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The Source of the Carbon Monoxide in the Classical Belousov−Zhabotinsky Reaction

Lavinia Onel

Department of Physical and Theoretical Chemistry and Materials Chemistry, Iaşi University "Al.I.Cuza", RO-700506 Iaşi, Romania

Maria Wittmann,* Krisztina Pelle, and Zoltán Noszticzius

Center for Complex and Nonlinear Systems and the Department of Physics, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

Luciana Sciascia

Dipartimento di Chimica Fisica "F. Accascina", Università di Palermo, 90128 Palermo, Italy

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CO and CO_2 evolution was measured in a cerium and in a ferroin-catalyzed Belousov−Zhabotinsky (BZ) reaction. These gases were stripped from the reaction mixture by a N_2 carrier gas, mixed with H_2, converted to methane on a Ni catalyst, and then measured by a flame ionization detector (FID). CO could be detected separately by absorbing CO_2 on a soda lime column. In separate experiments it was proven that CO is produced in a reaction of $BrO_2^\bullet$ radicals with bromomalonic acid (BrMA). To this end $BrO_2^\bullet$ radicals were generated in two different ways: (i) in the reaction $HBrO_2 + HBrO_3 \leftrightarrow 2\ BrO_2^\bullet + H_2O$ and (ii) by reducing $HBrO_3$ to $BrO_2^\bullet$ by Fe^{2+}. It was found that $^\bullet OH$ radicals − produced by Fenton's reagent − can also generate CO from BrMA. We propose that CO can be formed when an inorganic radical (like $BrO_2^\bullet$ or $^\bullet OH$) reacts with the enol form of BrMA producing an acyl radical which decarbonylates in the next step. Malonic acid (MA)−BrMA mixtures were prepared by a new method modifying Zaikin and Zhabotinsky's original recipe to minimize the production of dibromomalonic acid (Br_2MA).

1. Introduction

The classical Belousov−Zhabotinsky (BZ) reaction, the metal-ion-catalyzed oxidation and bromination of MA by acidic bromate, is the most studied chemical oscillator and a prime example for both temporal and spatial nonlinear phenomena in chemistry.[1−4] In spite of this, due to the complexity of the so-called organic reaction subset, there are important processes that are still not well understood. One of these problems is the origin of the periodic carbon monoxide evolution discovered by Noszticzius in 1977,[5] which cannot be explained by the known mechanisms[6−9] of the BZ reaction.

In this paper first we present experiments showing that an oscillatory CO and CO_2 evolution takes place both in cerium- and ferroin-catalyzed BZ systems when the substrate is MA but there are important differences regarding the gas evolution of these two BZ oscillators. Next we turn to our main aim to prove that most of the CO is produced in the bromomalonic acid (BrMA)−bromine dioxide radical ($BrO_2^\bullet$) reaction. This reaction can be studied even in the absence of any catalyst. To reach our aim, various batch and semibatch experiments were performed by applying a mixture of MA and BrMA. The mixture of the two organic substrates was produced by partial bromination of a MA solution. This way it was possible to avoid the problems associated with the synthesis of pure BrMA and the excess of MA also served as a hypobromous acid scavenger. In the first two series of experiments $BrO_2^\bullet$ radicals originated exclusively from the $HBrO_2$−BrO_3^- reaction but $HBrO_2$ was generated in two different ways. In the first series the only source of $HBrO_2$ was the reduction of acidic bromate by MA and BrMA whereas, in the second case, additional $HBrO_2$ was generated by adding formaldehyde to the reaction mixture. In the third type of experiments, not $HBrO_2$ but $BrO_2^\bullet$ radicals were generated directly in a reaction of acidic bromate with free (uncomplexed) Fe^{2+} ions. In the last experiments, it was demonstrated that CO can be also produced when BrMA reacts with other inorganic radicals, like $^\bullet OH$, for example. The $^\bullet OH$ radicals were generated by Fenton's reagent. Finally, a mechanistic explanation for the CO evolution is proposed.

2. Experimental Section

2.1. Chemicals. Malonic acid (Fluka, puriss), $Ce(SO_4)_2$ (Merck, p.a.), $NaBrO_3$ (Fluka, purum p.a.), NaBr (Merck, p.a.), H_2SO_4 (97%, Merck, p.a.), $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (Reanal, analytical grade), and H_2O_2 (Fluka, 30% in water) were used as received. Ferroin solution was prepared by mixing stoichiometric amounts of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 1,10-phenanthroline monohydrate (Fluka, purum p.a.). Formaldehyde stock solution was prepared by a 1 day hydrolysis of paraformaldehyde (Fluka puriss.) in 1 M sulfuric acid. All solutions were prepared with doubly distilled water.

2.2. Preparation of a Solution Containing a Mixture of Malonic and Bromomalonic Acids ("MB Mixture"). One possibility to prepare such a mixture is to dissolve MA and the potassium salt of BrMA in water and then mixing that solution with sulfuric acid. However, to prepare a pure K_2BrMA sample is not an easy task, as several recrystallization steps are necessary to get rid of the contaminating bromide.[10] In our hands the

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* Corresponding author. E-mail: wittmann@eik.bme.hu.

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recrystallization procedure gave a poor yield and the sample was still contaminated with some bromide. We attempted to remove the remaining bromide by titration with silver ions. In that case, however, silver ion contamination caused problems due to complex formation with BrMA. Thus, finally, we decided to apply a different method to prepare a mixture of MA and BrMA. That method is based on a recipe which was proposed originally by Zaikin and Zhabotinsky.[11] The recipe mixes bromate, bromide, and malonic acid in an acidic medium and assumes that BrMA will be formed according to the following stoichiometry:

$$3H^+ + BrO_3^- + 2Br^- + 3MA \rightarrow 3BrMA + 3H_2O$$

An advantage of this method is that the procedure is simple and no bromide remains in the end product. It is a problem, however, that some bromination of BrMA can also occur; thus the end product contains some dibromomalonic acid as well. To avoid this, we applied a great excess of malonic acid. The amount of the contaminating Br_2MA was checked experimentally and was also estimated by calculation. The concentration of Br_2MA was determined by measuring its decarboxylation rate r_{DC}, which is proportional with the Br_2MA concentration:

$$r_{DC} = k_{DC}[Br_2MA]$$

r_{DC} was determined from the steady-state ionic current of the FID, caused by the decarboxylation of Br_2MA in the reactor. As the rate constant of the reaction is known[12] the dibromomalonic acid concentration could be calculated.

