Periodic CO and CO_2 Evolution in the Oscillatory Briggs-Rauscher Reaction

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Received: October 27, 2006; In Final Form: November 10, 2006

While various reactions in the inorganic subset of the oscillatory Briggs−Rauscher (BR) reaction were clarified in the recent years, the organic subset of the present mechanisms contains only one process: the iodination of malonic acid. Further organic reactions can play a role, however, if malonic (MA) and iodomalonic (IMA) acids can be oxidized in the BR reaction. As CO_2 and CO should be products if such oxidations can take place, the main aim of this work was to learn whether these gases are produced in a significant amount in a BR system. In our BR experiments, a rather intense evolution of both gases was observed with an oscillatory and a nonoscillatory component. With the initial conditions applied here, one from every 6 carbon atoms was oxidized either to CO_2 or to CO in the course of the BR reaction. The amount of CO_2 was about 4 times higher than that of CO. Experiments are in progress to disclose the reactions which generate the measured gases and their role in the mechanism of the BR reaction.

Introduction

The sharp color changes displayed by the oscillatory Briggs−Rauscher (BR) reaction[1] make it probably the most "dramatic" oscillating reaction in solution as it was stated by Furrow and Noyes.[2] Sudden switches from a colorless or yellow state to a blue one can be observed when proper concentrations of hydrogen peroxide, iodate, malonic acid (MA), manganous salt catalyst, and starch indicator are applied in a continuously stirred aqueous acidic medium. As the BR reaction is an important example for nonlinear behavior in chemistry, both its mechanism[2−10] and its exotic dynamics[9,11] were studied by several authors. Recently, new substrates, such as acetone, were found[12,13] and the BR reaction was even applied as a test tool to measure the activity of certain antioxidants.[14−16]

In the classical Belousov−Zhabotinsky (BZ) reaction, which is another well-known halogenate based chemical oscillator also applying MA as an organic substrate, oxidation reactions of MA and BrMA (bromomalonic acid) and other organic intermediates, the so-called organic subset, play an important role in the negative feedback loop.[17] In the present theories of the BR reaction,[2−15] however, the organic subset consists of two reactions

$$\mathrm{MA} \leftrightarrow \mathrm{MA(enol)} \tag{1}$$

$$\mathrm{I_2 + MA(enol) \rightarrow IMA + I^- + H^+} \tag{2}$$

that is, the enolization of MA followed by the iodination of the enol. The only exception is the model of Vukojevic et al.[7] where the oxidation of iodomalonic acid (IMA) by hydrogen peroxide was included as a third organic reaction:

$$\mathrm{2\ IMA + H_2O_2 \rightarrow I_2 + products} \tag{3}$$

Considering the inorganic processes, the following global stoichiometry can be constructed describing the reduction of iodate to iodine:[10]

$$\mathrm{2\ IO_3^- + 9\ H_2O_2 + 2\ H^+ + 2\ MA \rightarrow I_2 + 6\ O_2 + 10\ H_2O + products} \tag{4}$$

A global stoichiometry for the oxidation of iodine to iodate can be written in a similar way:[10]

$$\mathrm{I_2 + 9\ H_2O_2 + 2\ MA \rightarrow 2\ IO_3^- + 8\ H_2O + 2\ H^+ + O_2 + products} \tag{5}$$

Reactions (4) and (5) can explain sudden switches between the yellow and blue colors in the presence of a starch indicator. Regarding the above two stoichiometric processes, generation of organic "products" could be expected in both phases of the BR reaction.

In an analogy with the BZ reaction, it seems reasonable to assume that CO_2 or CO or both might be among the undefined products.[18,19] Thus, the aim of the present work was to measure CO_2 or CO evolution in the BR reaction if there is any with a technique developed earlier to monitor the evolution rates of the these gases in the BZ reaction.

Experimental

Chemicals. Malonic acid (MA) (Fluka, puriss.), KIO_3 (Reanal, analytical grade), $MnSO_4$ (Reanal, analytical grade), H_2SO_4 (97%, Merck, p.a.), H_2O_2 (Fluka, 30% in water, puriss. p.a. not stabilized) were used as received. All solutions were prepared with doubly distilled water.

