J. Phys. Chem. A **2008,** *112,* 11649–11655

I(+1) Transfer from Diiodomalonic Acid to Malonic Acid and a Complete Inhibition of the CO and CO_2 Evolution in the Briggs−Rauscher Reaction by Resorcinol

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Received: July 21, 2008

A recent report on an intense CO_2 and CO evolution in the Briggs−Rauscher (BR) reaction revealed that iodination of malonic acid (MA) is not the only important organic reaction in the classical BR oscillator. To disclose the source of the gas evolution, iodomalonic (IMA) and diiodomalonic (I_2MA) acids were prepared by iodinating MA with nascent iodine in a semibatch reactor. The nascent iodine was generated by an iodide inflow into the reactor, which contained a mixture of MA and acidic iodate. Some CO_2 and a minor CO production was observed during these iodinations. It was found that in an aqueous acidic medium the produced I_2MA is not stable but decomposes slowly to diiodoacetic acid and CO_2. The first-order rate constant of the I_2MA decarboxylation at 20 °C was found to be $k_1 = 9 \times 10^{-5}\ s^{-1}$, which is rather close to the rate constant of the analogous decarboxylation of dibromomalonic acid under similar conditions ($7 \times 10^{-5}\ s^{-1}$). From the rate of the CO_2 evolution, the I_2MA concentration can be calculated in a MA−IMA−I_2MA mixture as only I_2MA decarboxylates spontaneously but MA and IMA are stable. Following CO_2 evolution rates, it was proven that I_2MA can react with MA in the reversible reaction $I_2MA + MA \leftrightarrow 2\ IMA$. The equilibrium constant of this reaction was calculated as $K = 380$ together with the rate constants of the forward $k_2 = 6.2 \times 10^{-2}\ M^{-1}s^{-1}$ and backward $k_{-2} = 1.6 \times 10^{-4}\ M^{-1}s^{-1}$ reactions. The probable mechanism of the reaction is I(+1) transfer from I_2MA to MA. The presence of I(+1) in a I_2MA solution is demonstrated by its reduction with ascorbic acid. To estimate the fraction of CO_2 coming from the decarboxylation of I_2MA in an oscillatory BR reaction, the oscillations were inhibited by resorcinol. Unexpectedly, all CO_2 and CO evolution was interrupted for more than one hour after injecting a small amount of resorcinol (10^{-5} M initial concentration in the reactor). Finally, some implications of the newly found I(+1) transfer reactions and the surprisingly effective inhibition by resorcinol regarding the mechanism of the oscillatory BR reaction are discussed. The latter is explained by the ability of resorcinol to scavenge free radicals including iodine atoms without producing iodide ions.

Introduction

The Briggs−Rauscher (BR) reaction[1] was originally developed to provide a spectacular demonstration of chemical oscillations by using simple reagents. Briggs and Rauscher discovered the reaction that bears their names by combining hydrogen peroxide and iodate of the Bray−Liebhafsky (BL) reaction[2,3] with malonic acid (MA) and Mn(II) ions of the Belousov−Zhabotinsky (BZ) reaction.[3−6] This way they found an "oscillating iodine clock" reaction that shows, in the presence of starch indicator, sudden cyclic changes in the following order: colorless → yellow → blue → colorless.[1] Since it was discovered, the BR system has attracted a high interest: both its mechanism[3,7−14] and its exotic dynamics[13,14] were studied in several laboratories. Various nonlinear phenomena, as complex oscillations[14] and chemical waves,[15] were reported in BR systems and also new organic substrates[16] were found beside MA. Moreover, it was found that the oscillations can be inhibited by small amounts of different perturbants.[17−19] On the basis of that observation the BR reaction was applied as a test tool to measure the activity and the concentration of different antioxidants.[20,21] Actually, this is an important functional dynamic aspect of the BR reaction where a change in the dynamics is applied for chemical analysis.

The present mechanisms of the BR reaction[7−14] give detailed schemes for its inorganic reactions but omit much of the complexity of the relevant organic reactions, usually reducing them to only two reactions:

$$MA \leftrightarrow MA(enol) \qquad (1)$$

$$I_2 + MA(enol) \rightarrow IMA + I^- + H^+ \qquad (2)$$

In the above schemes,[7−11,13,14] IMA stands for iodomalonic acid, which is regarded to be an inert end product of the BR reaction.