A theoretical estimate of $[Br_2MA]$ was based on the following two balance equations:

$$d[BrMA]/dt = k_1[MA] - k_2[BrMA]$$

$$d[Br_2MA]/dt = k_2[BrMA]$$

where $k_1[MA]$ and $k_2[BrMA]$ are the enolization rates of malonic and bromomalonic acid, respectively. This is because in these bromination reactions we can apply the assumption that the rate determining step is the rate of enolization independently of whether the brominating agent is bromine or hypobromous acid. (According to ref 9 $k_1 = 2.6 \times 10^{-3}$ s^{-1} and $k_2 = 1.2 \times 10^{-2}$ s^{-1}.) Dividing the two balance equations, we obtain the following differential equation:

$$d[Br_2MA]/d[BrMA] = k_2[BrMA]/\{k_1[MA] - k_2[BrMA]\}$$

which can be easily integrated whenever the assumption $[MA] \approx$ const holds. As malonic acid is applied in a great excess in our experiments, this is a reasonable assumption here. To make the approximation more accurate, however, we applied an average MA concentration in our calculations $[MA]_{AV} = ([MA]_0 + [MA]_F)/2$, where $[MA]_F$ is the final malonic acid concentration. The solution gives the following relationship:

$$[Br_2MA] = K \ln\{K/(K - [BrMA])\} - [BrMA]$$

where $K = (k_1[MA]_{AV})/k_2$. Moreover, the sum of the BrMA and Br_2MA concentrations is known:

$$[BrMA] + [Br_2MA] = [BrMA]_{ID}$$

Here $[BrMA]_{ID}$ is an "ideal" BrMA concentration, what the result of the bromination would be if no Br_2MA were formed. That is based on the ideal stoichiometry of the BrMA formation

$$[BrMA]_{ID} = 3[NaBrO_3]_0 = 1.5[NaBr]_0$$

where $[NaBrO_3]_0$ and $[NaBr]_0$ are the initial bromate and bromide concentrations in the brominating mixture. From these equations the BrMA and Br_2MA concentrations can be calculated.

TABLE 1: Measured and Calculated Ratio of the Concentrations of Br_2MA and BrMA for Different Initial MA Concentrations[a]

$[MA]_0$ (mol dm^{-3})	$[MA]_{AV}$ (mol dm^{-3})	$[Br_2MA]/[BrMA]$ (mol dm^{-3}) measured	calculated with $k_1/k_2 = 0.216$	calculated with $k_1/k_2 = 0.33$
0.156	0.138	0.35	0.72	0.45
0.396	0.378	0.14	0.24	0.15
1.24	1.22	0.045	0.07	0.045

[a] Other components, including the brominating agents, were applied in all experiments in the following concentrations: $[NaBr]_0 = 24$ mM, $[NaBrO_3]_0 = 12$ mM, and $[H_2SO_4]_0 = 1.2$ M. That is $[BrMA]_{ID} = 36$ mM in all three experiments. Here $[BrMA]_{ID}$ is an "ideal" BrMA concentration, what the result of the bromination would be if no Br_2MA were formed.

In Table 1 we present the directly measured and the calculated $[Br_2MA]/[BrMA]$ ratios for three different initial MA concentrations.

As can be seen, the calculated ratio is higher than the measured one by a factor of about 2. Most probably this is because the k_1/k_2 ratio applied in our calculations is too small. This hypothesis is supported by a calculation, the results of which are also displayed in Table 1, where the k_1/k_2 ratio was increased from 0.216 to 0.33 and the calculated values give a much better agreement with the experimental ones.

Most importantly, both the measurements and the calculations prove that, by applying such initial compositions, one can easily prepare solutions with known BrMA concentrations and the relative amount of Br_2MA can be rather small if the initial MA concentration is high enough.

The MB mixture (a mixture of MA and BrMA) was produced on the spot in the reactor of Figure 1 in the following way. As a first step a solution was prepared according to the third row of Table 1. For this purpose, first 1 mL of 3.09 M MA in 2 M H_2SO_4 was injected into the reactor, followed by 0.5 mL of 2 M H_2SO_4 and 0.5 mL of 0.12 M NaBr. Then, the nitrogen carrier gas stream was switched for 3 min to the reactor filled with water of the reference branch (see Figure 1). During this time 0.5 mL of 0.06 M $NaBrO_3$ in water was injected into the reactor to generate a mixture of HOBr and Br_2, which brominated MA rapidly. (The switch is necessary to avoid any loss of the elementary bromine which would occur if a continuous nitrogen gas stream had been maintained.) After bromination, the 2.5 mL MB mixture had the following concentrations: 1.2 M MA, 1.2 M H_2SO_4, 35 mM BrMA, and 1.6 mM Br_2MA.

The MB mixture was always produced freshly before the experiments, as BrMA solutions are not stable in an acidic medium.[12]

2.3. Apparatus and Methods for CO and CO_2 Measurements. The scheme of our CO/CO_2 measuring instrument is depicted in Figure 1.

Whenever the CO and CO_2 + CO currents were high enough, continuous measurements were applied (valves A and A′, open; valves B and B′, closed; as Figure 1 shows). In the case of low signals, however, an accumulation method was needed to increase the sensitivity of the measurement. To this end, first valves A and A′ were closed and valves B and B′ were opened for 3 min. During this time the nitrogen carrier gas bypassed