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10.1021/jp067070y CCC: $37.00

CO_2 and CO Measurements. A N_2 carrier gas was applied to remove the evolving CO and CO_2 from the reactor, which was thermostated to 20 °C and contained 2 mL of BR reaction mixture. The N_2 carrier was mixed with H_2, and CO and CO_2 were converted to methane on a Ni catalyst. Then all carbon atom-containing gases were measured with a flame ionization detector. Before the conversion to methane, a soda lime filter could be inserted to remove CO_2 so it was possible to measure CO selectively. Further details of our CO_2/CO measuring apparatus will be given in a subsequent paper.[19] (An earlier version of our apparatus can be seen in Figure 1 of ref 20. The main differences between the earlier version and the present apparatus are: (i) a combination of gas bubbling and magnetic stirring was applied in the reactor, (ii) the membrane permeator was omitted because our membrane was permeable only for CO_2 and not for CO, and (iii) a soda lime filter was applied whenever we wanted to measure CO separately.) In the present experiments, we applied higher than usual N_2 and H_2 streams (both were increased to 70 mL/min from the usual 40 mL/min flow rate). Moreover the N_2 stream after the reactor was split; only about 10% of the N_2 (containing the CO and CO_2 removed from the reactor) was mixed with the H_2, and 90% of the sample was not used. The split and the higher flow rates were applied in the present experiments for the following three reasons:

(i) To decrease the O_2 concentration in the catalytic converter. (This is because the BR reaction produces gaseous O_2 as well. As hydrogen and oxygen are burned to water vapor in the converter, too much oxygen can cause various problems.)

(ii) To decrease the usual sensitivity of our measuring system. (The BR reaction applied here produced far more CO and CO_2 than the usual BZ systems studied in our previous experiments with the same apparatus; thus without a split, the signal would have been too high and out of the linear range of the flame ionization detector),

(iii) To decrease the time constant of the measuring system to obtain a better resolution of the oscillations.

Preparation of the reaction mixture. *Mixture M.* One milliliter of solution A (0.1 M H_2SO_4) was mixed with 1 mL of solution B (0.16 M KIO_3 in water) and 1 mL of solution C (0.2 M MA and 0.026 M $MnSO_4$ in water).

Starting the reaction. A 1.5 mL portion of mixture M was filled into the reactor. The BR oscillating reaction was started by injecting 0.5 mL of solution D (2.64 M H_2O_2 in water) to reach the initial concentrations of the BR reaction in the reactor.

Results

Figure 1 displays the results of two parallel experiments. In the first measurement, shown in Figure 1a, the carrier gas bypassed the CO_2 filter; in this case, the sum of the CO and CO_2 evolution was recorded. In the second measurement, shown in Figure 1b, the carrier gas went through the CO_2 filter, which removed all CO_2 from it. Consequently, in this case it was possible to monitor CO selectively.

The intensity of the gas evolution is rather low at the start; nevertheless, oscillations in the gas evolution can be observed already at the beginning of both experiments. First, the amplitude of the oscillations is very small but it increases gradually suggesting a supercritical Hopf bifurcation. (As Vukojevic et al.[7] have already proved by quenching experiments, supercritical Hopf bifurcation can occur in the BR reaction.) It seems that the gas evolution has a nonoscillatory component as well that also increases in the first part of the experiment. Both the gas evolution rate and the amplitude of the oscillations reach a maximum between 400 and 500 s (this happens somewhat earlier for the CO evolution) then the amplitude decreases rapidly. Soon the oscillations disappear, probably again with a supercritical Hopf bifurcation, but the nonoscillatory gas evolution survives and continues with a decreasing intensity in the long postoscillatory regime. The curve in the postoscillatory regime is not entirely “smooth”, however, but somewhat “noisy”, even irregular “bursts” can occur in this regime.