It is known, however, that in the BZ reaction bromomalonic acid (BrMA), a compound analogous to IMA, is not an inert end product, but it is oxidized further by free radicals[22] and by the oxidized form of the catalyst.[23] Mostly, these reactions are responsible for the oscillatory CO_2 and CO production observed in the classical BZ reaction.[24,25] It is reasonable to assume that IMA can also participate in similar CO_2 and CO generating reactions in a BR system. In fact, when this expectation was checked, we discovered that there is an intense CO_2 and CO

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10.1021/jp8064163 CCC: $40.75

evolution in the BR reaction,[26] which can be even more intense than the one observed in the BZ reaction.

Naturally, the discovery of the oscillatory CO_2 and CO evolution in the BR reaction in itself does not prove that these gases are produced by a mechanism analogous to that of the BZ reaction. Thus, a main motivation of our present research was to identify the CO_2 and CO generating reactions of the BR oscillator and to clarify their mechanism. There are three possible organic molecules, or molecular intermediates, the reactions of which can lead to CO_2 and/or CO production: MA, IMA, and I_2MA (diiodomalonic acid). Our starting hypothesis[27] was that the reactions of the two iodinated species, IMA and I_2MA, constitute the major source of the CO and CO_2 evolution. Beyond the analogy with the BZ this hypothesis was also supported by our observation[26] that at the start of a batch BR experiment the CO_2 and CO evolution is very weak, but it gradually increases to a maximum after 7−8 min or 17−20 oscillations. (After that the amplitude of the oscillations decreases along with the intensity of the gas evolution.) Mahon and Smith[28] found by absorption spectroscopy that IMA is accumulating in the course of the BR reaction. This observation is in line with our assumption that CO_2 and CO are produced from the iodinated species. (There is another hypothetical mechanism, however, which cannot be excluded presently. According to that the increasing IMA concentration could also increase the concentration of inorganic free radicals, which can react not only with the iodinated species but also with malonic acid itself to generate some of the CO_2 and CO.)

As a first step to check the role of IMA and I_2MA in the CO_2 and CO evolution, we prepared these compounds by a method of Noszticzius et al.[29] By measuring CO_2 and CO evolution rates, we found that whereas IMA is stable, I_2MA decarboxylates slowly, just like Br_2MA[30] does. The decarboxylation rate of I_2MA was measured, and the rate constant of the reaction was calculated.

As I_2MA is the only CO_2 source in a MA−IMA−I_2MA mixture, the CO_2 evolution rate measured in that mixture is a measure of the I_2MA concentration there. It was observed that by adding MA to such mixtures or to a pure I_2MA solution, CO_2 evolution can be decreased or eliminated completely, indicating a reaction between I_2MA and MA. A reasonable assumption is that the product of such a reaction is IMA, in other words, I(+1) can be transferred from I_2MA to MA. The rate constants of the forward and backward reactions are calculated. With similar experiments, it was demonstrated that I(+1) in I_2MA can also react with ascorbic acid.

Next, the implications of these results for the BR reaction were studied. The first question was whether the decarboxylation of I_2MA makes an important contribution to the total CO_2 evolution in the BR reaction or not. While studying that problem, we discovered that micromolar concentrations of resorcinol can stop the otherwise intense CO and the CO_2 evolution in the BR reaction for a long time, which indicated that

i) the decarboxylation of I_2MA is not a significant source of CO_2 in the BR reaction,

ii) resorcinol can stop somehow the production of the "active species" needed for the gas evolution.

Finally, some implications of the newly found I(+1) transfer reactions and the surprisingly effective inhibition by resorcinol regarding the mechanism of the oscillatory BR reaction are discussed. The latter is explained by the ability of resorcinol to scavenge free radicals including iodine atoms ($I^•$) without producing iodide ions. The above observations suggest that I(+1) and $I^•$ might play a more important role in the mechanism of the BR reaction than it was assumed before.