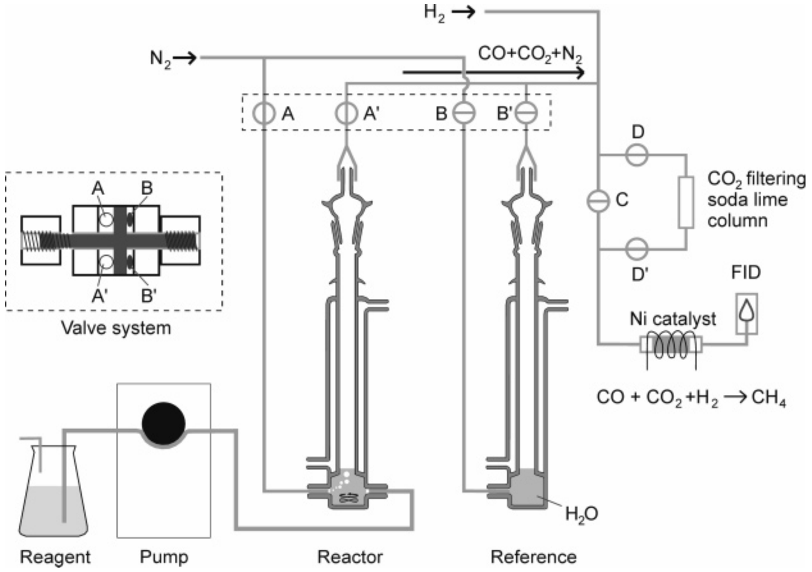


Figure 1. Schematic draft of the apparatus applied in the experiments. Nitrogen carrier gas (flow rate: 40 cm^3/min), containing the $CO + CO_2$ removed from the reactor, is mixed with a hydrogen gas (flow rate: 40 cm^3/min). Then CO and CO_2 is converted to methane on a nickel catalyst, and this methane current is measured by a flame ionization detector (FID). To measure the CO content of the mixture separately, CO_2 is adsorbed on a soda lime column (valve C, closed; valves D and D′, open). When the soda lime column is circumvented (valve C, open; valves D and D′, closed), a FID signal proportional to the $CO_2 + CO$ current can be recorded. See text for further details.

the reactor and CO_2 and CO evolving in the reaction were accumulating. In the next step, valves A and A′ were opened and valves B and B′ were closed for another 3 min. This way the signal due to the periodically collected gas appeared as a series of small peaks above the baseline and low evolution rates could be easily measured. The reactor-like reservoir with water in the reference branch was necessary to maintain the same N_2 flow rate in the whole instrument during the accumulation period.

2.4. Measuring CO_2 and CO Evolution in the Cerium-Catalyzed BZ Reaction. (Results are shown in Figure 2a.) The reactants were injected into the reactor in the following order: 2 mL of 0.2 M MA in 2 M H_2SO_4, 1 mL of 0.12 M $NaBrO_3$ in water. Then the reaction was started by the injection of 1 mL of 1.6 mM $Ce(SO_4)_2$.

2.5. Measuring CO_2 and CO Evolution in the Ferroin-Catalyzed BZ Reaction. (Results are shown in Figure 2b.) The same solutions as in the case of the cerium-catalyzed BZ reaction were introduced into the reactor, except the last one. This time the reaction was started by the injection of 1 mL of 8 mM ferroin.

2.6. Measuring CO_2 and CO Evolution from MA−BrMA−BrO_3^- Reaction Mixtures. 0.5 mL of 1.5 M $NaBrO_3$ was injected into the reactor, which already contained a 2.5 mL MB mixture. Experimental results are shown in Figure 3. To determine the CO_2 evolution rate due exclusively to the BrMA−BrO_3^- reaction, additional experiments were performed, as given in the Supporting Information.

2.7. Measuring the CO and CO_2 Evolution in Inorganic Radical−Substrate Reactions. (Experiments shown in Figures 4−6.) Two different substrate solutions, A and B were applied:

(1) Solution A, with MA substrate (2.5 mL). Three components were mixed: 1 mL of 3 M MA in 2 M H_2SO_4, 1 mL of distilled water, 0.5 mL of 2 M H_2SO_4.

(2) Solution B: Identical with the MB mixture.

In all experiments shown in Figures 4−6, 0.5 mL of inorganic oxidant (0.3 M $NaBrO_3$ or 3 M H_2O_2) was injected into the 2.5 mL solution of A or B. Thus the total liquid volume in the reactor was 3 mL in all cases and the following initial concentrations were established in the reaction mixture: $[H_2SO_4]_0 = 1$ M, $[MA]_0 = 1$ M in all experiments; $[BrMA]_0 =$ 29 mM, $[Br_2MA]_0 = 1.3$ mM in experiments with solution B; $[BrO_3^-]_0 = 0.05$ M in Figures 4 and 5; $[H_2O_2]_0 = 0.5$ M in Figure 6.

2.7.1. $BrO_2^\bullet$−Substrate Reaction. The $BrO_2^\bullet$ radicals were generated by two different methods, applying a short-lived reactant inflow into the reactor that contained the substrate and bromate:

2.7.1.1. Indirect Method by $HBrO_2$ Generation (Figure 4). Bromous acid formation was started by pumping 0.1 M CH_2O in 1 M H_2SO_4 into the reactor for 10 s with a 200 μL/min inflow rate.

2.7.1.2. Direct $BrO_2^\bullet$ Generation with the Ferrous Ion−Bromate Reaction (Figure 5). A periodic inflow of 0.2 M $(NH_4)_2Fe(SO_4)_2$ in 1 M H_2SO_4 was applied. A 200 μL/min inflow was switched on for 10 s and was stopped for 200 s before the next cycle.

2.7.2. $^\bullet OH$−Substrate Reaction. Hydroxyl radicals were produced by Fenton's reagent. In this case, the oxidant in the reactor was H_2O_2 and the same periodic inflow of ferrous ion solution was applied as in paragraph 2.7.1.2.

3. Results and Discussion

3.1. Oscillatory CO Evolution in a Cerium- and in a Ferroin-Catalyzed BZ System with Malonic Acid Substrate. In his paper Noszticzius[5] reported periodic CO and CO_2 evolution only in a cerium-catalyzed BZ system. In Figure 2, for comparison we present two analogous experiments with malonic acid substrate, one with cerium and the other with ferroin catalyst.

There are characteristic differences between the cerium- and ferroin-catalyzed systems. First of all, the induction period is missing when the catalyst is ferroin, as already observed by Smoes.[13] Second, the total amount of the gases ($CO_2 + CO$) is smaller in the case of the ferroin catalyst despite its 5 times higher concentration compared to cerium. The ratio of these gases is also markedly different: the relative amount of CO is much higher in the case of ferroin. On the other hand, if we compare the (CO peak area)/(total catalyst concentration) ratios,

