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Gas Production in the Bromate−Pyrocatechol Oscillator

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A significant amount of gas production has been observed in the bromate−pyrocatechol oscillator under high concentrations of bromate and pyrocatechol. The observation is in contrast to the general perception that aromatic compounds can form bromate-based oscillators that are free of gas bubbles, which is a desired property in investigating pattern formation. Analysis with ^{1}H NMR, ^{13}C NMR, mass spectrometry, and X-ray crystallography illustrate the production of 5-(dibromomethylene)-2(5*H*)-furanone from pyrocatechol, where the loss of one carbon atom from the aromatic ring causes the formation of gas bubbles. Possible mechanisms have been proposed to explain the observed phenomenon.

1. Introduction

The understanding of nonlinear chemical kinetics has been advanced significantly in the past three decades.[1−4] The investigation of oscillatory chemical reactions has also provided significant insights into similar phenomena encountered in physical, biological and other natural systems.[5−12] Simple reaction-diffusion schemes, for example, have remarkably reproduced biological pattern formation in plants and animals, where many different interactions between molecules, between cells, and between tissues are surely involved in the process of development.[13] Arguably, one of the most famous and best-understood chemical oscillators is the Belousov−Zhabotinsky (BZ) reaction, which is the oxidation and bromination of an organic substrate by acidic bromate in the presence of metal catalysts.[2]

When malonic acid is used as the organic substrate, as is often the case in the study of BZ reactions, the system produces CO_2. The formation of gas bubbles interrupts wave propagation in spatially extended media and subsequently causes the undesired transition to complex spatiotemporal behaviors. To address the above drawback, many attempts have been made to modify the classic BZ reaction with different organic substrates. These studies have led to the achievement of spontaneous oscillations in systems where acidic bromate reacts, respectively, with 1,4-cyclohexanedione (CHD), phenol, pyrocatechol, or 4-aminophenol.[14−20] Notably, no gas formation has been reported in those bromate−aromatic compound oscillators, which leads to the general impression that the aromatic ring is robust when reacting with acidic bromate. Therefore, employing aromatic compounds as the substrate is a promising direction in constructing new gas-free chemical oscillators. The absence of gas production, coupled with great photosensitivity, has made the CHD-BZ oscillator a new, attractive model system for the study of nonlinear spatiotemporal dynamics, in which a number of new phenomena have been observed, such as repelling and attracting pulses in capillary tubes and target patterns with anomalous dispersion relationship in a two-dimensional medium.[21−23]

In an attempt to expand the family of gas-free BZ oscillators, we have recently succeeded in achieving spontaneous temporal oscillations and pattern formation in the bromate-pyrocatechol system.[17,18] As a result of our continuous exploration of pattern formation in the ferroin−bromate−pyrocatechol medium, we noticed the appearance of gas bubbles in such a system when initial concentrations of bromate and pyrocatechol were high. This phenomenon motivated us to determine in this report whether the aromatic ring is indeed stable when reacting with acidic bromate and thus always forms gas free chemical oscillators. As illustrated in the following, our investigation shows the decarboxylation of pyrocatechol, resulting in the production of 5-dibromomethylene-2(5*H*)-furanone. To the best of our knowledge, this is the first report on the cleavage of the aromatic ring during an oscillatory reaction.

2. Experimental Section

All reactions were carried out in a thermal-jacketed 50 mL glass beaker (ChemGlass). The reaction temperature was kept constant at 25.0 ± 0.1 °C by a circulating water bath (Thermo NesLab RTE 7). A Teflon cap was placed on top of the reactor to hold the electrodes. The solution level was about 1 cm below the Teflon cap. The reaction solution was stirred with a magnetic stirring bar driven by a magnetic stirrer (Fisher Isotemp). Reactions were monitored with a platinum electrode coupled with a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode (Radiometer Analytical, XR200 and M231Pt-9). All measurements were recorded through a pH/potential meter (Radiometer PHM220) connected to a personal computer through a PowerLab/4SP data logger.

