

## A: Kinetics, Dynamics, Photochemistry, and Excited States

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# Unusual Chemistry in an Uncatalyzed Bromate-Aniline Oscillator: Ring-Contraction Oxidation of Aniline with Pulsative CO<sub>2</sub> Production

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#### Abstract

The bromate-aniline oscillatory reaction was discovered four decades ago, but neither the detailed mechanism, nor the key products or intermediates of the reaction were described. We report herein a detailed study of this reaction which yielded new insights. We found that oscillatory oxidation of aniline by acidic bromate proceeds, to a significant extent, via a novel reaction pathway with the periodic release of carbon dioxide. Several products were isolated and their structures, not described so far, were justified on the basis of MS and NMR. One of the main products of the reaction associated with the  $CO_2$  release route can be assigned to 2,2-dibromo-5-(phenylimino)cyclopent-3en-1-one. A number of known compounds produced in the studied reaction, including unexpected brominated 1-phenylpyrroles and 1-phenylmaleimides, were identified by comparison with standards. A mechanism is suggested to explain the appearance of the detected compounds, based on coupling of the anilino radical with the produced 1,4-benzoquinone. We assume that the radical adduct reacts with bromine to form a cyclopropanone intermediate which undergoes a Favorskii-type rearrangement. Further oxidation and bromination steps including decarboxylation lead to the found brominated phenyliminocyclopentenones. The detected derivatives of 1-phenylpyrrole could be produced by a one-electron oxidation of a proposed intermediate 2-phenylamino-5-bromocyclopenta-1,3-dien-1-ol followed by  $\beta$ -scission with the abstraction of carbon monoxide. Such a mechanism is known from the combustion chemistry of cyclopentadiene. The proposed mechanism of this reaction provides a framework for understanding the observed oscillatory kinetics.

# 1 Introduction

Oxidations of aniline are typically complex processes exhibiting extraordinarily rich chemistry. Depending on the oxidant and reaction conditions, the oxidation of aniline leads to a variety of products including 4-aminophenol, phenylhydroxylamine, nitrosobenzene, nitrobenzene, 1,4-benzoquinone, benzidine, 4-aminophenyl(phenylamine), azobenzene, azoxy-

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benzene,<sup>1</sup> oligomeric substances such as emeraldine and nigraniline,<sup>2,3</sup> and polyaniline.<sup>4,5</sup> The Boyland-Sims oxidation of aniline<sup>6</sup> produces 2-aminophenylsulfate and a polymeric material different from polyaniline, classified as a synthetic humic acid.<sup>7</sup> Oxidations of aniline are often complicated by the conjugation reactions of the parent aniline with its oxidation products such as quinones and quinone imines.<sup>8,9</sup> The mechanisms of oxidation and condensation/polymerization processes of aniline are still not fully understood, and current research is motivated mainly by the technological applications concerning the development of dyes<sup>10</sup> and conducting polymers.<sup>11,12</sup> As aniline and its derivatives are hazardous pollutants, searching for effective detoxification procedures based on oxidation strategies is also an active research field.<sup>13-16</sup>

An interesting example of the oxidation of aniline represents its reaction with bromate in aqueous sulfuric acid. Under the appropriate conditions, the reaction shows regular oscillations in the concentration of certain intermediates, monitored as temporal changes in the redox potential.<sup>17</sup> By varying the reaction conditions, more complex dynamic behavior with two separated oscillatory sequences can be observed.<sup>18</sup> Also, spatio-temporal structures in such a system have been reported.<sup>19</sup> The bromate-aniline oscillating reaction is a member of the uncatalyzed bromate oscillators (UBOs) family, derived from the classical Belousov-Zhabotinsky (BZ) reaction.<sup>20</sup> The class of UBOs differs from the original BZ reaction in the absence of metal catalyst and in nature of the substrate. The UBO substrates are oxidable organic compounds, such as derivatives of phenol or aniline<sup>17</sup> or their precursors, e.g. cyclohexane-1,4-dione.<sup>21,22</sup> The BZ system in both standard and modified versions has served for decades as an experimental and theoretical model in the study of nonlinear phenomena such as chemical oscillations, chaos, and traveling waves.<sup>23</sup> In particular, the UBOs and catalyzed BZ reactions with aromatic substrates remain in the focus of current research in the field of nonlinear dynamics  $^{24-30}$  as their mechanisms are still generally not known. Such research could open new insights into the oxidation pathways of organic substrates, help to clarify the role of free radicals in such reactions, and explore interactions between the organic and inorganic counterparts of oscillators from both the chemical and nonlinear dynamics points of view.

In the present work, we report the results of investigation into the sequential bromateaniline oscillator under the conditions described by Adamčíková and Ševčík.<sup>18</sup> Analysis of the reaction solution during the progress of the reaction has revealed a surprising conversion of aniline to compounds with proposed structures that cannot be found among the species already described in the literature. Such conversion is accompanied by contraction of the 6-carbon ring with the release of  $CO_2$  in a course that follows the oscillatory regime of the reaction. Although periodic  $CO_2$  and CO production is typical for the classical BZ systems,<sup>31,32</sup>  $CO_2$  oscillations have not yet been reported for a UBO. We suggest mechanisms that may account for the observed chemistry and discuss the nonlinear dynamic behavior of the system.

## 2 Experimental section

Oscillating reactions were performed using sodium bromate (puriss, p.a., Fluka), 95-97 %  $H_2SO_4$  (p.a., Merck), and distilled aniline (p.a., Merck). The standards used for the GC/MS analysis were either purchased from the suppliers or synthesized as described below.

The oscillatory kinetics were recorded potentiometrically using a pinhead Pt-electrode (0.5 mm diameter) and an Ag/AgBr electrode against a reference mercurosulphate electrode  $(1.2 \text{ M H}_2\text{SO}_4)$ . Alternatively, a saturated calomel electrode connected via a salt bridge was used as a reference electrode. The Ag/AgBr electrode was prepared from a silver wire (0.5 mm diameter) by a short dipping into liquid bromine. Usually, 20 mL of reaction solution was continuously stirred at 400 – 600 rpm in a 50 mL thermostated vessel (Figure S1).

The UV/vis spectrophotometry, separately or combined with the potentiometry, was also employed to monitor the reaction kinetics. For that purpose, the reaction was carried in a 1 cm quartz cell with continuous stirring, typically at 600 rpm, and UV/vis spectra were scanned every second on an Agilent 8453 diode-array spectrophotometer. To record spectra in a cell with a reduced optical path, the reaction was run in a stirred batch reactor filled with 150 mL of the reaction solution (Figure S2). The bulk reaction solution was driven by a peristaltic pump into a 1 mm-flow quartz cell with a flow rate of about 1.4 mL/min. This value was limited by the inlet to the flow cell through a microloader tip. The outflow from the cell was wasted into a container with a KCl solution, where a reference electrode was immersed. UV/vis spectra of the reaction solution in the cell were scanned every 5 s by the diode-array spectrophotometer. Simultaneously with the spectra, the potentials of Pt-electrodes in the batch reactor and the flow cell were recorded against the reference electrode.