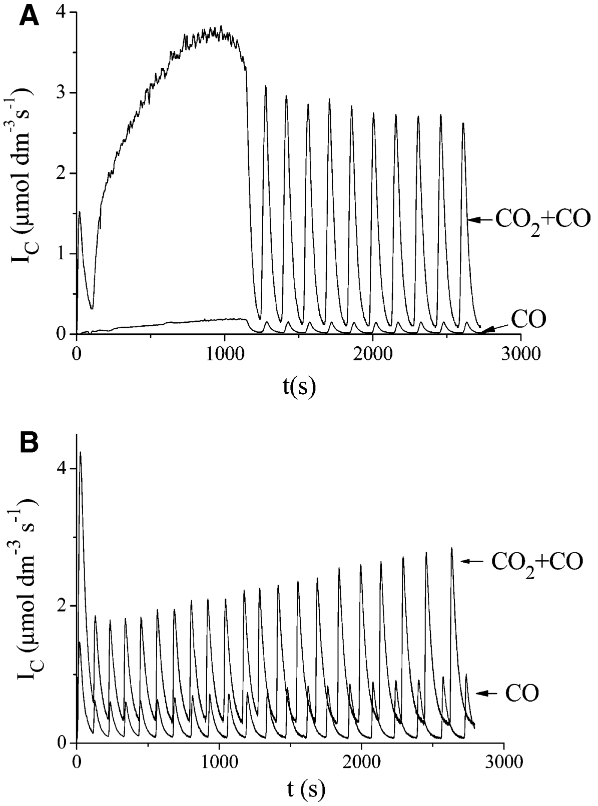


Figure 2. CO_2 and CO evolution in a cerium- and in a ferroin-catalyzed BZ reaction. I_C is the carbon atom current (μmol/s) measured by the FID, divided by the reactor volume given in dm^3. I_C is equal to I_{CO} when CO_2 is removed from the gas by the soda lime filter, and it is $I_{CO} + I_{CO_2}$ otherwise. CO_2 + CO and CO curves were measured in parallel experiments with initial conditions that were identical within experimental error. Conditions: $T = 20$ °C; reaction volume 4 mL; initial concentrations $[MA]_0 = 0.1$ M, $[NaBrO_3]_0 = 0.03$ M, $[H_2SO_4]_0 = 1$ M, and the catalyst (a) $[Ce(SO_4)_2]_0 = 4 \times 10^{-4}$ M and (b) $[ferroin]_0 = 2 \times 10^{-3}$ M (the catalyst concentration was increased to obtain a comparable level of the CO_2 + CO evolution rates). Based on the integrated areas of the CO_2 + CO and CO peaks the ratio CO/(CO_2 + CO) is (a) 4% and (b) 30%. (The small difference between the time period of the CO + CO_2 and CO traces is due to some minor deviation in the initial conditions.)

these are the same, within few percent, for the two different catalysts so the difference in the CO/(CO_2 + CO) ratio comes from the difference in the amount of CO_2 evolved. Most probably the higher CO_2 amount in the case of the cerium catalyst is due to the Ce^{4+}−mesoxalic acid (MOA) and the Ce^{4+}−oxalic acid (OA) reactions. This is supported by HPLC measurements on full BZ systems[9] where MOA and OA intermediates were found in a ferroin-catalyzed BZ system, but no MOA and only a minor amount of OA could be detected in a cerium-catalyzed one. Moreover, in some new experiments, we could prove that ferriin is not able to oxidize MOA, OA, and MA; only BrMA can be oxidized by it.[14] Thus the higher CO_2 amount appearing in the cerium system can be rationalized by the higher ability of Ce^{4+} to produce CO_2 from organic acids.

An additional deviation is that, in the cerium system, the peak height of the oscillations slowly decreases in time, whereas just the opposite tendency can be observed with ferroin. This tendency might be attributed to the effect of the accumulating intermediates among which, in this time span, the most important is BrMA, according to HPLC measurements.[9]

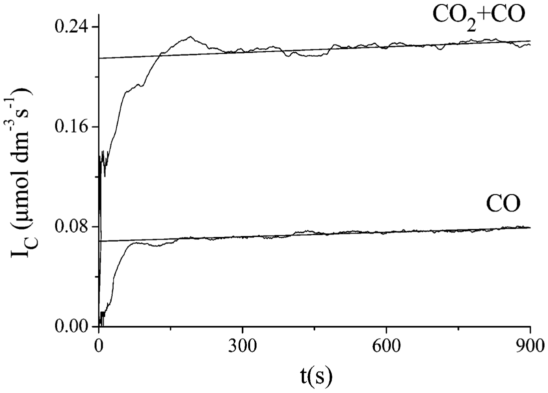


Figure 3. CO and CO_2 + CO evolution due to the BrMA−BrO_3^- reaction as a function of time. Initial conditions: $[BrMA]_0 = 0.029$ M, $[MA]_0 = 1$ M, $[NaBrO_3]_0 = 0.25$ M, $[H_2SO_4]_0 = 1$ M. In a steady state, the I_C value is equal to the rate of the gas producing reaction in the unit volume of the reactor. CO evolution occurred only in the presence of BrMA. Some CO_2, however, was produced from MA as well. To obtain the net CO_2 + CO current due to the BrMA−BrO_3^- reaction exclusively, the CO_2 current measured in a similar experiment, but without BrMA, was subtracted from the CO_2 + CO current measured with the MB mixed substrate. CO_2 evolution in the absence of BrMA (not shown here) has a character similar to the curves presented here, but the measured current is only a fraction of the current (about one-third) measured in the presence of BrMA.

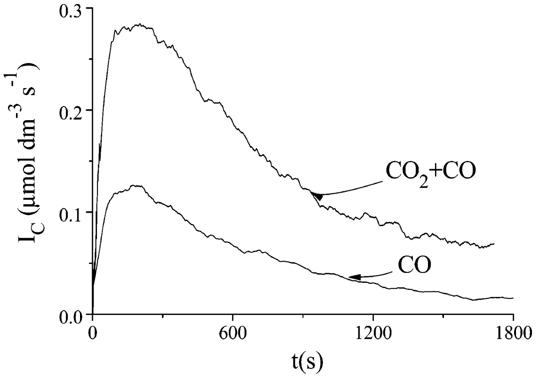


Figure 4. CO and CO + CO_2 evolution due to the BrMA + $BrO_2^•$ (generated by CH_2O) reaction. The curves are obtained as a difference of separate experiments as explained in the text. Initial concentrations in the experiment with CH_2O: $[CH_2O]_0 = 1.1$ mM, $[BrMA]_0 = 0.029$ M, $[MA]_0 = 1$ M, $[NaBrO_3]_0 = 0.05$ M, $[H_2SO_4]_0 = 1$ M.