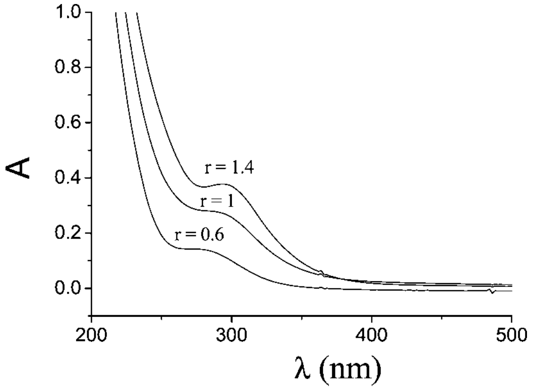

Figure 1. UV−vis absorption spectra of MA−IMA−I_2MA mixtures; path length 0.1 cm. The mixtures were produced by iodinating MA with nascent iodine (see text for details). The ratio $r = [I(+1)]/[MA]$ is indicated near the curves. $r = 0.6$, MA and IMA are the dominant species; $r = 1$, IMA is dominant; $r = 1.4$, a mixture of IMA and I_2MA.

Experimental Section

Chemicals. Malonic acid (Fluka, puriss.), $NaIO_3$ (Fluka, puriss. p.a.), KI (Riedel-deHaën, puriss. p.a.), H_2SO_4 (97%, Merck, p.a.), ascorbic acid (Reanal, analytical grade). All solutions were prepared with doubly distilled water.

Instrument for Spectrophotometric Measurements. The absorbance was monitored in the range of 190−820 nm with a Hewlett-Packard model 8452A diode array spectrophotometer.

Apparatus and Method for CO_2 and CO Measurements. The CO_2 and CO evolution rates were measured by the same instrument as in our previous publications.[22,26] Details of our CO_2/CO measuring apparatus, reactor, and method can be found in ref 22. In most of the experiments, N_2 and H_2 flow rates were 40 mL/min.

Preparation of Solutions Containing IMA and I_2MA. IMA and I_2MA were prepared applying the method suggested by Noszticzius et al.[29] First, the following two solutions were prepared:

Solution (A): 3 mL of 1 M MA, 1.6 mL of 5 M H_2SO_4, and 5 mL of 0.2 M $NaIO_3$;

Solution (B): 3 mL of 1 M MA, 2.6 mL of 5 M H_2SO_4, and 10 mL of 0.2 M $NaIO_3$.

First, in order to obtain the spectra, samples for spectrophotometric measurements were prepared by adding dropwise a solution of 0.4 M KI from a buret into solution (B). After each drop of the KI solution, we waited several seconds until the brown color of iodine disappeared. For measuring the absorbance, a 1 mL sample was taken from the mixture when the added volume of KI solution was 3, 5, and 7 mL, respectively. Each sample was diluted 25 times with distilled water before measurement. UV−vis absorption spectra of these mixtures with an increasing degree of iodination are presented in Figure 1.

All of these samples are mixtures containing different amounts of MA, IMA, and I_2MA. Nevertheless, in the sample where $r = [I(+1)]/[MA] = 1$, IMA is the dominant species, thus its spectrum can be compared with the one recorded by Mahon and Smith[28] for an IMA solution prepared by the method of Kőrös and Varga.[31] (Their method is based on the iodination of MA by molecular iodine in a water−ethanol mixture. Next, the potassium[31] or sodium[28] salt of IMA is formed, which is purified by recrystallization from ethanol.) Mahon and Smith dissolved the sodium salt of IMA in 0.2 M $HClO_4$ and obtained

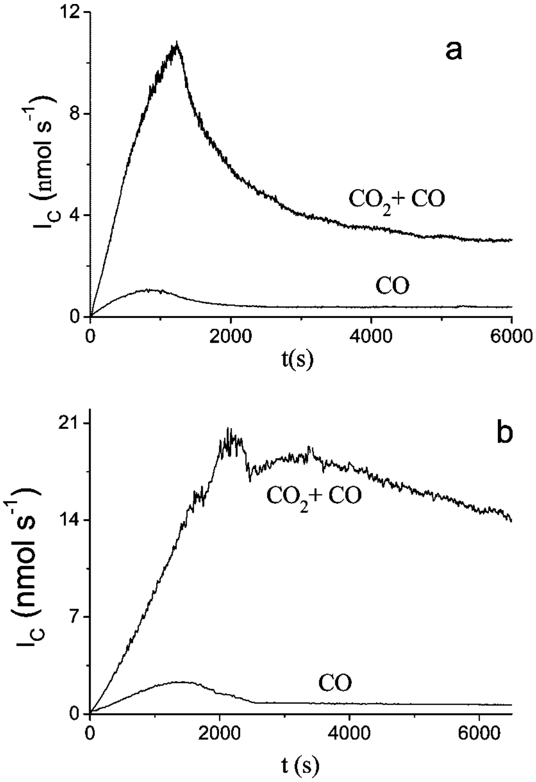

Figure 2. $CO_2 + CO$ and CO evolution rates measured in the course of the iodination of malonic acid. The process was stopped at different stages of iodination characterized by the following $r = [I(+1)]/[MA]$ ratios: (a) $r = 1$, (b) $r = 2$.