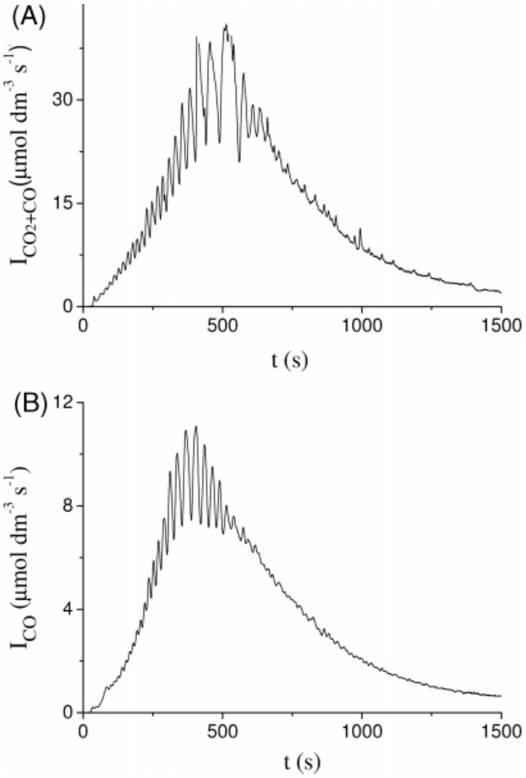

Figure 1. CO and CO_2 evolution rate in an oscillatory BR reaction. Initial concentrations: $[KIO_3]_0 = 0.04$ M, $[MA]_0 = 0.05$ M, $[MnSO_4]_0 = 6.5$ mM, $[H_2O_2]_0 = 0.66$ M, and $[H_2SO_4]_0 = 25$ mM. Total volume: 2 mL. (a) CO and CO_2 current as a function of time. (b) CO current as a function of time.

As we can see in Figure 1, both gases evolve in a significant amount. The integral of the experimental CO and CO_2 curve in Figure 1a is about 50 μmol. (Some gas evolution continues with an ever-decreasing intensity even after 1500 s, but its intensity drops below the detection limit around 4000 s; thus, the integral was taken between 0 and 4000 s.) Because the initial amount of MA is 100 μmol (equivalent to 300 μmol carbon atoms), our result suggests that 1 from every 6 carbon atoms is oxidized to CO or CO_2 in this BR reaction.

The integral of the I_{CO} shown in Figure 1b is about 10 μmol. This means that the CO/CO_2 ratio is 1:4 in the experiment shown in Figure 1.

Discussion

Present mechanisms of the BR reaction regard only two organic reactions: the enolization and the subsequent iodination of malonic acid. The only exception is model “Q” of Vukojevic, Sørensen, and Hynne[7] in which (*R*3), the oxidation of IMA by hydrogen peroxide is suggested, giving iodine and other products. It is obvious that the observed gases should be oxidation products in a reaction between some organic molecules and inorganic oxidants. IMA can be a good candidate for such an organic molecule, because in the BR reaction it is a product—and not an initial component—and according to Figure 1 at the beginning of the experiment the CO and CO_2 evolution is minimal. (Malonic acid itself, on the other hand, is a less likely candidate as its concentration is decreasing in the course of the BR reaction.) The oxidation probably is caused not by a single oxidant but by a mixture of various inorganic oxidants, including free radicals as well. While H_2O_2 is certainly such an inorganic oxidant, an explanation for the oscillatory CO and CO_2 evolution based exclusively on the IMA − H_2O_2 reaction would be problematic because H_2O_2 is not an oscillatory species. While in theory, oscillations could appear because of oscillations in the IMA concentration, such a rapid production and consumption of IMA is not realistic. In our opinion, a fast oxidation of IMA by $Mn(OH)^{2+}$ or by radical species like the $^{\bullet}OOH$ radical is a more probable explanation for the oscillatory gas evolution. This is because $Mn(OH)^{2+}$ and radical concentrations could easily oscillate. Moreover their reaction with organic molecules produces organic free radicals that can rapidly decarboxylate or decarbonylate. Similar processes are known in the BZ reaction.[19]

Finally, we note that if the gas evolution observed here really indicates the presence of organic free radicals, that would have important consequences for the mechanism of the BR reaction because these species could participate in various chain reactions including both organic and inorganic free radicals. Such a chain reaction was already found in a BZ system in which carboxyl radicals and bromine atoms were the chain carriers.[21] Present mechanisms of the BR reaction exclude the possibility of such chain reactions as none of the two inorganic radical species ($^{\bullet}OOH$ or $^{\bullet}IO_2$) is able to react with organic molecules according to the schemes. Nevertheless, such reactions probably can occur. To check this hypothesis, experiments are in progress with various subsystems of the BR reaction.

Acknowledgment. This work was partially supported by OTKA grants T-42708 and K-60867 and by the Bilateral Hungarian−Romanian Science and Technology Foundation RO-31/2005.

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