All ^{1}H NMR and ^{13}C NMR measurements were carried out using Bruker Avance 500 and 300 MHz spectrometers, and with the same sample that was used for mass spectrometry studies but dissolved in chloroform-*d* (99.8%) or acetone-d_6 (99.9%), purchased from Cambridge Isotope Laboratories. Stock solutions of $NaBrO_3$ (Aldrich, 99%), 0.6 M, and sulfuric acid (Aldrich, 95−98%), 4.0 M, were prepared with double-distilled water. Ferroin, 0.025 M, was prepared from a calculated amount of $FeSO_4 \cdot 7H_2O$ (Aldrich, 99+%) and 1,10-phenanthroline (Ald-

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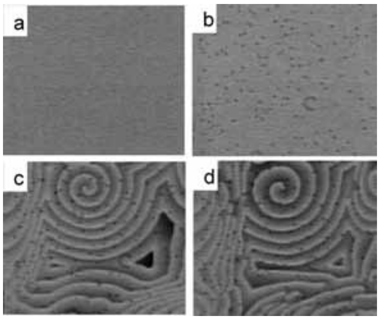


Figure 1. Snapshots of chemical waves in the ferroin-bromate-pyrocatechol reaction. These images were recorded at (a) 12, (b) 52, (c) 96, and (d) 124 min after mixing all reagents together. Reaction conditions are $[BrO_3^-] = 0.12$ M, $[H_2SO_4] = 1.1$ M, [ferroin] = 3×10^{-3} M, and [pyrocatechol] = 0.091 M. Dark and light color represents high concentrations of ferroin and ferriin, respectively. Gas bubbles, appearing as dark spots, are visible in the last three frames.

rich, 99+%). Pyrocatechol (Sigma, 99%) was directly dissolved in the reaction mixture. The volume of the reaction mixture was fixed at 30.0 mL in all experiments. X-ray crystallographic analysis was conducted on a single crystal covered in Nujol under a dry N_2 coldstream using a Kryoflex low-temperature apparatus on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.710\ 73$ Å); data were collected using the SMART software program.

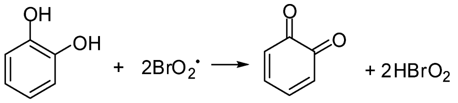
5-(Dibromomethylene)-2(5*H*)-furanone (**1**): IR (KBr) 3100, 1790, 1765, 1547 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (d, $J = 5.6$ Hz, 1H), 6.42 (d, $J = 5.6$ Hz, 1H); ^{13}C ($CDCl_3$) 167.8, 150.8, 140.7, 122.4, 81.9; MS (EI, 20 eV) 256/254/252 (M^+).

3. Results and Discussion

Figure 1 presents four snapshots showing the appearance of gas bubbles in the studied system. Here, reaction conditions are $[BrO_3^-] = 0.12$ M, $[H_2SO_4] = 1.1$ M, [ferroin] = 3×10^{-3} M, and [pyrocatechol] = 0.091 M. The reaction solution was held between two microscope slides to form a 0.5 mm thick solution layer. This configuration allows the gases produced in the reaction process to get trapped and aggregated to form bubbles with a visible size. While pattern formation has been achieved over broad reaction conditions as discussed in the earlier report, bubbles in the above reaction-diffusion medium appeared only when the initial concentrations of bromate and pyrocatechol were high. Another noticeable phenomenon is that under those conditions the reaction system produced a moderate amount of precipitate in a stirred batch reactor. The formation of precipitate offers us a way to decipher the source of gas production. To understand the reaction in a simplified environment, the experiment was repeated under otherwise identical conditions, but without ferroin present. Similarly, a precipitate (20−55 mg) was formed under these conditions.

The spectral data of this precipitate (**1**) were striking. The ^1H NMR spectrum ($CDCl_3$) possessed two doublets (at δ 7.68 and δ 6.42), each with a conspicuously small coupling constant ($J = 5.6$ Hz), ruling out both *o*-quinone and *o*-diprotiobenzenoid structures (Figure 2). The ^{13}C NMR spectrum displayed resonances at 167.8, 150.8, 140.7, 122.4, and 81.9, the former resonance being indicative of a carboxylic acid derivative and the latter resonance being exceptionally upfield for an sp^2 hybridized center (Figure 3). The infrared spectrum (KBr) supported the presence of the carbonyl function, by virtue of the two C═O stretching frequencies at 1791 and 1765 cm^{-1}. The EI mass spectrum (20 eV) gave a number of ions at 252−256, indicative of dibromination. Recrystallization of the precipitate from diethyl ether gave crystals suitable for X-ray crystallographic analysis, which showed **1** to be the known compound 5-(dibromomethylene)-2(5*H*)-furanone[24] (Figure 4). Compound **1** is striking in that it is both extensively rearranged from catechol and possessing one less carbon atom. While the 20−55 mg amounts of precipitated **1** correspond to 2−5% yield based on catechol, ^1H NMR spectroscopy of the diethyl ether extract of the aqueous filtrate demonstrated that a significant amount of **1** remained in solution. Finally, the ^1H NMR spectrum of the $CDCl_3$ solution of the precipitate in the ferroin containing reaction was identical to the that of the precipitate in the nonferroin containing reaction, although temporal series of the uncatalyzed and ferroin-catalyzed systems are quite different.[17,18] This confirms the formation of 5-(dibromomethylene)-2(5*H*)-furanone in both catalyzed and uncatalyzed systems.