The CO<sub>2</sub> measurements were performed using the experimental setup as previously described.<sup>33</sup> In brief, the reaction was run in a thermostated vessel (the reaction solution volume was 4 mL) with magnetic stirring. CO<sub>2</sub> was purged out from the reactor vessel by a carrier gas (high-purity N2, 40 mL/min) and then mixed with hydrogen. Afterward, CO<sub>2</sub> was converted to methane by means of a Ni catalyst operating at 400 °C and the CH<sub>4</sub> quantity was continuously determined with a flame ionization detector (FID).

The GC/MS or GC/HRMS analysis of the reaction intermediates and products was carried out in extracts from the reaction solution and in the precipitate formed during the reaction course. Typically, two extracts from different reaction time intervals were sampled for a particular analysis. To this end, the reaction was run in a 250 mL glass Erlenmeyer flask (the reaction solution volume was 200 mL) with magnetic stirring. For the first extract, after a given time from the start of the reaction, 100 mL of the reaction solution was replaced into a 200 mL glass Erlenmeyer flask and either directly extracted with 10 mL of distilled CHCl<sub>3</sub> or alkalized before the extraction. The alkalization was performed by a stepwise addition of a calculated amount of solid NaOH into the reaction solution that was continuously stirred and kept cooled in an ice bath. The extraction was carried by a vigorous shaking on a laboratory shaker for various time periods from 5 to 40 min. Finally, the bottom organic phase was separated and analyzed by the GC/MS. The second extract was obtained similarly from the rest 100 mL of the reaction solution in the 250 mL flask after an additional specified reaction time had elapsed. For the analysis of the reaction precipitate, this was filtered from the reaction solution, washed by water, then dried and dissolved in CHCl<sub>3</sub>.

In order to isolate reaction intermediates or products, 520 - 1500 mL of the reaction solution was extracted at a specific reaction time by 50 - 100 mL CHCl<sub>3</sub> for 10 - 20 min. The water phase was separated and extracted again with the same amount of CHCl<sub>3</sub>. The solvent was evaporated from the collected organic phase in the presence of a 65/40 silicagel (Merck) and the residue was eluated by a mixture of hexanes and ethylacetate 7:1 on a column filled with the same silicagel. This way several substances were separated in a sufficient purity proven by the GC/MS analysis.

The GC/MS measurements were performed on an Agilent Technologies 6890N gas chromatograph with a 5973 Network mass-selective detector (Agilent, Palo Alto, CA, USA). The 1 µL of sample injection operated at the temperature of 280 °C in the splitless injection mode with a purge time of 2 min. The oscillation reaction products were separated using capillary column 30 m  $\times$  0.25 mm i.d. coated with a film thickness of 0.25 µm of (5 %-phenyl)-methylpolysiloxane HP-5 as stationary phase (Agilent, CA, USA). The column temperature was 50 °C initially, then the temperature was increased to 300 °C at the ramp rate of 15 °C min<sup>-1</sup>. The temperature was held at the final value of 300 °C for 5 min. Helium carrier gas with constant flow of 1.5 mL min<sup>-1</sup> was used. The transfer line temperature was set at 300 °C. Quadrupole conditions were as follows: electron energy 70 eV, and ion source temperature 230 °C. Mass spectral data were obtained by the Full Scan mode in the range 45 - 600 m/z.

The GC/HRMS recordings were performed with a Pegasus<sup>®</sup> GC-HRT high-resolution time-of-flight (TOF) mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) with a Folded Flight Path<sup>®</sup> multiple reflecting geometry mass analyzer coupled with an Agilent 7890A gas chromatograph (Agilent, Palo Alto, CA, USA). The instrument is capable of acquiring high-resolution (up to 50,000 at FWHH in ultra-high-resolution mode) and highmass-accuracy (~1 ppm) data at a very high acquisition rate (up to 200 full mass range spectra per second). The system was controlled by ChromaTOF-HRT<sup>®</sup> software version 1.90 (LECO Corporation), which was also used for data collection and data processing. The data were collected using 8 full spectra (45 - 600 m/z range) per second in the highresolution mode (25,000 at FWHH). The electron ionization source was kept at 250 °C. Chromatographic separation was performed using an Rxi<sup>®</sup>-5Sil MS column (30 m length, 0.25 mm internal diameter, phase thickness 0.25 µm) with the carrier gas helium at the constant flow of 1.2 mL min<sup>-1</sup>. The column temperature was programmed as follows: 50 °C (1 min), 20 °C min<sup>-1</sup> to 300 °C. The transfer line temperature was 300 °C. 1 µL of sample was introduced into the injector heated at 280 °C at a split ratio of 20:1.

The NMR spectra of some isolated intermediates/products of the studied reaction were recorded in a 5 mm NMR tube on a Varian VNMRS 600 MHz spectrometer (600 MHz for  $^{1}$ H and 150 MHz for  $^{13}$ C) in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard.

The IR spectra were acquired from KCl pellets on a Shimadzu IRPrestige-21 FTIR spectrometer.

## 3 Results and discussion

## 3.1 General description of the oscillating reaction

A potentiometric record of the oscillatory oxidation of aniline by bromate under the conditions of Adamčíková and Ševčík<sup>18</sup> is shown in Figure 1. Several different phases can be distinguished in the reaction progress. After an induction period, which usually lasts 13-20 min, a first sequence of 8-15 almost sinusoidal oscillations with increasing amplitude follows. The second oscillatory sequence shows a train of 3-9 high amplitude pulses during a period of 8-10 min. The oscillatory sequences are separated by an intermediate period (a mesophase) with a duration of approximately 4-6 min. The intermediate period often shows several low amplitude oscillations. Occasionally, a split of the mesophase into two peaks can be observed (Figure 1b), and the absence of a transition phase was recognized in some experiments that showed a set of continuous oscillations (Figure S3 in Supporting Information).



Figure 1: Time records of (a) Pt-electrode potential and (b) Pt-electrode and Ag/AgBr electrode potentials for the bromate-aniline oscillating reactions at 25 °C. Initial concentrations: 25 mM NaBrO<sub>3</sub>, 2 mM aniline, 1.2 M  $H_2SO_4$ ; reaction volume: 20 mL.

Interestingly, the Pt and Ag/AgBr potentials oscillate in phase during the first sequence, but shortly after the mesophase, the Ag/AgBr signal undergoes a phase shift and the recorded potentials show anti-phase oscillations (Figure 1b).

Disregarding the various types of mesophase, the observed dynamic behavior was usually well reproducible and did not significantly depend on the stirring rate and illumination by daylight. Bubbling of the reaction solution by nitrogen with flow rates up to 400 mL min<sup>-1</sup>, before or during the reaction, showed no considerable effect. Independence of the reaction system from stirring, illumination and the presence of oxygen has been previously reported.<sup>18</sup>

The reaction progress is accompanied by changes in the color of the reaction solution. The initially colorless solution turns pale fuchsia soon after the reaction is started. The color intensity gradually increases to hot magenta at the beginning of the first oscillatory period. However, experiments with a lower initial aniline concentration, and hence a shorter induction period, suggest that the intensity of the violet color is probably not correlated with the onset of oscillations. During the first oscillatory period, the reaction solution turns deep cerise and becomes turbid. The mesophase is represented by a brown color of the reaction solution that turns dark orange during the second oscillatory period with simultaneous production of a dark brown precipitate. Coloring of the reaction solution at 19, 43, and 62 min from the start of the reaction can be seen in Figure S1.

