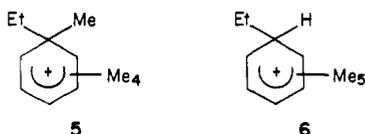


ceivably open to Me_2O involves elimination of ethylene



While the lack of necessary data prevents exact calculations, reasonable estimates suggest that neither process should significantly depart from thermoneutrality. Dimethyl ether is known to undergo fast R^+ transfer from gaseous cations,⁶ and its reaction with $\text{C}_6\text{MeEt}_6^+$ is probably favored by the limited steric requirements, the high concentration attainable in the gas, and the relatively high temperature (120 °C) of the system.

Alkylation of Pentamethylbenzene. The results are of special interest, allowing quantitative comparison between the rate of ipso substitution and that of alkyldeprotonation of the same substrate. The latter process is found to predominate by an order of magnitude, despite its unfavorable statistical factor. In line with foregoing considerations, the bias against ipso substitution can be plausibly ascribed to the different rates of the processes which convert the charged intermediates into neutral aromatic products. In fact, it can be argued that demethylation of the ipso-alkylated adducts **5**



is slower than deprotonation of the intermediate **6** from the attack at the unsubstituted position of PMB. This is a reasonable proposition if one considers that proton-transfer processes are comparatively very fast in the gas phase and that the formation of proton-bound clusters can allow deprotonation of **6** even by relatively weak *n*-type bases. It seems likely that the observed bias in favor of alkyldeprotonation is enhanced by the partial isomerization into **6** of the unreactive intermediate **5** via facile 1,2 Et⁺

Conclusions

The complementary results from different experimental techniques, i.e., CI mass spectrometry, CID spectrometry, and gas-phase radiolysis, provide convincing evidence for the occurrence of gaseous heptaalkylbenzenium ions having the σ -complex (Wheland intermediate) structure as stable species in the dilute gas state. The ions represent the charged intermediates of the gas-phase ipso substitution promoted by the attack of Et^+ , Me_2F^+ , and Me_2Cl^+ cations on hexaalkylbenzenes.

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Registry No. **1**, 3043-52-5; **4** (R, R' = Me), 27175-04-8; **4** (R, R' = Et), 56726-05-7; **4** (CR = Et; R' = Me), 95069-55-9; HMB, 87-85-4; HEB, 604-88-6; pentamethylbenzene, 700-12-9.

A New Halogen-Free Chemical Oscillator: The Reaction between Sulfide Ion and Hydrogen Peroxide in a CSTR¹

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Abstract: Periodic oscillation and bistability occur in the potentials of Pt redox, pH, and sulfide ion selective electrodes when sulfide ion reacts with hydrogen peroxide in a continuous flow stirred tank reactor. The S^{2-} - H_2O_2 system is one of the few known and probably the simplest of the non-halogen chemical oscillators. It is the first of these systems to show bistability and the only chemical oscillator known to oscillate between acid and basic pH.

The overwhelming majority of the known homogeneous oscillatory chemical reactions are based on the chemistry of oxyhalogen anions.² Recently, two new discoveries have extended the realm of chemical oscillation beyond group 17¹² of the Periodic Table. Jensen³ reported oscillation in the reaction of benzaldehyde with oxygen in the presence of Br^- and Co(II) . Field and Burger⁴ have found oscillatory behavior in the potential of a Pt electrode and in the absorbance at 668 nm when sulfite, sulfide, methylene blue, and oxygen react in a continuous flow stirred tank reactor (CSTR). In contrast to the almost universal association of bistability with oscillation in oxyhalogen systems, neither of the above two reactions has been shown to exhibit multiple stationary states.

We report here on a halogen-free system, with apparently simpler constituents than either the Jensen or Burger-Field reactions, which gives both bistable and oscillatory behavior in a CSTR. The reaction, which involves only sulfide ion and hydrogen peroxide, has been studied previously in other contexts by several

authors,⁵⁻⁷ since it offers a potentially cheap and convenient route to eliminate H_2S generated by industrial and municipal wastewater systems.