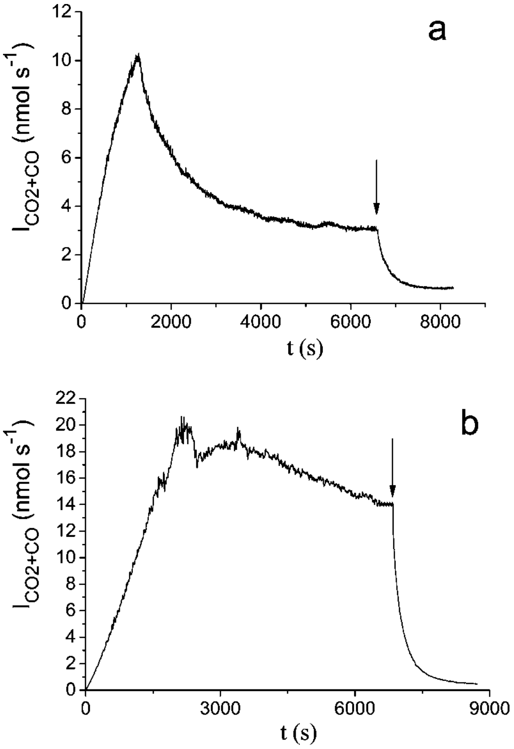

Figure 3. Reaction of I_2MA with MA as indicated by the drop in the decarboxylation rate of I_2MA. At the time marked by ↓ 0.5 mL 0.5 M MA in 0.5 M H_2SO_4 was injected to start the reaction. The MA−IMA−I_2MA mixtures were produced for (a) and (b) like in parts a and b of Figure 2, respectively.

a similar UV−vis spectrum like the one depicted in Figure 1. Small deviations between Figure 1 and the spectrum recorded by Mahon and Smith are due to the presence of some contaminants − like iodate and I_2MA − in our samples prepared with an acidic mixture of iodate and iodide (this is the so-called "nascent iodine"[32−34]) and to the differences in the acidic medium (0.2 M $HClO_4$ and 0.025 M H_2SO_4, respectively). Thus, we can see that iodination with nascent iodine and with molecular iodine give similar products. However, iodination in the presence of an excess iodate is closer to the chemistry of the BR reaction, where iodate is always present in the reaction mixture.

Figure 1 also proves that further iodination of IMA with nascent iodine is also possible. Figure 1 ($r = 1.4$) shows the spectrum of a IMA−I_2MA mixture produced this way.

Measurement of CO_2 and CO Evolution in the Course of Iodinating MA and IMA. Reaction of I_2MA with MA and with Ascorbic Acid. To monitor CO_2 and CO evolution during the preparation of IMA and I_2MA, we performed the iodination in a reactor containing solution (A) or (B) and fed 0.4 M aqueous KI solution into the reactor continuously with a peristaltic pump.

Part a of Figure 2 shows CO_2 and CO evolution during and after the iodination of malonic acid. Part a of Figure 3 and part a of Figure 4 show CO_2 evolution in similar experiments, but here after the CO_2 evolution reaches a quasi steady state malonic acid (part a of Figure 3) and ascorbic acid (part a of Figure 4) is injected into the reaction mixture in amounts indicated in the figures. In these experiments the reactants for the iodination were applied in a ratio assuming the following theoretical stoichiometry:

$$3\,H^+ + IO_3^- + 2\,I^- + 3\,MA \rightarrow 3\,IMA + 3\,H_2O \qquad (3)$$

To this end, 2.4 mL of solution (A) (containing 0.75 mmol MA and 0.25 mmol $NaIO_3$) was placed into thereactor, and 1.25 mL 0.4 M KI solution (i.e., 0.5 mmol KI) was pumped into the reactor with a constant flow rate of 62.5 μL/min for 20 min.