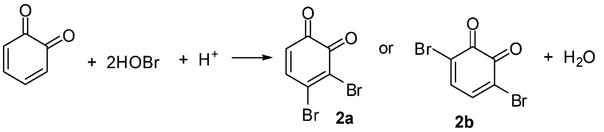
The most plausible mechanism for the formation of **1** from catechol involves initial oxidation to the *o*-quinone. The oxidation process is expected to involve bromine dioxide radicals, which forms an autocatalytic nonlinear feedback (processes 1 and 2), a key dynamic condition for constructing chemical oscillators.



(1)

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2BrO_2^\bullet + H_2O \qquad (2)$$

The *o*-quinone may then react with HOBr, a well-known intermediate in bromate-based oscillatory reactions, to produce **2a** or, more likely, **2b**, through process 3.



2a **2b** (3)

Further oxidation to the dicarboxylic acid by a Baeyer−Villiger-like process to give a dicarboxylic acid (**3a** or **3b**) and subsequent Michael-type addition−elimination of either of these intermediates would afford furanone-carboxylic acid **4** (Scheme 1, eqs 4 and 4a). The catechol to dicarboxylic acid to furanone-carboxylic acid transformation under oxidative conditions has several precedents.[25] It is based on these precedents that oxidation prior to bromination is proposed, as initial electrophilic bromination of the catechol would be expected to result in bromine incorporation on the furanone ring. Finally, under the oxidative conditions present, the most likely source of the conversion of **4** to **1** involves a radical halogenative decarboxylation via an acyl hypobromite (**5**, eq 5), often referred to as a Hunsdiecker reaction.[26] The last process leads to the formation of gas bubbles.

4. Conclusions

This research shows the formation of gases in the ferroin−bromate−pyrocatechol reaction and illustrates that the aromatic ring is broken in the reaction process. Such a result is in contrast to the general perception that the aromatic ring is stable in acidic bromate solution and thus suitable for developing bubble free chemical oscillators. In contrast to the malonic acid-BZ reaction, in which gases are produced even under mild reaction condi-

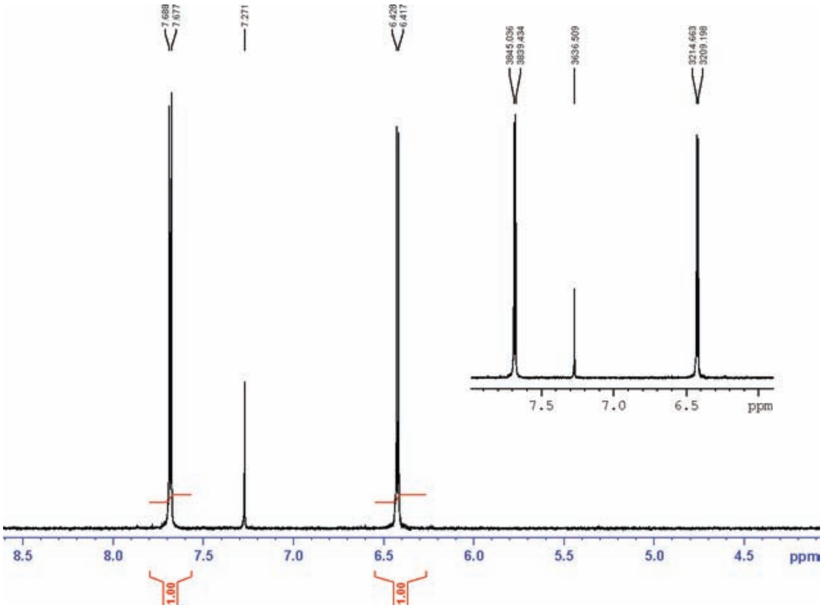


Figure 2. ^{1}H NMR spectrum of **1** ($CDCl_3$, 500 MHz).