Several other features of the S^{2-} - H_2O_2 system should be noted. It not only exhibits both oscillations and bistability but also provides an almost classic example of the cross-shaped phase diagram,⁸ which led to the first systematically designed chemical oscillators.⁹ While all oxyhalogen systems and the Jensen reaction

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oscillate only in acidic solution and the Burger-Field oscillator runs at pH 11, the present reaction undergoes oscillation between acidic and basic pH's, and the acidity may indeed be one of the key factors responsible for the dynamical behavior. Finally, the simplicity of composition of this system makes it an attractive candidate for detailed mechanistic analysis.

Experimental Section

Materials and Apparatus. Hydrogen peroxide (Fisher Certified A. C.S., 30%) and Na₂S·9H₂O (Fisher Reagent) were used for preparation of the input solutions. Stock solutions of H₂O₂ were titrated with 0.1 M KMnO₄ in H₂SO₄ solution, while the sulfide stock solutions were standardized by titrating in the presence of starch a known amount of iodide generated by reacting KIO₃ with KI in acidic (HCl) solution. Stock solutions were prepared frequently because of the possibility of decomposition of H₂O₂ and air oxidation of S²⁻. The concentration of the input H₂SO₄ (0.003 M) was checked with a glass electrode connected to a pH meter.

The reactor was similar in design to that employed in earlier studies,⁹ but was made of plexiglass to eliminate slow decomposition of H₂O₂ catalyzed by glass. The CSTR had a volume of 40.3 cm³ and was thermostated at 25.0 ± 0.1 °C. Potentiometric measurements employed a Radiometer K601 Hg|Hg₂SO₄|K₂SO₄ reference electrode and two of the following: Pt electrode (Radiometer P101), combined glass electrode (Orion 91-04), or sulfide ion selective electrode (Orion 94-16). The platinum and reference electrodes were connected directly to the chart recorder, while the combined glass and sulfide electrodes were connected through a pH meter (Orion digital ionalyzer 501). The construction of the reference electrode precluded contact between the mercury and the reactant solution. Control experiments in which the Pt electrode was removed and only the glass electrode was used for monitoring showed that the platinum surface did not affect the reaction. The reactor was fed by a Sage 375A peristaltic pump and was stirred by a magnetic stirrer at constant speed of 600 rpm. No air gap was present between the surface of the solution and the reactor cap.

Methods. In the batch experiments, solutions of Na₂S, H₂O₂, and H₂SO₄ were mixed in a beaker and the electrode potentials recorded vs. time. To establish the stoichiometry, HCl was used to adjust the acidity and the sulfate content determined by gravimetric analysis as BaSO₄.

For the flow experiments, the reactor was filled at the highest available pump speed. After a steady state was attained, the flow rate was lowered and a new steady or oscillatory state was established. This procedure was continued until the flow rate reached zero. The flow rates were then increased stepwise to the maximum. When the entire range of flow rates had been probed for one set of input concentrations, the sequence was repeated for a new feed composition. The input flow consisted of three streams: the H₂O₂, Na₂S, and H₂SO₄ solutions. The concentrations given as [X]₀ are the values of [X] in the reactor immediately after mixing, i.e., one third of the concentrations in the input reservoirs.

In order to test for the effects of dissolved oxygen, which are crucial in the Burger-Field oscillator,⁴ several runs were carried out with the reactor continuously purged by argon gas introduced through one of the input tubes. No difference in behavior could be found in any of these experiments, and the argon purges were discontinued. The oscillatory behavior was also unaffected by replacing H₂SO₄ by HCl in the input stream.

Results

Batch Experiments. When Na₂S, H₂O₂, and dilute H₂SO₄ solution are combined in a beaker, the mixture initially turns to clear yellow as the result of transient formation of polysulfides (mainly S₄²⁻ and S₅²⁻).^{7,10} At low initial acid concentrations, these species are then oxidized further to colorless sulfate. If the initial [H⁺] is sufficiently high, instead of sulfate formation one observes the precipitation of white elementary sulfur. The oscillatory region corresponds to the low initial acid regime.