# 3.2 UV/vis spectrophotometry of the reaction

We examined the sequential oscillator under study by recording absorption spectra in intervals of 1-5 s during the reaction progress. It turned out that the oscillatory behavior can be conveniently monitored by recording the absorbance at 427 nm in a stirred cuvette with a 1 cm optical path (Figure S3 in Supporting Information).

To gain data also from the UV region, where aromatic species show high absorptivity, the oscillating reaction was run in a stirred bulk from which the solution was continuously fed into a flow cuvette with a 1 mm optical path (Figure S2). The outflow from the cuvette was wasted, as returning it back to the bulk resulted in quenching of the oscillations. The redox potential both in the bulk and flow cuvette was simultaneously recorded and the spectra were scanned repeatedly. It can be seen (Figure 2a, Figure S4) that the amplitudes of the two oscillatory sequences differ in their spectral characteristics: the first sequence exhibits higher amplitudes for 427 nm while the second one is at 305 nm. Such amplitude properties suggest that the difference spectral analysis could reveal useful information about the oscillating species, as shown below. The oscillations of the absorbance and redox potential measured in the flow cuvette are in phase. However, the oscillatory dynamics of the bulk solution differs from that observed in the flow (Figure 2b). Despite the time (approx. 70 s) required to deliver the reaction solution from the bulk to the flow cuvette, the bulk and

flow oscillations are synchronized very soon after the reaction is started. As the reaction approaches the intermediate period, a small phase shift is developed. Then, the flow subsystem enters the mesophase with temporal suppression of the oscillatory amplitude, while such a transient period is not recognized in the bulk behavior. This observation indicates that the mesophase arises from nonlinear mechanisms, such as coupling between two suboscillators,<sup>28</sup> rather than from an essentially altered chemistry in the sequentially and continuously oscillating systems. It has been demonstrated<sup>34</sup> that BZ systems with mixed substrates exhibit sequential oscillations showing both an intermediate period with damped oscillations and a fluent transition to the next oscillatory sequence.



Figure 2: Time records of (a) absorbance for 305 and 427 nm in the flow cuvette (optical path 1 mm) and (b) Pt-electrode potential in the flow cuvette and the bulk reactor for the bromate-aniline oscillator. Conditions as for Figure 1; initial reaction volume: 150 mL. The arrows point to the onset of single pulses selected for the difference spectral analysis (see Figure 3).

Changes in UV/vis spectra in the course of the reaction occur in several regions. During the induction period absorbance from 213 nm to 360 nm monotonically rises and a broad band, 470-700 nm, with a maximum at 540 nm is developed. The onset of the oscillatory activity is associated with the formation of a 240-260 nm band. The 470-700 nm band increases further until the end of the first oscillatory period. The most articulated oscillations in absorbance can be observed for wavelengths 254, 305, and 427 nm with significant oscillatory activity in the whole subregion of 370-470 nm. At the end of the first oscillatory period, a maximum at 218 nm is formed. During the mesophase, the 240-260 nm band continues rising and develops a maximum at 245 nm, while the 470-700 nm band transforms to a shoulder around 500 nm. The second oscillatory phase shows no significant global changes in the observed spectra, merely a small increase of the 240-260 nm band and a small decrease in the 470-700 nm band. The oscillatory activity is observed in the subregions of 280-340 nm and 370-470 nm. When the oscillations cease, the UV/vis spectrum of the reaction solution remains almost unaltered in the whole spectral width of 190-900 nm.

A difference analysis of amplitudes for the selected pulses revealed three main spectral bands (Figure 3) with the maxima at 254, 305, and 427 nm. The difference spectra in Figure 3 were calculated as  $\Delta A = A(t) - A(t_{min})$ , where t is a selected time during a single pulse (usually the time of a maximum in the absorbance) and  $A(t_{min})$  is the absorbance at the minimum of the pulse. As the relative portion of the bands varies for the difference spectra taken from diverse oscillations, it can be deduced that the bands correspond to three different substances.

The spectral band with a maximum at 254 nm compares quite well with the UV spectrum of 1,4-benzoquinone, taking into account that the band extracted from the oscillatory reaction is somewhat wider, probably due to contamination with other species absorbing below 254 nm (aniline and bromoanilines) as well as above this wavelength. On closer inspection, one more band can be detected, overlaid by the peak at 254 nm. As the absorption for 254 nm does not show true oscillations, but accumulates in a stepwise manner, it can be eliminated by sampling the difference spectra from the descending part of the examined pulse. Such an approach reveals a small band centered at 265 nm. If the 265 nm band is subtracted from the 254 nm band, excellent agreement is obtained with the 1,4-benzoquinone



Figure 3: Difference absorbances vs. wavelength plots for amplitudes of the selected oscillations from the experiment shown in Figure 2. The times of the absorbance sampling are given as subscripts in seconds (see also arrows in Figure 2a). The details are explained in the main text and in Supporting Information (Figure S5).

absorption band with a maximum at 246 nm (Figure S5b).

The small band with a maximum at 265 nm is most likely due to the tribromide anion, which shows an absorption maximum at 266 nm.<sup>35</sup> Although the extracted band is narrower than the  $Br_3^-$  band measured in 1.2 M H<sub>2</sub>SO<sub>4</sub> (Figure S5b), such a discrepancy can be ascribed to a negative contribution from the overlapping 305 nm band (see Figure S5c).

The bands at 305 and 427 nm seem to be attributable to the anilino radical and the aniline radical cation, respectively, but such assignment has the following drawbacks: (1) the  $pK_A$  value for the equilibrium between the acidic and basic forms of this radical is 7.05,<sup>36</sup> so the unprotonated anilino radical should not show detectable absorbance in a solution of 1.2 M sulfuric acid; (2) both the conjugate pairs should preserve the ratio given by the rapid acid-base equilibrium and hence should not behave as independent substances; (3) the absorption band reported for the aniline radical cation has two well-defined maxima at 406 and 423 nm,<sup>36</sup> but we did not find the maximum at 406 nm; (4) the shape of the band of aniline radical cation differs from that shown in Figure 3.

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Rastogi and Srivastava<sup>37</sup> observed the transient appearance of a rather broad band at 310 nm in a similar bromate-aniline oscillating system. The intensity of the band increased in an oscillatory manner in phase with the redox potential oscillations, then decreased and finally disappeared. The authors discussed ascribing the band to the anilino radical and the redox oscillations to the pair  $PhNH_2/PhNH^{\bullet}$ .

An alternative option to rationalize the 427 nm band is its attribution to 1,2benzoquinone. An aqueous solution of this substance shows an absorption maximum at 389 nm (ref.<sup>38</sup>), which is, however, a substantially lower than the observed value. In addition, comparison of the shapes of the examined spectral bands (Figure S5b) demonstrates a difference. Considering that the 427 nm band is little contaminated by other light-absorbing species, the attribution to 1,2-benzoquinone is unlikely.