Figure 2b, Figure 3b, and Figure 4b show experiments analogous to those in part a of Figure 2, part a of Figure 3, and part a of Figure 4, respectively, except in the iodination the reactants were applied to meet the following stoichiometry:

$$6\,H^+ + 2\,IO_3^- + 4\,I^- + 3\,MA \rightarrow 3\,I_2MA + 6\,H_2O. \qquad (4)$$

To this end, 1.95 mL of solution (B) (containing 0.375 mmol MA and 0.25 mmol $NaIO_3$) was placed into the reactor, and 1.25 mL 0.4 M KI solution (i.e., 0.5 mmol KI) was pumped to the reactor with a constant flow rate of 31.25 μL/min for 40 min.

Originally, we expected that the iodination will follow the applied stoichiometry. However, in the first case, as our experiments (Figure 2a, Figure 3a, and Figure 4a) proved, the product was not pure IMA but a mixture of MA, IMA, and I_2MA. The last compound decarboxylates slowly, and this decarboxylation is the source of the CO_2 after the iodination is over.

Measurement of the CO_2 + CO Current During the Perturbation of the BR Reaction. The BR reaction was produced by the recipe described in our previous article.[26] Two mL of the BR reaction mixture was prepared this way. At 157 s after the start, the BR reaction was perturbed by injecting 0.5 mL 50 μM aqueous resorcinol solution. The flow rates of N_2 and H_2 were maintained at high values, 70 mL/min each of them, in the course of this measurement.

All kinetic measurements in Figures 2–5 were performed in a reactor thermostatted to 20 °C.

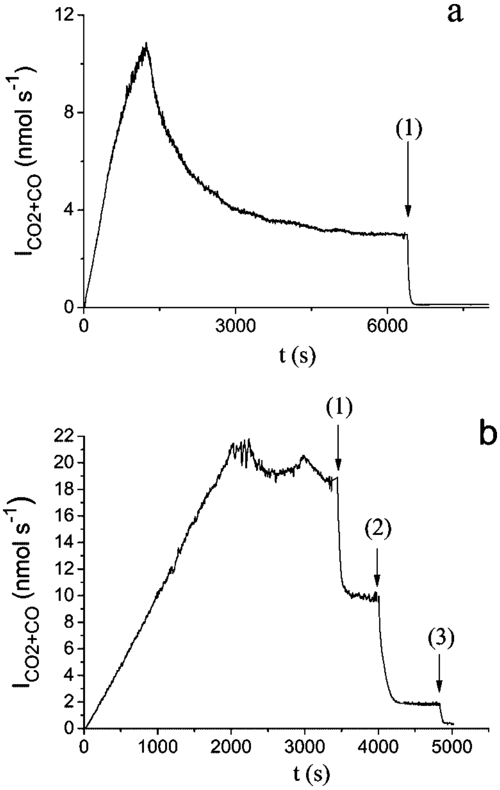

Figure 4. Reaction of I_2MA with ascorbic acid as indicated by the drop in the decarboxylation rate of I_2MA. At the time marked by ↓ different volumes of 0.5 M ascorbic acid in 0.5 M H_2SO_4 were added: (1) 0.15 mL, (2) 0.1 mL, and (3) 0.1 mL. The MA−IMA−I_2MA mixtures were produced for (a) and (b) like in parts a and b of Figure 2, respectively.