Potential traces for the Pt, glass pH, and sulfide ion electrodes in a typical batch experiment are shown in Figure 1. The appearance of multiple inflection points in each trace suggests that the reaction takes place in several distinct steps. All portions of the traces lengthen significantly with decreasing [H₂O₂], but the reaction rate is relatively insensitive to variation of [Na₂S]. Either increasing or decreasing [H₂SO₄] by an order of magnitude causes the inflection points to disappear. In the former case, sulfur

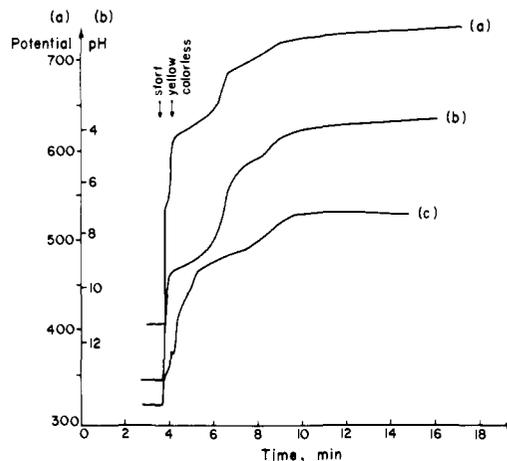


Figure 1. Batch experiment with initial concentrations [H₂O₂] = 0.4 M, [Na₂S] = 0.0167 M, [H₂SO₄] = 0.001 M: (a) potential of Pt electrode; (b) potential of the glass pH electrode; (c) potential of the sulfide electrode (uncalibrated).¹¹ The above composition shows oscillations in the CSTR at reciprocal residence times $k_0 = (1.5-6.0) \times 10^{-4} \text{ s}^{-1}$.

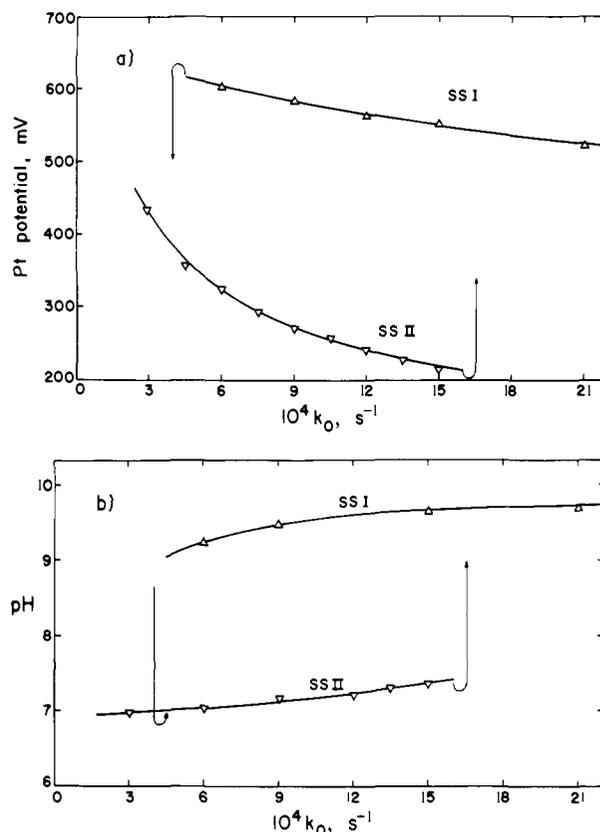


Figure 2. Hysteresis between steady states in the CSTR with the concentrations [H₂O₂]₀ = 0.40 M, [Na₂S]₀ = 0.01 M, [H₂SO₄]₀ = 0.001 M: (a) potential of the Pt electrode; (b) pH measured by the glass electrode.

precipitation and H₂S evolution are also observed.

Flow Experiments. When the reaction is carried out in the CSTR, one may observe either of two steady states (SSI or SSII), bistability between them, or sustained oscillations, depending upon the input concentrations and flow rate. The steady states and bistability (shown as hysteresis with variation of the flow rate k_0) are illustrated in Figure 2.