Another explanation for the presence of the band with a maximum at 427 nm in our observations provides the possible production of bromine in the studied system. It is well known that  $Br_2$  is formed in BZ reactions, but substrates such as phenol and aniline are easily brominable and hence no  $Br_2$  can accumulate in UBOs of this type.<sup>39</sup> A calculation using a known value<sup>40</sup> for the molar absorptivity coefficient of  $Br_2$  at 390 nm (173 M<sup>-1</sup> cm<sup>-1</sup>) predicts that 87 % of aniline should be converted to produce the assumed stoichiometric amount of  $Br_2$  within a single pulse. This is undoubtedly not realistic. Moreover, the bromine band with a maximum at 394 nm in 1.2 M H<sub>2</sub>SO<sub>4</sub> (Figure S5b) is significantly broader than the 427 nm band in Figure 3. As discussed below, we incline to the interpretation that the oscillating activity in this spectral region can be ascribed to a semiguinone radical.

## 3.3 $CO_2$ production in the reaction

Our preliminary results<sup>41</sup> reporting on the identification of brominated N-phenylpyrrole in the aniline UBO pointed to a possible opening of the 6-carbon ring during the oxidation of aniline by bromate. Also, the Wang group has shown clear evidence of the production of a brominated protoanemonin, 5-(dibromomethylene)-2(5H)-furanone, in a BZ oscillator with pyrocatechol both in catalyzed and uncatalyzed systems.<sup>24</sup> Such observations cast doubt<sup>24–26</sup> on the previous perception that UBOs represent gas-free systems. We examined the studied reaction for the possibility of  $CO_2/CO$  production (see Experimental section for the methodology) and found pulsative evolution of  $CO_2$  that follows the oscillatory dynamics described above. Figure 4 illustrates a typical experiment with the two oscillatory sequences and the mesophase.



Figure 4: Oscillatory evolution of  $CO_2$  from the bromate-aniline reaction. Conditions as for Figure 1; reaction volume: 4 mL. Inset: zoomed-in view of the initial spike in the  $CO_2$  production.

Interestingly, the system shows an initial large spike in  $CO_2$  production (Figure 4, inset) with an oscillatory pattern. After 1 minute,  $CO_2$  production is suppressed and the system enters the induction period. The initial burst of  $CO_2$  appears under Orbán-Kőrös conditions;<sup>17</sup> moreover, a reproducible oscillatory pattern of the spike can also be resolved (Figure S6).

During the followed time period of the reaction (0 - 3075 s) in Figure 4, 1.5 µmol of CO<sub>2</sub> was produced. This amount represents approximately 19 molar % of the amount of aniline initially present in the reaction. No detectable production of carbon monoxide was found in

the studied system.

## 3.4 GC/MS analysis of the reaction intermediates/products

In order to uncover the chemistry underlying the observed oscillatory behavior, we tried to analyze the reaction solution and the produced precipitate using several techniques. Gas chromatography combined with mass spectrometry (GC/MS) was the most fruitful approach. We analyzed extracts of the oscillating reaction mixture in chloroform sampled at various periods of the reaction progress. The extracts were obtained either directly from the reaction solution or the reaction solution was alkalized by addition of solid NaOH before the extraction. Representative GC records are shown in Figure 5. The picture appeared to be somewhat more complex than we expected. Besides the anticipated substances that have been already corroborated in the bromate-aniline oscillator,<sup>42</sup> such as 1,4-benzoquinone (**BQ**) with its brominated derivatives (**BQBr**, **BQBr**<sub>2</sub>) and the bromoanilines (*o*,*p*-**ANBr**, **ANBr**<sub>2</sub>, **ANBr**<sub>3</sub>), a series of unknown compounds (**U1–U6**) was found. Also, small peaks assigned to species, which are interesting from the mechanistic point of view (**S1–S4**), are selected in Figure 5. The obtained mass spectra of **U1–U6** suggest that this series may be treated as derivatives of **U1** with various extent of bromination and their isomers (all the mass spectra are included in Supporting Information).

The substance **U1** is formed very soon after mixing the reactants and it can be detected, even with traces of **U2**, in the initial GC record (Figure 5, red line). Approximately at the time when the first oscillatory sequence begins, **U1** represents the most dominant peak in the GC records of extracts (Figure S7). Later on, **U2** takes over dominance, but **U1** remains in a steady state for at least 10 minutes. During the second oscillatory sequence, the concentration of **U1** decreases, while **U2** preserves a steady state level. The dominant abundance of **U2** was observed also in the precipitate (Figure S8). Handlířová,<sup>42</sup> using thin layer chromatography, reported the occurrence of a dimer or a higher condensation product of aniline (the precise composition was not determined) in the final reaction phase of the





Figure 5: Gas chromatograms of samples extracted from the bromate-aniline oscillating reaction solution at various stages: the reaction was stopped after the start by the addition of NaOH (red line); the reaction was stopped after the first oscillatory sequence by the addition of NaOH (magenta line); the reaction solution after the first oscillatory sequence was directly extracted for 15 mins (green line). The labels 'AN' and 'BQ' denote aniline and 1,4-benzoquinone, respectively; others are explained in the text.

bromate-aniline oscillator. This product could be attributed to U2.

The mass spectrum of **U1** (page S44 in Supporting Information) shows a molecular ion with a mass of 249/251, and it can be deduced that one atom of bromine is present. The base mass ion of 170 can be interpreted as a fragment that lost the Br atom. Subsequently, it loses a small fragment of 28 to form an ion with a mass of 142. The ions 51 and 77 suggest the presence of an unsubstituted benzene ring. It took us quite a long time to propose a reasonable structure for **U1**. An initial hypothesis assumed a Schiff base type conjugate of cyclohexen one with aniline  $^{41}$  which might be further oxidized to release  $\mathrm{CO}_2$  and brominated to produce 1,2,3,4-tetrabromo-N-phenylpyrrole (NPPBr<sub>4</sub>). NPPBr<sub>4</sub> was reliably identified earlier in our experiments.<sup>41</sup> Such a Schiff base was prepared in the unbrominated form and its fragmentation pattern fitted well in series with the monobrominated **U1** and dibrominated **U2.** However, we were not able to suggest a plausible mechanism for the formation of such a compound in the bromate-aniline reaction. A possible explanation had emerged after reconsideration of the proposed structure for U1. The fragment 28 leaving the ion 170, originally interpreted as a  $-CH_2-CH_2$  moiety from cyclohexene, can be replaced by carbonyl -CO- and the ring reinterpreted as cyclopentenone. This hypothesis suggests that  $\mathrm{CO}_2$  is released in a reaction step before the formation of  $\mathbf{U1}$ , consistent with the observed initial burst of  $CO_2$  (Figure 4). The proposed structures of the selected substances found in the GC/MS record in Figure 5 are shown in Chart 1.



Chart 1: Proposed structures of the selected substances found in the bromate-aniline oscillator.