3.2. A Negative Result: Reaction of the Oxidized Form of the Catalyst with BrMA is Not a Major CO Source in BZ Systems. Regarding the results of the above experiments, our first hypothesis was that CO is produced in a reaction of the oxidized form of the catalyst (Ce^{4+} or ferriin) with BrMA. The results of some preliminary semibatch experiments,[15] however, contradicted this hypothesis: we found only traces of CO in such reactions. CO was measured with the accumulation method (see the Experimental Section) and its amount was about 2 orders of magnitude smaller than that found in the oscillatory reactions.

Finally, a suitable experimental approach (a method to identify the reagents which generate CO in the BZ) was discovered, while we studied the reaction of acidic bromate with a mixture of MA and BrMA.

3.3. CO Evolution from a MA−BrMA−BrO_3^- Reaction Mixture. The original aim of this research was to synthesize a mixture of MA and BrMA acids (MB mixture; see the Experimental Section) to check our previous results[12] on the BrMA−BrO_3^- reaction. When we applied the MB mixture as a substrate for this reaction, however, we could observe not only CO_2 but also a CO evolution. This result greatly influenced our further search for the CO source in the BZ, as it indicated that CO can be generated without the catalyst as well. It is also

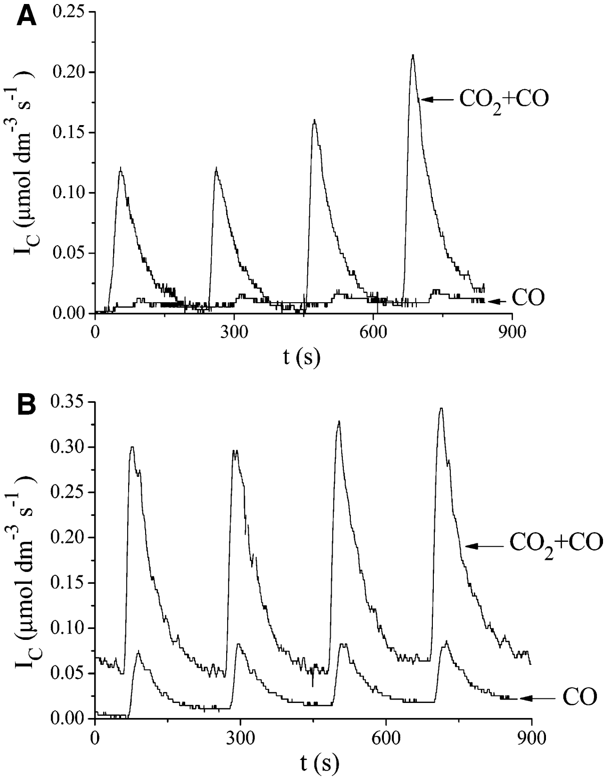


Figure 5. CO and CO + CO$_2$ evolution in the BrO$_2^•$−substrate reactions. The BrO$_2^•$ radicals were generated in the Fe^{2+}−BrO$_3^-$ reaction, by pumping Fe^{2+} into the reactor for 10 s, which caused a stepwise 2.2 × 10^{-3} M increase in the iron concentration there. Pumping of Fe^{2+} was periodically repeated after a waiting period of 200 s with no inflow. Substrate: (a) 1 M MA; (b) 1 M MA + 0.029 M BrMA.

important that repeating the experiment with pure MA, we could detect only CO$_2$. Figure 3 shows the results of the experiments with the MB substrate.

Thus we were able to find CO evolution in the acidic bromate−BrMA reaction but, at the beginning, it was not clear which oxybromine species reacts with BrMA, producing CO and CO$_2$. The candidates were BrO$_3^-$, BrO$_2^•$, HBrO$_2$, and HOBr. BrO$_3^-$ can be easily ruled out, however, because (according to HPLC measurements) the bromate concentration decreases monotonically and the BrMA concentration does not oscillate either in the course of the BZ reaction. Consequently, a BrO$_3^-$−BrMA reaction cannot explain the oscillatory CO evolution observed in BZ systems. HOBr can produce carbon dioxide[12] in a reaction with BrMA but not CO. In the presence of 1 M MA, however, the steady-state HOBr concentration is too low to contribute significantly even to the CO$_2$ evolution. (One aim of applying a high MA concentration in the reaction mixture was just its ability to scavenge HOBr without any gas production.) Thus HOBr could be also removed from the list of candidates. After this, only two candidates remain: HBrO$_2$ and BrO$_2^•$. Several arguments support that BrO$_2^•$ is the CO generating reagent and the next paragraph discusses this working hypothesis.

3.4. Proposed Working Hypothesis: CO is a Product of the BrO$_2^•$−BrMA Reaction. One argument is based on the oscillatory character of the CO evolution in the BZ reaction as shown in Figure 2. The decarbonylation reaction should be fast as it follows the oscillations. Decarbonylation of radicals is usually much faster than that of molecules and a reaction of HBrO$_2$ with BrMA could produce only molecular intermediates. On the other hand, it is known that acyl radicals can decarbonylate rapidly[16,17] and the reaction of BrO$_2^•$ with the enol form of BrMA can produce such radicals:

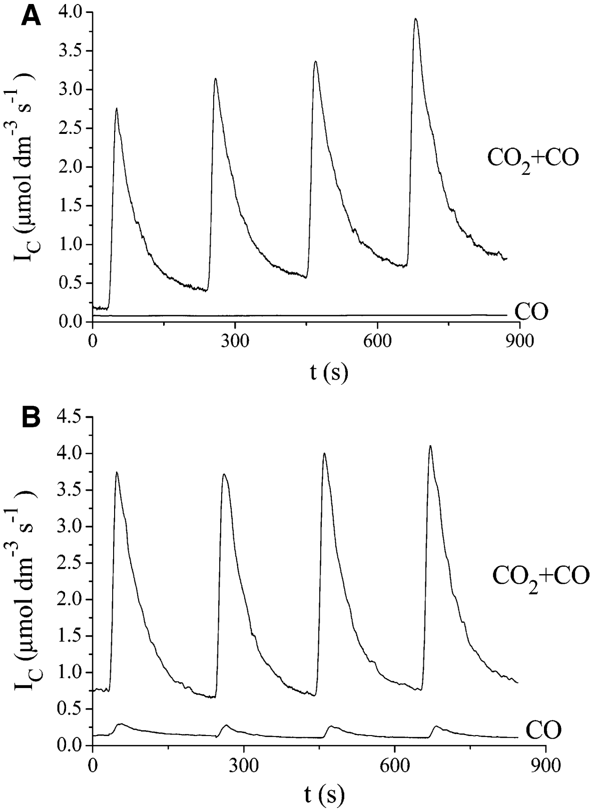
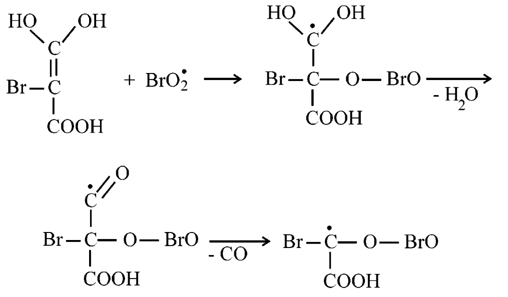


Figure 6. CO and CO + CO$_2$ evolution in the •OH−substrate reactions. •OH radicals were generated by applying the Fe^{2+}−H$_2$O$_2$ reaction (Fenton's reagent), by pumping Fe^{2+} into the reactor in the same amount and with the same period as in Figure 5. Substrate: (a) 1 M MA; (b) 1 M MA + 0.029 M BrMA.



