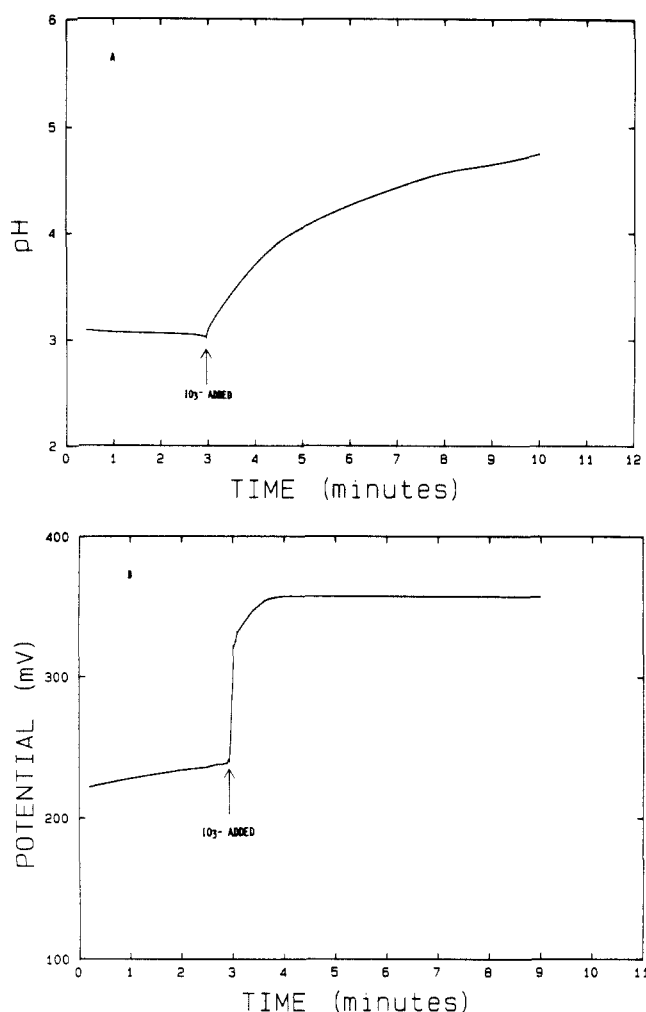


Figure 3. (A) pH and (B) Pt potential vs. time responses for the iodate-ferrocyanide system in batch.

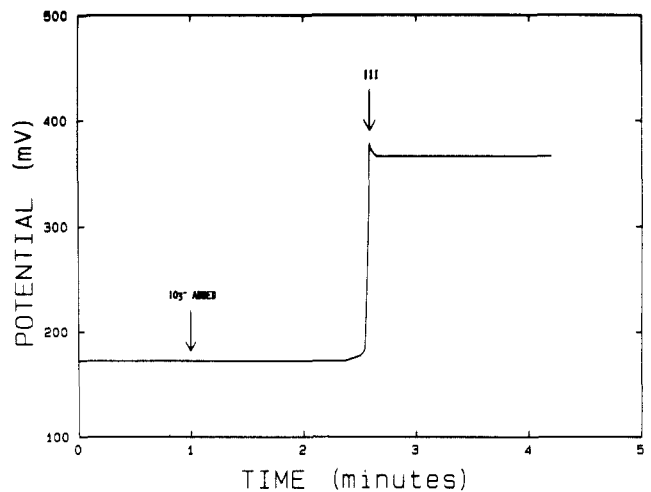


Figure 4. Pt potential response for the mixed system in batch.

input concentration plane for the oscillations to be reproducible.

At elevated temperatures ($\geq 30 \text{ °C}$), the characteristic cross-shaped phase diagram¹² is found. As the temperature is raised the region of oscillation grows (Figure 6). This broadening is also accompanied by a rightward shift of the bistable and oscillatory regions of the phase diagram. Just as in batch, the peaks of the