The mass detected for U1 by the high resolution mass spectrometry, 170.0600, conforms to the calculated value of 170.06059 for the proposed molecule. However, a number of attempts to synthesize a compound with the proposed structure for U1 or U2 and to use it as a reference failed. Fortunately, the substances U2, U3a, and U5 were isolated from the reaction solution and characterized by GC/HRMS, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR, and UV/vis spectra. All the data obtained for the isolated compounds, available in Supporting Information, are consistent with the proposed structures (Chart 1). Thus, one of the main products of the bromate-aniline oscillator, substance U2, can be identified as 2,2-dibromo-5-(phenylimino)cyclopent-3-en-1-one. Substances **U3b** and **U4** (Figure 5, not shown in Chart 1) are suggested to be 2-bromophenylimino and 4-bromophenylimino analogues of U2, respectively, and substance U6 is most probably a 4-bromophenylimino analogue of U3a. An isomeric structure of U6 has been suggested for a substance reported by Ma et al. (6c' in ref.<sup>43</sup>): 3,5,5-tribromo-4-[(4-bromophenyl)imino]cyclopent-2-en-1-one. The NMR data for the 6c' of Ma et al. demonstrate that this compound is not identical with substance U6 (see Supporting Information, page S47). This fact justifies the proposed neighboring 1,5-positions for the carbonyl and phenylimino groups in the structures of the U-series substances. In addition, such a configuration is consistent with a proposed fragmentation scheme for U1(page S45 in Supporting Information) as well as with the proposed mechanisms of the ring contractions discussed below.

Substance **U3b** frequently forms a mixed peak with **NPPBr**<sub>4</sub> in GC-records (Figure 5). These species can be separated using an appropriate column (Figure S8), or by a deconvolution method (pages S45, S46 in Supporting Information). **NPPBr**<sub>4</sub> usually occupies 60-70 % of the area of mixed peaks.

Substances S1 and S2 are known compounds and the structure of S1 was verified by comparison of the retention time and mass spectrum with a prepared counterpart. Also, the structures S3 and S5 are well known and were identified using commercially available *N*phenylmaleimide and a prepared dibromo derivative. Substance S4 (Figure 5, not shown in

Chart 1) can be most probably assigned to the corresponding monobromo derivative. Details on the identification of the known compounds and justification of the proposed structures for the unknown species found in the studied reaction together with all the measured spectral data can be found in Supporting Information.

#### 3.5 Proposed mechanisms for the carbon-release processes

The evidence of the presence of compounds with 5-member rings in the bromate-aniline oscillator provides a basis for the elucidation of  $CO_2$  liberation in the studied system. However, the question as to the reaction mechanisms responsible for the generation of such unexpected substances should be addressed. A possible route for the proposed ring contraction suggests the Favorskii rearrangement, a mechanism widely used in organic synthesis.<sup>44,45</sup> It is well known that the Favorskii reaction on an  $\alpha$ -halocyclohexanone leads to derivatives of cyclopentanecarboxylic acid.<sup>46-50</sup> Although the detailed mechanism of the Favorskii rearrangement is still a subject of debate,<sup>51,52</sup> it is generally accepted that one of the established reaction pathways occurs via a cyclopropanone intermediate (**B** in Scheme 1). Such an intermediate could be produced by a Michael addition of aniline to 5,6-dibromocyclohex-2-ene-1,4-dione (**A** in Scheme 1), which is known to be formed in the bromination of 1,4-benzoquinone.<sup>53</sup> Further oxidation, decarboxylation, and bromination of **C** in Scheme 1 could lead to **U1**.



Scheme 1: A possible route to the Favorskii rearrangement in the bromate-aniline oscillator.

However, serious objections can be raised to Scheme 1: (1) the reaction of 1,4benzoquinone with bromine under the conditions of the studied system is very slow, even in the presence of 0.1 M bromide ions; (2) a mixture of 2 mM aniline with 2 mM 1,4benzoquinone in 1.2 M  $H_2SO_4$  shows no GC/MS detectable products after 40 min, hence the proposed Michael addition is probably not feasible under the given conditions as well; (3) 5,6-dibromo-cyclohex-2-ene-1,4-dione undergoes fast hydrolysis in aqueous solutions.<sup>53</sup>

Considering the weak spots in Scheme 1, but clinging to the concept of a Favorskii-type rearrangement, we suggest an alternative mechanism based on the coupling of anilino radicals with 1,4-benzoquinone (Scheme 2).



Scheme 2: Suggested mechanism for the formation of substance U1 in the bromate-aniline oscillator. F and G are tautomers of B and C in Scheme 1, respectively.

Such a coupling is realistic as very fast additions of various radicals including methyl, phenyl, hydroxyl, and  $\beta$ -hydroxyethyl to 1,4-benzoquinone have been reported.<sup>54–56</sup> The initially formed adduct (**D** in Scheme 2) is stabilized by tautomerization to an aromatic 4-hydroxyphenoxy radical **E**.<sup>55</sup> Radical bromination in  $\beta$ -position and rearrangement of the electron-density lead to a cyclopropanone intermediate **F**, typical for the Favorskii reaction. Nucleophilic addition of water on the carbonyl carbon of **F** is accelerated by the presence of acid. The subsequent 1,4-elimination of HBr relieves the cyclopropane ring strain and creates the carboxyl group. The ring-contraction leads to a compound **G** and the following sequence of oxidation, decarboxylation and bromination steps provides the detected intermediate **U1**. As neutral 4-hydroxyphenoxy (semiquinone) radicals show absorption maxima in aqueous

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solutions above 400 nm,<sup>55,57</sup> the intermediate  $\mathbf{E}$  is a plausible candidate for the species responsible for the 427 nm band observed in the difference spectra (Figure 3).

As a first guess, we assumed that the substances accounting for the minor peaks S1 and S2 in the GC/MS record (Figure 5) are brominated cyclopent-3-ene-1,2-diones produced by the partial hydrolysis of U2 and U3a. However, the compounds U2 and U3a are surprisingly stable, showing no change in the UV/vis spectra in 1.2 M  $H_2SO_4$  for at least one hour. Moreover, comparison with the prepared 2,2-dibromocyclopent-4-ene-1,3-dione showed that substance S1 can be reliably identified with this compound. Thus, we speculate that, instead of hydrolysis, S1 and S2 could be formed by a similar mechanism including the Favorskii rearrangement proposed for the production of the U-compounds. Such a reaction might be initiated by the coupling of a bromo-radical with 1,4-benzoquinone.

Obviously, another carbon-release mechanism accounts for the formation of the *N*-phenylpyrrole derivatives identified as additional minor products of the studied reaction (**NPPBr**<sub>4</sub>, **S3**, and **S4** in Figure 5 and Chart 1). The oxidation of the intermediate **K** (Scheme 2) is likely to proceed via a substituted cyclopenta-1,3-dienoxy radical. Such radicals undergo ring-opening by  $\beta$ -scission with the subsequent abstraction of carbon monoxide.<sup>58,59</sup> The formed substituted butadienyl can be stabilized by a second bromination and by an intramolecular cyclization, eliminating the first bromine atom as suggested below (Scheme 3).



Scheme 3: Proposed mechanism for the formation of 2-bromo-N-phenylpyrrole in the bromate-aniline oscillator.

Although we have not observed any release of CO from the reaction solution, the proposed

scheme could be acceptable, assuming that this reaction channel is less significant than the  $CO_2$  release channel, as it can be deduced from the GC/MS records (Figure 5). Therefore, the amount of CO produced is probably much lower in comparison with the amount of  $CO_2$  produced and falls below the detection limit. Alternatively, CO could be immediately converted to  $CO_2$  in the highly oxidative reaction environment.