The carbon atoms in the radical formed after the decarbonylation will give finally CO$_2$ or CO and we know that their ratio in the overall process is 1.65. Any mechanistic proposal for the further fate of the radical BrC•(COOH)OBrO would be too hypothetical now but two parallel processes can be suggested with the following stoichiometries:

(A) one yielding a carbon dioxide and a carboxyl radical:

$$\mathrm{BrC^•(COOH)OBrO} \rightarrow \mathrm{Br_2} + \mathrm{CO_2} + {}^•\mathrm{COOH}$$

(B) one yielding a carbon monoxide and a carboxyl radical:

$$\mathrm{BrC^•(COOH)OBrO} + \mathrm{H_2O} \rightarrow 2\mathrm{HOBr} + \mathrm{CO} + {}^•\mathrm{COOH}$$

Carboxyl radicals will be further oxidized to CO$_2$ so oxidation of BrMA via route A gives 2CO$_2$ + 1CO and via route B 1CO$_2$ + 2CO. The combination of these two routes gives the measured ratio if route A is 7 times faster than route B.

The first step in the above scheme is analogous to the addition of an initiator radical to a vinyl monomer in free radical chain polymerization. In this respect it is interesting to mention that Pojman and co-workers[18,19] observed periodic polymerization of acrylonitrile in the BZ reaction. Enolization is also common for other BZ substrates like acetone[20,21] or cyclohexanedione;[22] thus similar reactions can occur in other BZ systems as well. The reaction of bromine dioxide radical with the enol form of these substrates does not yield an acyl radical, however; thus no CO evolution can be expected after the BrO_2−enol reaction in these cases.

The $BrO_2^\bullet$ radicals can be formed in the following reaction sequence. First MA reduces acidic bromate[23] to produce $HBrO_2$:

$$\mathrm{MA} + 2\mathrm{H}^+ + 2\mathrm{BrO_3}^- \rightarrow \mathrm{MOA} + 2\mathrm{HBrO_2} + \mathrm{H_2O}$$

then $HBrO_2$ forms $BrO_2^\bullet$ with acidic bromate:[2,9]

$$\mathrm{HBrO_2} + \mathrm{H}^+ + \mathrm{BrO_3}^- {-} \mathrm{H_2O} \leftrightarrow \mathrm{Br_2O_4} \leftrightarrow 2\mathrm{BrO_2}^\bullet$$

3.5. Revision of the Rate Constant of the BrMA−BrO_3^- Reaction. Although it is rather probable that CO is produced in the $BrO_2^\bullet$−BrMA reaction, presently it is not clear, however, whether CO_2 can be also found among the products of the same reaction or of a parallel one, also between $BrO_2^\bullet$ and BrMA. If both CO and CO_2 are produced in such reactions, then what is the CO_2/CO ratio? If CO_2 does not come or originates only partially from the BrMA−$BrO_2^\bullet$ reaction, then the remaining CO_2 should be a product of the direct BrMA−BrO_3^- or of the BrMA−$HBrO_2$ reaction. As $HBrO_2$ disproportionates rapidly in acidic medium, most probably, the excess CO_2 comes from the BrMA−BrO_3^- reaction. As explained in the Supporting Information, we were able to give an upper limit for the rate constant of the BrMA−bromate reaction: $k_{BB} = 2.02 \times 10^{-5}$ M^{-1} s^{-1}. As we shall see later, however, the CO_2 also comes from the $BrO_2^\bullet$−BrMA reaction, where the CO_2/CO ratio is 1.65. Calculating with this data $k_{BB} = 4.7 \times 10^{-6}$ M^{-1} s^{-1}. This is close to rate constant of the MA−BrO_3^- reaction, where for the so-called mesoxalic acid channel $k_{MOA} = 2.46 \times 10^{-6}$ M^{-1} s^{-1}.

Comparing these results, however, to the value suggested by us previously ($k_{BB} = 3.8 \times 10^{-4}$ M^{-1} s^{-1}), we can see that even the maximum estimate is more than 1 order of magnitude smaller than the earlier value. When looking for the reason of this strong deviation, it was realized that the solid samples of K_2BrMA used in our earlier experiments contained bromide.[24] Thus the strong CO_2 evolution observed formerly with acidic bromate was, unfortunately, an artifact, as it was mainly due to the decarboxylation of the Br_2MA formed in the reaction of Br^-, BrO_3^-, and BrMA, and only a small part of the observed CO_2 evolution was generated by the BrMA−BrO_3^- reaction.

3.6. Enhancing $HBrO_2$ Production with Formaldehyde. According to our working hypothesis, CO appears in the $BrO_2^\bullet$−BrMA reaction. In the experiment depicted in Figure 3 the direct BrO_3^-−MA reaction[23] was the only source of the $HBrO_2$ necessary for the $BrO_2^\bullet$ formation. It is known,[25,26] however, that formaldehyde is also able to reduce acidic bromate to $HBrO_2$ rather rapidly:

$$\mathrm{CH_2O} + \mathrm{H}^+ + \mathrm{BrO_3}^- \rightarrow \mathrm{HCOOH} + \mathrm{HBrO_2}$$

Thus, in the next experiment we decreased the BrO_3^- concentration from 0.25 to 0.05 M (to decrease the share of the BrO_3^-−MA reaction in the $HBrO_2$ production) and applied an initial CH_2O concentration of 1.1 mM. The net CO and CO + CO_2 evolution due to the $BrO_2^\bullet$−BrMA reaction initiated by the formaldehyde injected at $t = 0$ is shown in Figure 4.