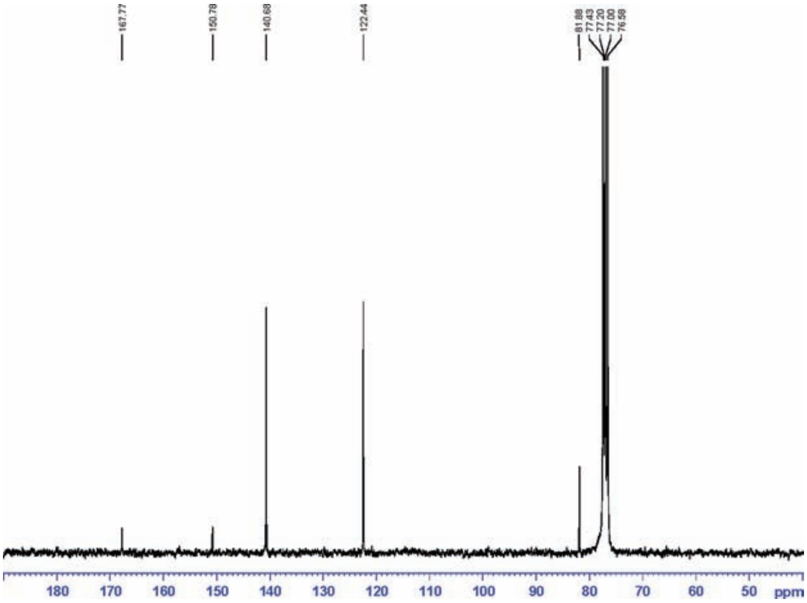


Figure 3. ^{13}C NMR spectrum of **1** ($CDCl_3$, 75 MHz).

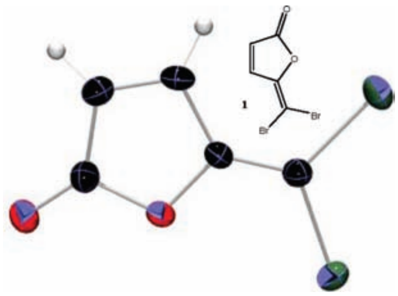
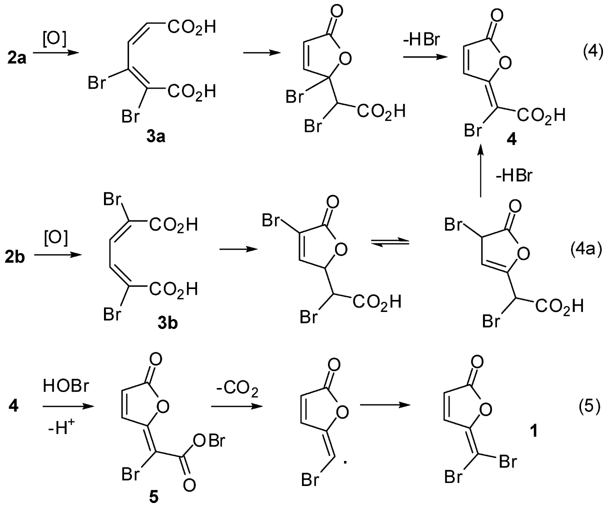


Figure 4. ORTEP 3 representation of X-ray crystallographic structure of the precipitate. The precipitate was prepared under the conditions $[BrO_3^-] = 0.20$ M, $[H_2SO_4] = 1.4$ M, and [pyrocatechol] = 0.12 M.

tions, a significant amount of gas production can only be obtained when the concentrations of bromate and pyrocatechol are high. This may explain why no gas bubble formation has been reported in bromate-aromatic compounds reactions. Nevertheless, the cleavage of the aromatic ring is confirmed here

SCHEME 1: Proposed Mechanism of Formation of 5-(Dibromomethylene)-2(5*H*)-furanone (1)



through the characterization of the precipitate, which becomes visible several hours after the start of the reaction. The result presented in Figure 1 shows that the cleavage of benzene ring commences at an early stage of the reaction. Our experiments also confirm that there is a significant amount of **1** in solution.

While the underlying mechanism of the oscillatory phenomenon remains to be understood, our analytical measurements suggest that an intermediate dibromoquinone is involved, which leads to a final product of 5-(dibromomethylene)-2(5*H*)-furanone. The above result is significant in future study of bromate-based oscillators, including the bromate-phenol and the popular bromate-CHD systems. Given that the bromate-phenol oscillator is known to produce both catechol and *o*-benzoquinone,[27] and that the CHD-BZ oscillator also produces dibromoquinones as intermediates, gas bubbles could be formed in these systems as well. The study of whether such gas evolution or 5-(dibromomethylene)-2(5*H*)-furanone formation occurs in these systems is in progress, and will be reported in due course.

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Supporting Information Available: The crystal structural data for **1**, including structural refinement details, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and torsional angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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