It is well known<sup>60</sup> that *N*-phenylpyrrole is preferentially brominated on the pyrrole ring to form bromo-*N*-phenylpyrroles, including the tribromo- and tetrabromo-*N*-phenylpyrroles (**NPPBr**<sub>3</sub>, **NPPBr**<sub>4</sub>) found in the reaction mixture. Apparently, an oxidation pathway also takes place, producing the *N*-phenylmaleimides S3 - S5.

Proposed mechanisms accounting for the organic substances identified or suggested to be formed in the bromate-aniline oscillator are collected in Scheme S1 in Supporting Information.

## 3.6 Global reaction kinetics

Although a precise quantitative analysis of the concentration changes of the particular intermediates during the reaction progress is needed, the obtained results allow for a putative sketch summarizing the overall kinetics of the whole complex process under study. The detection of substance **U1** at an early stage of the reaction (Figures 5 and S5) suggests that the initial oxidation/conjugation processes are surprisingly fast, probably proceeding in an autocatalytic way. This is supported by the observation of the burst in the  $CO_2$  production at the beginning of the reaction (Figure 4). The oscillatory nature of the initial release of  $CO_2$  and its sudden suppression points to inhibitory feedback that developes concomitantly with the starting processes. A detailed investigation into this initial period of the reaction could give insights to the nonlinear mechanisms controlling the oscillatory dynamics of the entire system.

During the induction period, 1,4-benzoquinone is produced by the oxidation of aniline by bromate, which is reduced to oxy-bromine compounds in lower oxidation states (HBrO<sub>2</sub>,

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HOBr) and bromide ions. Bromides react rapidly in acidic solution with bromate present in excess, producing bromine. Bromination of aniline yields bromoanilines with a major proportion of 2,4-dibromoaniline  $(ANBr_2)$  at this stage of the reaction. At the end of the induction period, **U1** can be found in a considerable amount.

During the first oscillatory phase, substance U2 significantly accumulates together with the continuing production of **BQ** and 2,4,6-tribromoaniline (**ANBr**<sub>3</sub>). Also, the formation of U3 and U4 is observed. The concentration of **ANBr**<sub>2</sub> culminates at the beginning of this phase. The substance U1 does not accumulate further, but we assume that it reaches a steady state, wherein the rates of the production and decay are equal. Most probably, U1 is consumed in the process of its conversion to U2. Such a conversion could proceed via the addition of Br<sub>2</sub> or HOBr to the enol-form of U1, or as a radical bromination at the  $\alpha$ -position to the carbonyl group.

During the second oscillatory phase, the concentration of **U1** is significantly reduced, but the concentration of **U2** remains almost unchanged. We deduce that the production of **U2** from **U1** is compensated for by the consumption of **U2** in subsequent bromination processes producing **U3a**, **U3b**, **U4**, **U5**, and **U6**. An additional depletion of **U2** from the reaction solution is due to its precipitation. Formation of a precipitate is obvious at this stage of the reaction and the analysis showed that substances **U2–U5** represent the major peaks in the GC record of the dissolved precipitate (Figure S8 in Supporting Information). **BQBr** and **NPPBr**<sub>4</sub>, both produced in the first oscillatory period, continue accumulating. The direct reaction of **BQ** with  $Br_2$  can be excluded as mentioned above, thus the production of **BQBr** is likely due to the oxidation of bromoanilines. Eventually, both **BQBr** and **NPPBr**<sub>4</sub> can be formed by radical bromination of the parent compounds. Only a small decrease in the concentration of **ANBr**<sub>3</sub> can be detected, while **ANBr**<sub>2</sub> almost vanishes during this reaction phase.

It can be summarized from the presented data that the studied reaction proceeds via four principal reaction channels (RCs). The product of the primary oxidation of aniline by bromate is, as expected, 1,4-benzoquinone (RC1). The reduction of bromate produces bromine, which is rapidly consumed by aniline, forming another final product, 2,4,6-tribromoaniline (RC2). In parallel, a third channel comes into play, initiated, as suggested, by the addition of an anilino radical to **BQ**. This CO<sub>2</sub>-producing channel, later on, splits to a major branch (RC3a), resulting in brominated cyclopentendionephenylimines referred to as the U-species (the intermediate U1 and the products U2-U6) and to a minor branch (RC3b). Here, release of an additional carbon (presumably CO) leads to derivatives of Nphenyl(pyrrole/maleimide) as the final products. The proposed structures of the U-species have not been previously described. The signals attributed to these compounds occupy a major area in the GC/MS records of both the reaction solution extracts and the dissolved precipitate, hence the substances of the U-series (primarily U2) are strong candidates to form a dominant group among the products of the studied reaction. Although additional research is needed to assess the relative significance of the particular reaction channels, a rough estimate for  $CO_2$  releasing channel can be made. As mentioned above, the released  $CO_2$  represents 19 molar % of the total amount of aniline. Considering that two molecules of aniline are consumed in this channel to produce one molecule of  $CO_2$ , it comes out that more than one third of the aniline enters this reaction pathway. Details on the reaction channels and mechanisms are outlined in Subsection 3.8.

#### 3.7 Oscillating kinetics and mechanism

As shown above, the UV/vis difference spectra point to at least four species involved in the oscillatory kinetics. The first one, identified as the product **BQ**, shows a stepwise accumulation in each cycle of the first oscillatory phase, but **BQ** net production is negligible in the second oscillatory phase. However, it cannot be excluded that the concentration of **BQ** is kept at a steady state level in this phase.

The other two species related to the absorption bands with the maxima at 305 and 427 nm are in-phase oscillating intermediates, which we refer to as **I305** and **I427**. The relative

contribution of these intermediates to the observed oscillations depends on the dynamic state of the system. The initial oscillations show moderately higher difference absorbance for 305 nm ( $\Delta A_{305}$ ) than for 427 nm ( $\Delta A_{427}$ ). As the amplitude  $\Delta A_{427}$  increases faster than that of  $\Delta A_{305}$ , later on,  $\Delta A_{427}$  becomes higher than  $\Delta A_{305}$ . On the contrary, the second oscillatory phase is characterized by the prevalence of the 305 nm amplitude over that recorded for 427 nm. Interestingly, if the system remains in continuously oscillating mode, i.e. shows no transition to the second oscillatory phase, with the exception of the initial oscillations,  $\Delta A_{427}$  remains significantly higher than  $\Delta A_{305}$  for the entire oscillatory period.

The fourth species engaged in the oscillatory cycle accounts for the absorption band centered at 265 nm. It can be resolved from the second oscillatory phase, where  $\Delta A_{265}$  is not overlaid by the 1,4-benzoquinone absorption, that this intermediate oscillates with a phase shift of approximately  $\pi/2$  in comparison with the **I305** and **I427** oscillations. This fact suggests that the intermediate is associated with the negative feedback of the cycle. Such a finding agrees with the recognition of the species as  $Br_3^-$ , provided that  $Br^-$  ions, as discussed below, take the inhibitory control of the oscillator. When the oscillations stop, a decay of this intermediate is observed.

Identification of the intermediates I305 and I427 remains unsolved. As already mentioned, the adduct E (Scheme 2) of the anilino radical with BQ is a feasible option for I427. The I305 oscillations show higher amplitudes in the second phase together with the increased production of  $CO_2$ . So, it can be assumed that this intermediate is involved in the carbon releasing mechanism. The radical J (Scheme 2) could stand for an initial guess for the identification of I305.