Under bistable conditions, the state established at high k_0 , the flow branch SSI, is associated with a higher Pt potential and higher pH in the reactor. As k_0 is lowered a critical value is reached at which transition to the thermodynamic branch SSII takes place via a small maximum in Pt potential and minimum in pH. After this transition, the solution becomes slightly turbid (or at some concentrations pale yellow) as a result of sulfur precipitation. On

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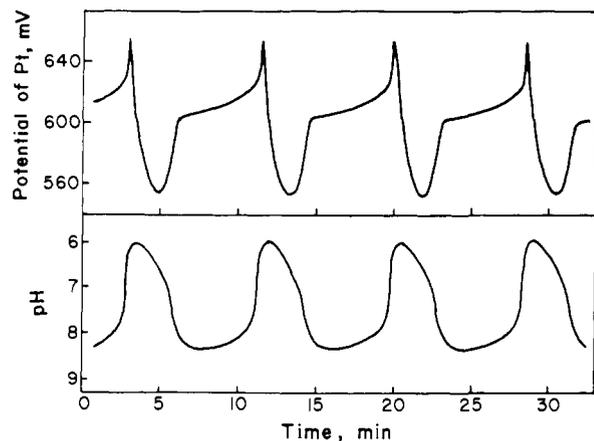


Figure 3. Oscillations in (a, top) the potential of a Pt electrode and (b, bottom) the pH with $[H_2O_2]_0 = 0.4$ M, $[Na_2S]_0 = 0.0167$ M, $[H_2SO_4]_0 = 0.001$ M, $k_0 = 6 \times 10^{-4} s^{-1}$.

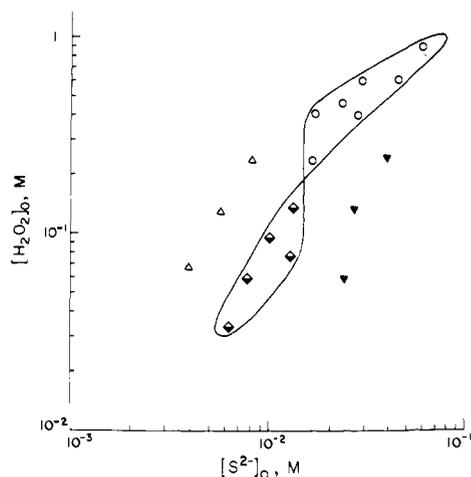


Figure 4. Phase diagram in the $[H_2O_2]_0$ - $[Na_2S]_0$ plane with $k_0 = 4.5 \times 10^{-4} s^{-1}$, $[H_2SO_4]_0 = 0.001$ M, temperature = 25 °C: (O) oscillations; (◊) bistability; (Δ), SS; (▼) SSII.

increasing the flow, the reverse transition is observed at a second, higher critical flow rate. The SSII-SSI transition is relatively slow, is accompanied by the clearing of the solution, and at low $[Na_2S]_0$ is marked by low-amplitude, high-frequency, damped oscillations.

At appropriate values of the input concentrations, the system possesses a range of flow rates under which it exhibits sustained oscillation. Typical oscillatory traces are shown in Figure 3.

The oscillations are marked by visible changes in the state of the reactor. In the high pH phase, the solution is clear and colorless until just after the peak in the Pt potential. Then colloidal white sulfur begins to appear, and turbidity increases until the potential passes its minimum. The solution then clears and remains clear until the Pt potential maximum is reached again.

When the oscillatory state is approached from the high flow rate (SSI) side, the system shows excitability in a range of k_0 values just above the oscillatory range. Approach to oscillation from the SSII side (low flow rate) gives damped oscillation as k_0 is increased toward the critical value for oscillation.

The sizable change in pH during the oscillations enables us to make the oscillations dramatically visible by the addition of acid-base indicators. For example, with Gramercy Universal Indicator (Fisher) added to one of the input solutions, the system oscillates between a deep blue and a striking yellow.