In Figure 4 the curves are differences of separate experiments. For example, the CO curve in Figure 4 is a difference between the CO experiment with the initial concentrations given in the figure caption and another reference CO experiment with the same initial concentrations, but without CH_2O. This way, the CO curve shows only that fraction of CO that is due to the added CH_2O exclusively.

According to our experiments, CO could be formed only from BrMA. CO_2, however, can be also formed from MA. Thus if we add CH_2O to a mixture of BrMA, MA, and acidic bromate, the extra CO_2 will be produced by both substrates, when they react with the extra $BrO_2^\bullet$ radicals due to the added CH_2O. To obtain the extra CO + CO_2 coming exclusively from BrMA, we made the following calculations. First, the result of the reference CO + CO_2 experiment (all components present except CH_2O) was subtracted from the result of a CO + CO_2 experiment with all components, including CH_2O. This difference, however, also contains an extra CO_2 coming from MA. The amount of that CO_2 was estimated by subtracting the result of a CO + CO_2 experiment where only MA and acidic bromate was present from another one with the same components, but with added CH_2O. This way we were able to depict a net CO + CO_2 curve in Figure 4, which shows only the part of CO + CO_2 that satisfies two conditions: (i) it is generated by the added CH_2O and (ii) it originates from BrMA.

Comparing the two curves of Figure 4, we can calculate the CO_2 /CO ratio for a case when both CO_2 and CO come from the $BrO_2^\bullet$−BrMA reaction. That ratio, according to Figure 4, varies with time increasing from 1.3 to 1.66 in the first 28 min of the experiment.

Figure 4 also shows that the maximal CO and CO + CO_2 evolution occurs only after 150−200 s following the CH_2O injection. As the time constant of our apparatus[12] is about 5 times smaller than this, most of the observed delay is due to the reaction kinetics. A feasible explanation for the delay is based on the fact that $HBrO_2$ is only a precursor of the $BrO_2^\bullet$ radical. Thus, although the generation of $HBrO_2$ starts as soon as CH_2O is injected, that generation is not too rapid, and a certain time is required for the accumulation of enough $HBrO_2$ to produce $BrO_2^\bullet$ radicals with a higher intensity.

3.7. Generating $BrO_2^\bullet$ Radicals with the Fe^{2+}−BrO_3^- Reaction. The aim of these experiments was to generate $BrO_2^\bullet$ radicals in a direct fast reaction, without a delay like what we could see in the experiments with formaldehyde. As we were not aware of any recipe (except the BZ reaction and its subsystems) for a direct and fast generation of $BrO_2^\bullet$ radicals, we tried to reduce acidic bromate with Fe^{2+} ions because it was reasonable to assume that the following fast reaction sequence

$$\mathrm{Fe}^{2+} + \mathrm{H}^+ + \mathrm{BrO_3}^- \rightarrow \mathrm{Fe(OH)}^{2+} + \mathrm{BrO_2}^\bullet$$

$$\mathrm{Fe(OH)}^{2+} + \mathrm{H}^+ \rightarrow \mathrm{Fe}^{3+} + \mathrm{H_2O}$$

could generate $BrO_2^\bullet$ radicals directly. Thus we hoped to see a near instantaneous CO and CO_2 production if Fe^{2+} is injected into a MB−BrO_3^- mixture in an experiment similar to that in the previous paragraph, but using Fe^{2+} instead of CH_2O. Figure 5 shows the results of such experiments, which lived up to our expectations.

As Fe^{2+} reacts much faster with acidic bromate than CH_2O does, now it was possible even to repeat the experiments within a short time. The results of four repeated experiments are depicted in Figure 5. Figure 5a shows reference experiments without BrMA. In this case, practically no CO evolution can be detected. Due to some BrMA production and accumulation in the reaction, however, some trace amount of CO can be observed, especially in the fourth experiment. On the other hand, as Figure 5b shows, a characteristic CO evolution was recorded if BrMA was present in the reaction mixture. All of these and also the sharp jump and the fast decay in the gas evolution (governed practically by the time constants of our apparatus) were in accordance with our working hypothesis. These experiments with injected Fe^{2+}, however, could still allow the possibility that the CO and CO_2 generating oxybromine species is $HBrO_2$ instead of $BrO_2^\bullet$. This is because, when injecting Fe^{2+} to generate $BrO_2^\bullet$ radicals, we cannot exclude that these radicals react further with Fe^{2+} rapidly to give bromous acid:

$$Fe^{2+} + BrO_2^\bullet \rightarrow Fe^{3+} + BrO_2^-$$

$$BrO_2^- + H^+ \rightarrow HBrO_2$$

Thus we wanted to perform an experiment where inorganic radicals react with BrMA producing CO and CO_2, but in the absence of $HBrO_2$. Obviously, we had to choose an inorganic radical different from $BrO_2^\bullet$ as, in the presence of that radical, $HBrO_2$ might also appear. Thus our choice was the hydroxyl radical.

3.8. CO_2 and CO Evolution in the MA−$^\bullet$OH Radical and BrMA−$^\bullet$OH Radical Reactions. Hydroxyl radicals were generated by Fenton's reagent,[27] but in a 1 M sulfuric acid medium:

$$Fe^{2+} + HOOH \rightarrow Fe(OH)^{2+} + {}^\bullet OH$$

$$Fe(OH)^{2+} + H^+ \rightarrow Fe^{3+} + H_2O$$

At pH = 3, which is usual for a Fenton's reagent, the next step is a reduction of Fe^{3+} by HOOH:

$$Fe^{3+} + HOOH \rightarrow [FeOOH]^{2+} + H^+$$

$$[FeOOH]^{2+} \rightarrow Fe^{2+} + {}^\bullet OOH$$

However, at the high acidity applied in our experiments, the above reduction of Fe^{3+} was mostly suppressed; thus the usual Haber−Weiss catalytic cycle[28] was mostly inactive here. This way the reaction could be controlled by an Fe^{2+} inflow: stopping the flow stopped most of the reaction.

The experimental conditions applied here to generate $^\bullet$OH radicals were nearly identical with the ones used to generate $BrO_2^\bullet$ radicals described in the previous paragraph; the only difference was that here the inorganic oxidant was 0.5 M H_2O_2 and was 0.05 M BrO_3^- previously. All other concentrations were the same. The results are shown in Figure 6.