To uncover the origins of the observed oscillatory behavior is a difficult task. Suggestion of a detailed reaction mechanism allowing for the construction of an oscillatory kinetic model would require quite a number of additional studies. At this stage of knowledge, we confine ourselves to propose some tentative explanations and possible skeleton mechanisms. In general, chemical oscillators are based on coupling of positive and negative feedback loops. Oscillations emerge from a periodic switching between the loops that is regulated by a controlling intermediate. Particularly, in bromate oscillators, the positive feedback is represented by an autocatalytic production of bromous acid according to a scheme suggested by Noyes et al.:<sup>61</sup>

$$BrO_{3}^{-} + HBrO_{2} + H^{+} \rightarrow 2BrO_{2}^{\bullet} + H_{2}O$$
(1)

$$\operatorname{BrO}_2^{\bullet} + \operatorname{H}^{\bullet} (\text{or } e^- + \operatorname{H}^+) \to \operatorname{HBrO}_2$$
 (2)

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$$
(3)

A donor of the electron in step (2) is usually a metal catalyst, as it is the case for the classical Belousov-Zhabotinsky systems. For the UBO class, however, the origin of electrons is not as clear. Orbán, Kőrös, and Noyes<sup>62</sup> suggested for step (2) hydrogen atom abstraction from a dihydroxybenzene substrate. Liu and Scott<sup>63</sup> have shown by kinetic simulations that the electron may come rather from a quinone-intermediate produced by a two-electron oxidation of the original organic reactant. A key role of continuously produced intermediates such as hydroquinone and semiquinone as one-electron donors in (2) was pointed out by Szalai and Kőrös for the UBO with cyclohexane-1,4-dione.<sup>22</sup>

It is generally accepted<sup>64</sup> that both catalyzed and uncatalyzed bromate-driven oscillators are controlled by bromide ions, which mediate the negative feedback loop via the inhibition of HBrO<sub>2</sub> production:<sup>65,66</sup>

$$HBrO_2 + Br^- + H^+ \to 2HOBr \tag{4}$$

As for the electrons in the positive feedback loop, the source of Br<sup>-</sup> in the inhibitory step (4) is questionable for UBOs. The original skeleton mechanism of UBOs,<sup>62</sup> known as the Orbán-Kőrös-Noyes (OKN) mechanism, suggested a reaction of HOBr with organic radicals

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producing Br<sup>-</sup> in two one-electron transfer processes. Although simulations using a model based on the OKN mechanism have shown oscillations,<sup>67</sup> such negative feedback was criticized. Györgyi et al.<sup>68</sup> reasoned that HOBr is rather a fast brominating agent kept at a very low concentration that is not sufficient as the Br<sup>-</sup> source for step (4). They suggested a new route for Br<sup>-</sup> regeneration from bromoorganic species via the oxidation of bromoorganic radicals by bromate, producing exclusively 1,2-benzoquinones. Conversely, other successful simulation models mentioned above assume a two-electron reduction of HOBr by the reactant<sup>63</sup> or both by the reactant and the intermediate<sup>22</sup> as the only source of Br<sup>-</sup> for the negative feedback loop.

The observed coexistence of different periodic regimes suggests that various oscillatory mechanisms may function simultaneously in the envisaged system. It can be assumed, in accordance with the OKN mechanism for phenolic substrates, that autocatalytic HBrO<sub>2</sub> production is initiated and maintained by abstraction of a hydrogen atom from aniline or most likely from the anilinium cation. The formed aniline radical cation can be oxidized further to **BQ** or coupled with the **BQ** already produced. The adduct exhibits unusual chemistry with CO<sub>2</sub> release as proposed in Scheme 2. As CO<sub>2</sub> evolution always accompanies the oscillations, the carbon-releasing reaction channel (RC3) seems to be essential to establish the periodic cycle. This notion is supported by preliminary experiments showing that an initial presence of **BQ** in the reaction solution shortens or even abolishes the induction period.

The  $CO_2$ -releasing route provides with additional candidates for H-donors for step (2), namely with the intermediates **G** and **K**. As **BQ** accumulates during an oscillation together with  $CO_2$  production, we mean that both aniline and the **G** take part in the positive feedback loop, at least for the first oscillatory period. The relative contribution of both species to the autocatalytic process (1-3) may vary during the course of the reaction and may also depend on the oscillatory regime. We assume that high amplitude oscillations in the second oscillatory phase are driven mainly by the intermediate **G**. A minor contribution of the **K**  might also be considered, as one-electron oxidation of  $\mathbf{K}$  is proposed for the formation of N-phenylpyrrole derivatives (Scheme 3).

The presented results show no evidence that the controlling species are other than  $Br^-$  ions in the studied system. The observed oscillations of  $Br_3^-$  support this assumption; however, the particular contribution of  $Br_2$  and  $Br^-$  to the  $Br_3^-$  formation is not resolved. Accepting bromides as the key inhibitor in step (4), the major mechanistic question<sup>68</sup> regarding UBOs is concerned with the source of  $Br^-$  regeneration. Although we do not have a conclusive answer at the present time, the studied reaction brings additional information on the subject.

HOBr is a plausible source of  $Br^-$  for the studied system, as it can oxidize a variety of organic materials present in the reaction, including aniline and bromoanilines. We point namely at the intermediate **K**, which seems to be amenable to two-electron oxidation, producing the detectable intermediate **U1**. One can speculate that one-electron oxidation of **K** by  $BrO_2^{\bullet}$  or  $Br^{\bullet}$  follows the minor *N*-phenylpyrrole route, while two-electron oxidation by HOBr leads to the one of the main products, **U2**. However, bromination reactions of HOBr, mainly with aniline, cannot be excluded. The alternative source of  $Br^-$  suggested by Györgyi et al.<sup>68</sup> could be, perhaps, realized also in the bromate-aniline system by the oxidation of bromoaniline radicals by bromate. But, in contrast with the phenol UBO, we have detected no 1,2-benzoquinone in the reaction mixture.

The questions concerning the detailed functioning of the described oscillator, in particular, the mechanisms underlying the observed sequential periodic behavior, remain open for future research.

## 3.8 Proposed reaction pathways

The mechanisms suggested for the formation of the substances detected in the reaction mixture of the studied system are gathered in Scheme 4. As reported above and in Supporting Information, the detected substances were: in part identified as known compounds (**BQ**, **BQBr**, *o*-**ANBr**, **S1**, *p*-**ANBr**, **S3**, **ANBr**<sub>2</sub>, **ANBr**<sub>3</sub>, **S5**, **NPPBr**<sub>4</sub>; in several cases

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isolated and their structures have been proposed (U2, U3a, and U5; and in other cases assigned to the structures suggested on the basis of GC/MS and GC/HRMS data (**BQBr**<sub>2</sub>, **S2**, **S4**, **NPPBr**<sub>3</sub>, **U1**, **U3b**, **U4**, **U6**) in relation with the previous proposed structures. The identifiers of the detected substances are blue highlighted in the scheme. The red highlighted identifiers, **E** and **J**, point to the radical intermediates that are plausible candidates accounting for the observed UV/vis-spectral bands with maxima at 427 and 305 nm (Figure 3), respectively.