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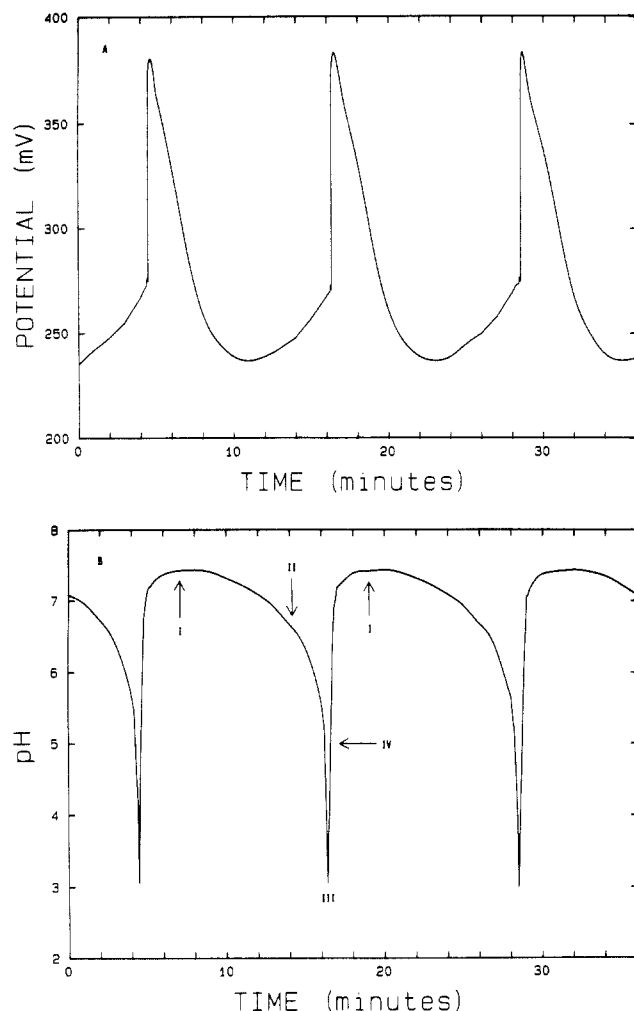


Figure 5. Oscillations in the iodate-sulfite-ferrocyanide system at 40 °C. $[\text{IO}_3^-]_0 = 0.075 \text{ M}$, $[\text{SO}_3^{2-}]_0 = 0.0893 \text{ M}$, $[\text{Fe}(\text{CN})_6^{4-}]_0 = 0.0204 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.0045 \text{ M}$, $k_0 = 0.0022 \text{ s}^{-1}$.

pH and Pt oscillations occur simultaneously. The oscillations appear to take place between the two steady states observed in batch. Platinum oscillations are approximately 100 mV in magnitude, similar to the change in iodate-ferrocyanide batch experiments. The pH difference, pH 3 to 7, is the same as that for the iodate-sulfite system in batch.

Temperature Effects. The effect of increased temperature was studied for the iodate-sulfite, iodate-ferrocyanide, and ferrocyanide-sulfite reactions. Little change in rate was found for the original Landolt system. The pH rises 1.6 times faster at 40 °C than at 25 °C for the IO_3^- - $\text{Fe}(\text{CN})_6^{4-}$ reaction. The largest effect is observed in the ferricyanide-sulfite system. Here a 20 °C increase causes the rate to increase by a factor of 2.6.

Discussion

With the aid of the reactions proposed above it is possible to explain, at least qualitatively, the observed oscillatory behavior. We shall refer to the pH response curve of Figure 5B, as the pH electrode offers the advantage of responding to a single species, H^+ , which occurs in most of the reactions 1-6.

At point I the solution is alkaline because of the high basicity of the sulfite ion. From point I to point II the dominant reaction is the relatively slow reaction of iodate and sulfite, eq 1. The pH begins to decrease slowly due to the hydrogen ions produced in this step. After point II the reaction speeds up. This sudden change is the result of the autocatalytic formation of I^- and H^+ , reactions 2 + 3. The process continues in this manner until point III, when all the SO_3^{2-} is used up. Without sulfite, reactions 1 and 3 can no longer take place. Until this point the shape of the pH oscillation is exactly the same as that of the Landolt system in batch (Figure 1A). Thus, the ferrocyanide does not appear