The most important result of the experiments displayed in Figure 6 is that, although no CO evolution can be observed in the case of pure MA substrate (Figure 6a), CO appeared among the reaction products when the Fenton experiment was performed with MB mixed substrate. This is in accordance with our expectations, as the experiment proves that (i) CO is coming from BrMA and (ii) CO can be generated from BrMA by another inorganic radical, namely, $^\bullet$OH.

Comparing Figure 6a,b, we see an additional difference between the CO_2 evolution of the two images. Before the addition of iron, the CO_2 evolution is minimal in the case of MA substrate, but there is a steady CO_2 evolution when BrMA is present. This indicates an uncatalyzed reaction between BrMA and H_2O_2. In Figure 6a, as the amount of iron is increased, the steady CO_2 evolution is also growing, suggesting that Fe(III) can also play some catalytic role in the case of MA. On the other hand, the initially high steady-state CO_2 evolution is not growing in Figure 6b with the increasing amount of iron. Thus some Haber−Weiss cycle is possible in the case of MA, but BrMA inhibits the process somehow (e.g., by capturing some chain carrier radical species or by complex formation with Fe(III)).

We can assume that the $^\bullet$OH radicals can also react with the enol form of BrMA to form an acyl radical, which can decarbonylate, as in the case of $BrO_2^\bullet$ radicals.

It is worth mentioning that, recently, CO evolution was detected in the Briggs−Rauscher reaction[29] as well, where the source of the oscillatory component of the CO evolution might be an analogous reaction between $^\bullet$OH radicals and iodomalonic acid.

3.9. Comparing the CO_2/CO Ratios Obtained in the Formaldehyde and in the Fe^{2+} Experiments with Those Measured in the Oscillatory Systems. As Figure 4 shows, when $BrO_2^\bullet$ radicals react with BrMA, the reaction gives CO_2 and CO simultaneously. The n_{CO_2}/n_{CO} ratio can be calculated from the integral of the CO_2 + CO and the CO curves (773 and 290 nmol, respectively).[30] The result is $n_{CO_2}/n_{CO} = 1.66$. In this experiment, $BrO_2^\bullet$ radicals were produced from bromous acid, which was generated by reducing acidic bromate with formaldehyde. However, as shown previously, $BrO_2^\bullet$ radicals can also be produced directly in a reaction of Fe^{2+} with acidic bromate. It can be expected that the n_{CO_2}/n_{CO} ratio for the $BrO_2^\bullet$−BrMA reaction should be the same, independent of the $BrO_2^\bullet$ generation method. Actually, if in the first experiment of Figure 5 we regard the CO_2 + CO amount (this is the difference between the integrals of the CO_2 + CO curves depicted in parts b and a of Figure 5, that, is 28.7 nmol) and the amount of CO (10.8 nmol), the n_{CO_2}/n_{CO} ratio is also 1.65. That is, if in a reaction system both CO_2 and CO are coming from the $BrO_2^\bullet$−BrMA reaction, we can assume that their relative amount should be around 1.65 ± 0.05.

There are various CO_2 producing reactions in an oscillatory BZ system but, according to our experiments, there is only one significant CO source, which is the $BrO_2^\bullet$−BrMA reaction. Accepting that hypothesis of the one dominant CO source, the fixed n_{CO_2}/n_{CO} ratio can be applied to estimate the other sources (different from the $BrO_2^\bullet$−BrMA reaction) of CO_2 in an oscillatory BZ reaction.

(i) For example, in the Ce^{4+}/Ce^{3+}-catalyzed BZ oscillator shown in Figure 2a $n_{CO}/(n_{CO_2} + n_{CO}) = 0.04$ thus $n_{CO_2}/n_{CO} = 24$ is much larger than 1.65. Obviously, other reactions are the dominant CO_2 sources as the $BrO_2^\bullet$−BrMA reaction is responsible only for a small fraction (1.65/24 = 6.9%) of the CO_2. As Ce^{4+}, the oxidized form of the catalyst, can react rapidly with oxalic, mesoxalic, and bromomalonic acids to form carbon dioxide,[9] it is reasonable to assume that in a cerium-catalyzed system most of the CO_2 is produced in such reactions.

(ii) In the case of a ferroin-catalyzed system the situation is different, however. In that case, ferriin, the oxidized form of the catalyst, can react only with BrMA but not with malonic, oxalic, and mesoxalic acids.[14] As $n_{CO}/(n_{CO_2} + n_{CO}) = 0.3$, $n_{CO_2}/n_{CO} = 2.33$, which means that in this case the majority of CO_2 (1.65/2.33 = 71%) is produced in the $BrO_2^\bullet$−BrMA reaction.

4. Conclusions and Outlook

In the classical version of the BZ reaction when the substrate is malonic acid, both CO_2 and CO evolution can be observed.

The amount of these gases, however, depends on the chemical nature of the catalyst. Although the amount of CO generated in one cycle and normalized to the catalyst concentration is roughly the same for cerium and ferroin catalysts, cerium generates much more CO_2. It was found that CO is produced exclusively in the $BrO_2^\bullet$−BrMA reaction but numerous other reactions can contribute to the CO_2 evolution, especially in the case of cerium-catalyzed systems. The $BrO_2^\bullet$−BrMA reaction also generates some CO_2 and the CO_2/CO ratio is 1.65 in this process, suggesting different decomposition routes of an intermediate to CO and CO_2. As free radicals react readily with a double bond, the reaction partner of $BrO_2^\bullet$ is most probably the enol form of BrMA, forming an acyl radical that can easily decarbonylate. It is known that $BrO_2^\bullet$ plays an important role in the autocatalytic cycle of the BZ oscillators; thus its reaction with the enol form of a substrate can modify the dynamics and the bifurcation structure of these systems.

In the present experiments it was found that two inorganic radicals ($BrO_2^\bullet$ and $OH^\bullet$) can generate CO when reacting with BrMA. It is rather probable that CO also appears when BrMA reacts with other inorganic radicals. As CO can be measured selectively and sensitively with our method, this can be a basis for a new method to detect and measure inorganic radicals in a reaction mixture simply by adding BrMA to it and measuring the CO generated in the inorganic radical−BrMA reaction. Iodomalonic acid can be a similar detector of inorganic radicals. Experiments are in progress in our laboratories to reveal these possibilities.

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Supporting Information Available: Evaluation of the experimental results partly shown in Figure 3 to determine the CO_2 evolution rate due exclusively to the BrMA−BrO_3^- reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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