In Figure 4, we show a phase diagram obtained by varying $[Na_2S]_0$ and $[H_2O_2]_0$ at fixed input acid, flow rate, and temperature. The behavior in the neighborhood of the critical point which joins the bistable and oscillatory regions has the characteristic "cross-shape" predicted by the model of Boissonade and De Kepper.⁸

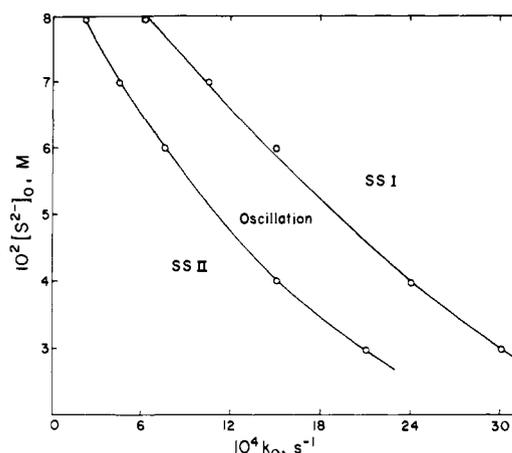


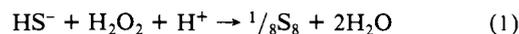
Figure 5. Phase diagram in the $[Na_2S]_0$ - k_0 plane with $[H_2O_2]_0 = 1.0$ M, $[H_2SO_4]_0 = 0.001$ M.

A different shape of phase diagram is obtained if one fixes one input reactant concentration and varies the flow rate and the other input concentration. Such a plot is shown in Figure 5.

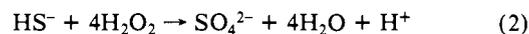
Discussion

The system reported here is only the second sulfur-based chemical oscillator. It appears to be of considerably simpler composition than the Field-Burger reaction,⁴ both because of the absence of methylene blue and because mass transfer processes (i.e., the dissolution of O_2) are of little consequence. The S^{2-} - H_2O_2 oscillator is thus a prime candidate for mechanistic study. While our data and the available knowledge of sulfur-hydrogen peroxide chemistry are not yet sufficient for us to propose a full mechanism here, we offer a few observations on which future mechanistic investigations may build.

Hoffmann⁷ gives eq 1 and 2 for the stoichiometry of the sulfide-hydrogen peroxide reaction



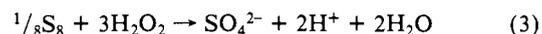
when $[H_2O_2] \sim [Na_2S]$, and



when $[H_2O_2] \gg [Na_2S]$.

Our batch studies under the conditions of Figure 1, where $[H_2O_2]/[Na_2S] = 24$, confirm eq 2. We note that eq 2 produces H^+ , while eq 1 consumes that species. By examining the pH and potential traces of Figures 2 and 3 and considering the changes in turbidity that occur in the reactor, we may draw some tentative conclusions. It appears that in SSI, where the potential and pH are high and the solution clear, the chemistry is dominated by eq 2. In SSII, where turbidity appears, eq 1 characterizes the principal stoichiometry. Similarly in the oscillatory state, the turbid, low-pH period following the Pt potential peak is described by eq 1, while eq 2 gives the major stoichiometry during the clear basic portion of the oscillation.

The flow of 0.001 M sulfuric acid is essential for the oscillations. The system will not oscillate in the presence of a buffer. Hydrogen ion appears to be a key species in this reaction and may provide a source of autocatalysis. If reaction 1 is followed by the process



and if (1) is rate determining, then the net reaction 1 + reaction 3 has the stoichiometry of the overall process 2 and is autocatalytic in H^+ while allowing for the destruction of the colloidal sulfur.

(11) The sulfide electrode responds specifically to $[S^{2-}]$ only above pH 12.

(12) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering, e.g., III \rightarrow 3 and 13.)

Dissection of these processes into elementary steps is a goal currently being pursued in this laboratory.

While many questions, including the importance of heterogeneous processes, remain, the $S^{2-}-H_2O_2$ system offers considerable promise for advancing our knowledge of chemical oscillation and related phenomena. By introducing the sulfide in a slow, controlled manner, perhaps through an organic sulfur compound, it should prove possible to produce a batch oscillator of this type. Given the possibility of visualizing the oscillations by the addition of

acid-base indicators, such a system would be an outstanding candidate for the study of wave propagation and spatial structures.