Aniline  $(\mathbf{AN})$  is in part initially oxidized by bromate to 1,4-benzoquinone  $(\mathbf{BQ})$ .  $\mathbf{BQ}$  is both intermediate and one of the main products of the studied reaction. The formation of  $\mathbf{BQ}$  from  $\mathbf{AN}$  occurs via a one of the three major reaction channels denoted as RC1 (the upper-left part of Scheme 4). An additional root for the  $\mathbf{BQ}$  production is oxidation of p-ANBr.

The reduction of oxobromates by aniline and the other organic intermediates leads to the formation of bromide ions and subsequently to  $Br_2$ , which is consumed in a number of bromination steps. A significant part of **AN** is brominated to another main product **ANBr**<sub>3</sub> in the second major reaction channel (RC2: **AN**  $\rightarrow$  **o**,**p**-**ANBr**  $\rightarrow$  **ANBr**<sub>2</sub>  $\rightarrow$ **ANBr**<sub>3</sub>, the left part of Scheme 4). As  $Br_2$  is not reactive toward **BQ** under the given reaction conditions, we suggest formation of **BQBr** via oxidation of **ANBr**<sub>2</sub>. Alternatively, or in parallel, **BQBr** could be formed by addition of Br' radical to **BQ**. This is supported by the detection of **BQBr**<sub>2</sub>, which is most probably a product of such radical addition, as the oxidation of **ANBr**<sub>3</sub> to **BQBr**<sub>2</sub> can be excluded because of the low reactivity of **ANBr**<sub>3</sub>.

The third major reaction channel (RC3:  $\mathbf{BQ} + \mathbf{AN}^{\bullet} \to \mathbf{E} \to \mathbf{F} \to \mathbf{G} \to \mathbf{J} \to \mathbf{K}$ , upper part of Scheme 4) is a multiple channel with several branches initiated by coupling of the produced  $\mathbf{BQ}$  with  $\mathbf{AN}^{\bullet}$ . The proposed Favorskii-type rearrangement provoked by a reaction of the radical  $\mathbf{E}$  with  $\mathbf{Br}_2$  leads in several steps to an intermediate  $\mathbf{K}$ . The oxidation of  $\mathbf{G}$ to  $\mathbf{J}$  is supposed to play a crucial role in the oscillatory cycle, suggesting the intermediate  $\mathbf{G}$  to be a hydrogen-donor for the autocatalytic production of  $\mathbf{HBrO}_2$ . Also, the observed



Scheme 4: Proposed mechanisms for the formation of the intermediates/products detected in the bromate-aniline oscillator. Deatails are explained in the text.

production of  $CO_2$  is assumed to occur at this step.

A minor channel is responsible for the production of **S1** and **S2** (middle-left part of Scheme 4). We speculate that these substances could be formed by a similar mechanism as the RC3, started by addition of Br<sup>•</sup> radical to **BQ**. One-electron oxidation of the intermediate **K** by Br<sup>•</sup> and/or BrO<sub>2</sub><sup>•</sup> is suggested as the initiation of a minor, but significant branch of the RC3 channel accounting for the formation of the *N*-phenylpyrrole derivatives (RC3b: **K**  $\rightarrow$ **L**  $\rightarrow$  **N**  $\rightarrow$  **P**  $\rightarrow$  **Q**  $\rightarrow$  **R**, central part of Scheme 4). The radical intermediate **L** undergoes a  $\beta$ -scission followed by CO release and the formed radical **P** is stabilized by bromination. Then, an intermediate **R** is formed by closing of the pyrrole ring. **R** can be brominated to produce the detected compounds **NPPBr<sub>3</sub>** and **NPPBr<sub>4</sub>** or oxidized before the bromination producing the detected *N*-phenylmaleimides **S3**, **S4**, and **S5** (the bottom part of Scheme 4).

A direct two-electron oxidation of **K** by HOBr, and possibly also with two successive one-electron oxidations of **K** (via the intermediate radical **L**), establish a major branch of the reaction channel RC3 (RC3a:  $\mathbf{K} \rightarrow \mathbf{U1} \rightarrow \mathbf{U2} + \mathbf{U3a} + \mathbf{U3b} + \mathbf{U4} + \mathbf{U5} +$  $\mathbf{U6}$ , the central-right part of Scheme 4). The observed intermediate  $\mathbf{U1}$  undergoes various bromination reactions leading to a mixture of the detected products  $\mathbf{U2} - \mathbf{U6}$ . The twoelectron reduction of HOBr to  $\mathbf{Br}^-$  provides a plausible key step for the negative feedback loop controlling the oscillatory cycle.

## 4 Conclusion

The presented study of an uncatalyzed bromate-aniline oscillator yielded several new findings. Differential UV/vis spectrophotometry revealed four species showing activity during the oscillatory cycle. One of them was identified as the accumulating product 1,4benzoquinone and another one as the oscillating intermediate tribromide ion. Two other oscillating intermediates, possibly organic radicals, with absorption maxima at 305 and 427 nm, remain unidentified. An oscillatory evolution of  $CO_2$  from the reaction solution was detected, probably for the first time for an uncatalyzed bromate oscillator. Carbon-releasing mechanisms based on the decarboxylation and decarbonylation of organic radicals were proposed to explain this phenomenon.

The GC/MS analysis of samples extracted from the reaction solution brought surprising results. In addition to the expected reaction products such as 1,4-benzoquinone and tribromoaniline, an unknown compound (**U2**) showing as the main signal in the GC/MS record was detected. This compound was isolated from the reaction solution and was identified as 2,2-dibromo-5-(phenylimino)cyclopent-3-en-1-one. The proposed structure is consistent with the obtained MS, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and IR spectra. Other unexpected structures, namely derivatives of *N*-phenylpyrrole and *N*-phenylmaleimide, were attributed to some minor peaks in the GC/MS record by comparison with the synthesized standards.

The occurrence of the compounds with a contracted ring in the studied system was elucidated with the proposed mechanism based on coupling of the anilino radical with the 1,4-benzoquinone molecule. We suggest that the addition of a bromine atom to the coupled radical constitutes an intermediate amenable to a Favorskii-type rearrangement; subsequent oxidative decarboxylation explains the observed  $CO_2$  production. Further oxidation of the decarboxylated intermediate may lead to **U2** (a major branch) or produce the *N*phenylpyrrole derivatives via  $\beta$ -scission, followed by the release of CO (a minor branch). Although additions of various radicals to benzoquinones have been reported, a reaction of the anilino radical with 1,4-benzoquinone has not yet been described, to our knowledge. Such a reaction could be of general importance as it may occur also in other oxidation processes of aniline, for example, in polyaniline preparation.

The measured stoichiometry of the produced  $CO_2$  indicates that the carbon-releasing reaction route is significant, and we assume that it is crucial to establishing the observed oscillatory behavior. Although a detailed kinetic model of the studied reaction is not provided yet, the potential origins of the positive and negative feedback loops in the studied system

were discussed within the scope of the Orbán-Kőrös-Noyes mechanism.

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# Supporting Information Available

Experimental setups, supplemental figures, and spectroscopic data (pdf)

The following files are available free of charge.

- U2 NMR.zip: NMR data of substance U2
- U3a NMR.zip: NMR data of substance U3a
- U5 NMR.zip: NMR data of substance U5

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# Graphical TOC Entry





