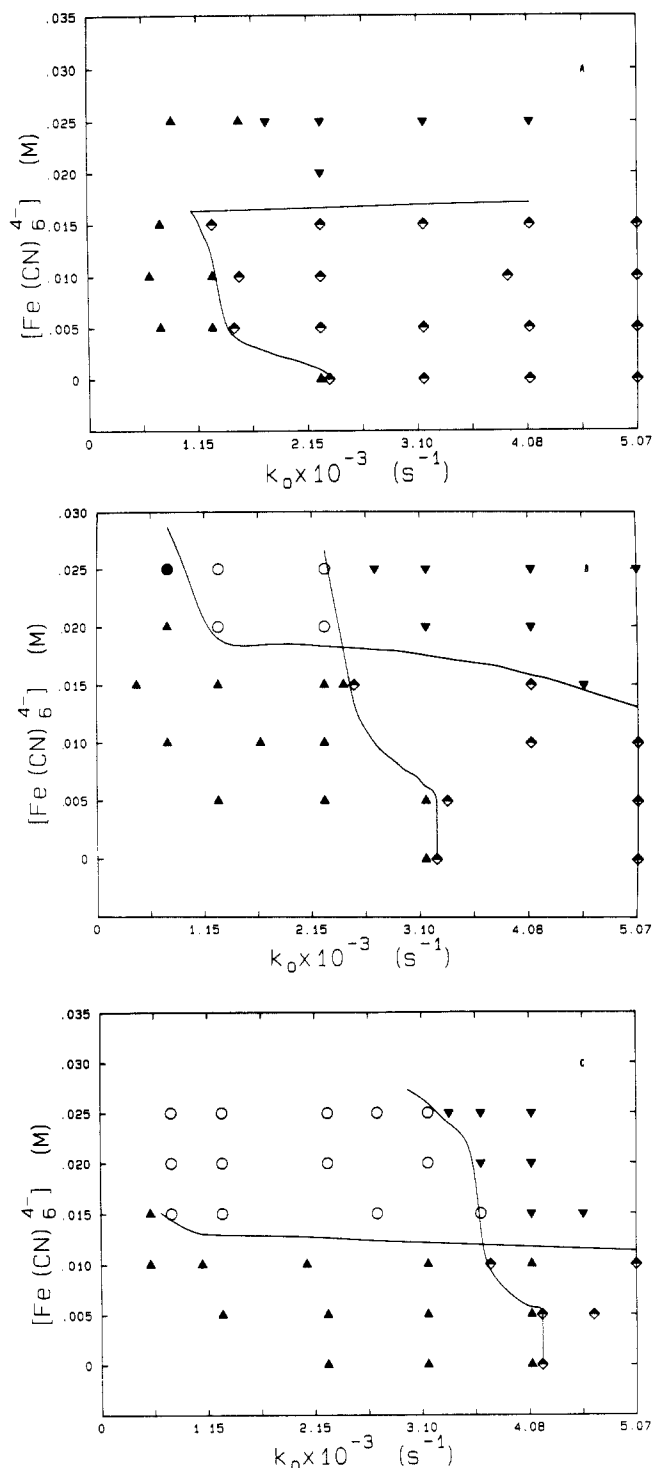
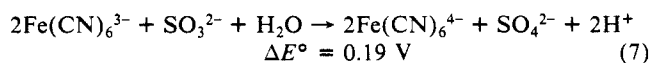


Figure 6. Phase diagrams in the k_0 - $[\text{Fe}(\text{CN})_6^{4-}]_0$ plane at (A) 20 °C, (B) 30 °C, and (C) 40 °C. Fixed concentrations are the same as those in Figure 5. Symbols: ▼ = SSI, ▲ = SSII, ◆ = bistability, ○ = oscillations, ● = excitability.¹⁹

to be a major reactant during this portion of the oscillation. As noted above, at the pH minimum a transient brown color is observed which is followed by a rapid rise in potential. These observations are explained by the presence of iodine. From III to IV, the I_2 produced by reaction 2 is consumed primarily in reaction 6. In order for the next oscillation to begin time is required to replace the reactants, to "reset the clock". Iodate has now been replenished and sulfite ion is being flowed into the reactor yet the next oscillation does not begin immediately. We suggest that the following reaction may account for this delay:



Higginson and Marshall²⁰ determined that reaction 7 becomes important at pHs higher than 5. As the pH is increased this process becomes faster and more complete. The ferricyanide oxidation of the sulfite results in a lag period in the oscillation. The sulfite cannot build up to a level where the Landolt reaction can resume, point I, until the ferricyanide is either reduced back to ferrocyanide or is washed out of the reactor.