Acknowledgment. We thank Mohamed Alamgir and Kenneth Kustin for helpful discussions. This work was made possible by NSF Grant CHE8204085 and by a U.S.-Hungarian Cooperative grant from the National Science Foundation (INT 8217658) and the Hungarian Academy of Sciences.

Registry No. S^{2-} , 18496-25-8; H_2O_2 , 7722-84-1.

Geometric Structure and Pseudorotational Potential of Pyrrolidine. An ab Initio and Electron Diffraction Study

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Abstract: The geometric structure of pyrrolidine was studied by ab initio gradient techniques and gas electron diffraction. According to both methods, the envelope conformation with the N out of plane and the imino hydrogen in the axial direction is the lowest in energy. The calculation of the energy profile for pseudorotation results in a second energy minimum for the envelope conformer with equatorial position of the amino hydrogen. The energy difference between these two conformers is predicted to be about 1 kcal/mol and the barrier to pseudorotation to be 1.66 kcal/mol. The following skeletal geometric parameters were obtained from the electron diffraction study (r_a values): C-N = 1.469 (10) Å, C-C = 1.543 (8) Å, \angle CNC = 105.2 (35)°, flap angle of CNC plane $\alpha = 39.0$ (14)°. This corresponds to a puckering coordinate $q = 0.38$ (2) Å. These values agree very well with the ab initio calculations. Attempts to combine electron diffraction and microwave data had to be abandoned because of a low-frequency, large-amplitude puckering vibration (65 cm^{-1}).

The structures, conformations, and dynamic behavior of saturated five-membered rings have attracted much interest from experimentalists and theoreticians for several decades.²⁻⁴ While the geometric structures of cyclopentane, tetrahydrofuran, and several substituted derivatives have been studied by theoretical and experimental methods, no complete structure determination for the isoelectronic pyrrolidine (PY) or any substituted derivative has been reported so far. The structure of PY, however, is of great interest, since this nitrogen heterocycle is a basic building block of amino acids and peptides. In a structure determination of PY, a large number of possible conformations which occur along the pseudorotational path have to be considered. If pseudorotation is described by a phase angle φ , ten envelope conformations ($E \pm n$) and ten twist conformations (Tm) occur along a full circle (Figure 1). n indicates the atom, which is above (+) or below (-) the plane of the four other ring atoms. m is the atom on the twist axis. Only six envelope conformations ($E + 1$, $E - 5$, $E + 4$, $E - 3$, $E + 2$, and $E - 1$), and five twist conformations, however, are different from each other.

Thermodynamic studies of PY^{5-7} indicate a puckered five-membered ring with free or almost free pseudorotation. McCullough⁷ derived a barrier of 300 cal/mol. From calculations of strain energies, Pitzer and Donath⁸ obtained a barrier of 1.3 kcal/mol, where the twist conformer (T1) is predicted to be the

most stable one. Vibrational spectroscopy leads to controversial conclusions. Baldock and Katritzky⁹ assume a mixture of various conformers of similar energy and Krueger and Jan¹⁰ interpret the vibrational spectra in terms of a mixture of two twist conformers. Khoan et al.¹¹ demonstrate that the vibrational frequencies are not sensitive toward axial or equatorial position of the amino hydrogen ($E + 1$ or $E - 1$). The most recent vibrational study including FIR spectra in the gas phase and matrix spectra was performed by Schrem.¹² 1H NMR,¹³ ^{13}C NMR,¹⁴ and ^{15}N NMR studies¹⁴ give no answer with respect to conformation. Rademacher and Koopmann¹⁵ interpret electron diffraction intensities in terms of a mixture of various conformers. This interpretation is based on force field (CECAL) and semiempirical (MINDO/2) calculations which show very small energy differences between various conformers. A recent microwave study¹⁶ of the parent and N-deuterated species demonstrates that the rotational constants are compatible only with an envelope conformation with the nitrogen atom out of the plane containing the carbon atoms and with the amino hydrogen in axial position. Analysis of vibrationally excited states indicates a relatively high barrier to pseudorotation. The aim of the present study is the determination of the conformation and geometric structure of pyrrolidine by gas

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