In general, the oscillation begins with the Landolt reaction. The ferrocyanide does not disturb the reaction, since it reacts much more slowly with the iodate than does the sulfite. The Landolt reaction proceeds until all the sulfite has been consumed. At this point the $\text{Fe}(\text{CN})_6^{4-}$ comes into the picture as it reacts with the I_2 formed in the Landolt reaction. The product of this reaction, $\text{Fe}(\text{CN})_6^{3-}$, serves as an inhibitor to the Landolt reaction. Only after the ferricyanide is removed can the oscillation begin again. Thus the ferrocyanide-ferricyanide redox couple serves two purposes. First, by reacting with the I_2 it permits the system to return to SSI. Second, by slowing down the sulfite buildup the ferricyanide creates a time lag which results in oscillatory rather than steady-state behavior. It is necessary that the temperature be high enough so that this reaction can take place sufficiently rapidly.

The discovery of the iodate-sulfite-ferrocyanide oscillator is of significance to the study of chemical oscillations for several reasons. It provides an almost classic example of the utility of the cross shaped phase diagram approach^{11,12} in searching for new oscillators. It suggests that the family of iodate oscillators may well be comparable in size to the other oxyhalogen families, though the search may have to be carried out above room temperature.

Finally, this system seems ideal for both dynamical and mechanistic studies. In addition to the pH and redox probes on which we have focused in this report, it is possible to measure $[\text{I}^-]$ potentiometrically and $[\text{I}_2]$, $[\text{Fe}(\text{CN})_6^{4-}]$, and $[\text{Fe}(\text{CN})_6^{3-}]$ spectrophotometrically. Such data would facilitate both the generation of multidimensional phase portraits and the development and testing of detailed mechanisms. Studies are now under way in our laboratories to determine several of the relevant rate constants so that the mechanistic suggestions sketched above can be converted to a full mechanism for this fascinating system.

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The Generalized Resonating Valence Bond Description of Cyclobutadiene

Arthur F. Voter[†] and William A. Goddard, III*

Contribution No. 7151 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received February 13, 1985

Abstract: The low-lying electronic states of square and rectangular cyclobutadiene (CBD) are calculated by using the generalized resonating valence bond (GRVB) method and compared with the results from Hartree-Fock and configuration interaction wavefunctions. We find that simple valence bond concepts correctly predict the sequence of excited states (including ground-state singlet) and the distortion to a rectangular geometry for the ground state. Contrary to common expectation, we find that the singlet ground state of square CBD has 22 kcal of resonance energy (relative to a single valence bond structure). Thus, CBD is *not* antiresonant, though it is much less stable than normal conjugated systems.

I. Introduction

Cyclobutadiene (CBD), the simplest cyclic four-electron π system, has provided an interesting counterpoint to benzene for many years. In agreement with simple Hückel theory arguments, the molecule is highly unstable, though it has been isolated in low-temperature matrix studies¹ and observed as a short-lived intermediate in solution.^{2,3} Two features of CBD are particularly intriguing. First, the most stable geometry is found to be rectangular (both experimentally¹⁻³ and theoretically⁴⁻⁷), with the square geometry (6-12 kcal higher) representing a saddle point for interconversion of the two rectangular structures.⁸ Second, the lowest state at the square geometry is found to be a singlet, in contradiction to the prediction of a triplet ground state from molecular orbital (MO) theory.

The resonating valence bond (VB) model offers a useful alternative view of CBD, providing a simple rationalization of spin state and geometry; the CBD molecule thus provides a good vehicle for contrasting the VB and MO theories. In the following we discuss the electronic structure of square cyclobutadiene at a qualitative level from both points of view. We then quantify these arguments by using the orbitally-optimized generalizations of MO and VB theory and compare these results with accurate config-

uration interaction (CI) calculations. Finally, we consider distortions from the square geometry to give the observed rectangular geometry.

The orbitally-optimized representation of MO theory is simply the Hartree-Fock (HF) wave function, while for VB theory it is the generalized valence bond⁹ (GVB) wave function. Because the resonance of more than one VB wave function is important for CBD, we will also apply the recently developed resonating GVB (R-GVB) method¹⁰ in which two (or more) GVB wave functions are mixed, leading to a resonance-stabilized state and one or more antiresonant states. The true generalization of resonating-VB theory is the generalized resonating valence bond (GRVB) wave function¹¹ in which the GVB subwave functions are allowed to

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[†] Present address: Theoretical Division, MS J569, Los Alamos National Laboratory, Los Alamos, NM 87545