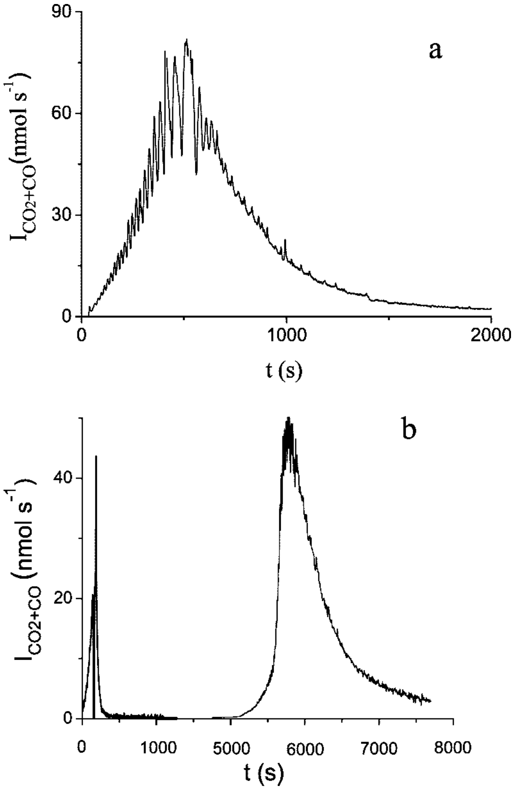

Figure 5. Perturbation of the BR reaction with resorcinol. Concentrations in the BR reaction at time zero: $[NaIO_3]_0 = 0.04$ M, $[MA]_0 = 0.05$ M, $[MnSO_4]_0 = 6.5$ mM, $[H_2O_2]_0 = 0.66$ M, $[H_2SO_4]_0 = 25$ mM. CO_2 + CO evolution (a) without perturbation, (b) with perturbation at $t = 157$ s followed by a long quiescent regime without any measurable CO_2 + CO evolution. Concentration of the perturbant in the reaction mixture right after its injection: 10 μM.

Results and Discussion

CO_2 and CO Evolution During and After the Iodination of MA and IMA. As the main motivation of our present research was to identify the CO_2 and CO generating reactions of the BR oscillator, we decided to check whether these gases do evolve during the iodination of MA by nascent iodine. To this end a MA−acidic iodate mixture was placed into a semibatch reactor and a continuous potassium iodide inflow was established with the aid of a peristaltic pump. (See the Experimental Section for concentrations and other parameters of the experiment.) During and after the iodide inflow the component currents I_{CO_2+CO}, or I_{CO} (CO_2 + CO or CO currents, respectively) leaving the reactor were recorded.[22] The result can be seen in parts a and b of Figure 2.

As it can be seen, a partial iodination of MA (part a of Figure 2) and especially its complete iodination to I_2MA (part b of Figure 2) is accompanied by CO_2 evolution and also by a relatively minor CO production. The small CO evolution can be observed mostly in the course of the iodination. This indicates that CO is probably produced when inorganic free radicals of the nascent iodine react with IMA. The mechanism of such a reaction, however, is not the subject of the present article. Here, we focus exclusively on the regime after the iodination, where the CO evolution is already insignificant.

When the iodination is stopped (at 1200 s in part a of Figure 2 and at 2400 s in part b of Figure 2 after the start of the experiment), CO evolution drops to a very low level but an intense CO_2 evolution continues, especially when the end-product of the iodination is I_2MA. This suggests that the source of CO_2 is the decarboxylation of I_2MA,

$$I_2MA \rightarrow I_2AcA + CO_2 \qquad \text{(R1)}$$

where I_2AcA denotes diiodoacetic acid. The hypothesis of the spontaneous decarboxylation of I_2MA is also supported by an analogous reaction of Br_2MA.[30] From part b of Figure 2, even k_1, the first-order rate constant of the I_2MA decomposition, can be determined by fitting an exponential decay curve to the I_{CO_2} versus time diagram after the iodination. The result is $k_1 = 9 \times 10^{-5}$ s^{-1}, which has the same order of magnitude as the analogous rate constant measured for the decarboxylation of Br_2MA.[30] (The final H_2SO_4 concentration in the I_2MA solution is 0.4 M. The rate constant of the Br_2MA decarboxylation at such a H_2SO_4 concentration is about 7×10^{-5} s^{-1}, according to Figure 1 in ref 30.)

If we accept that $k_1 = 9 \times 10^{-5}$ s^{-1} then n_{I_2MA}, the mole number of I_2MA in the reactor, can be calculated from I_{CO_2} using the following equation,

$$I_{CO_2} = \frac{dn_{CO_2}}{dt} = -\frac{dn_{I_2MA}}{dt} = k_1 n_{I_2MA} \qquad (5)$$

provided that no other CO_2 producing reaction occurs in the reactor.

Equilibrium 2 IMA ↔ I_2MA + MA. Reaction of I_2MA with MA. If we assume that the measured CO_2 current I_{CO_2} is due to the decomposition of I_2MA, then changes in the CO_2 evolution displayed in parts a and b of Figure 2 are to be explained on the basis of that assumption. To interpret the experiment shown in part b of Figure 2, no additional hypothesis is needed: first I_{CO_2} increases as more and more I_2MA accumulates in the reactor and when the iodination is over it slowly decreases due to the gradual decomposition of I_2MA. Less trivial is the interpretation of the curve in part a of Figure 2. First of all, we can see CO_2 evolution in this case too, indicating that the reaction mixture should contain not only IMA but also some I_2MA as well. Another interesting feature can be observed when the iodination is over: I_{CO_2} drops sharply and levels off at a lower intensity, which decreases further more slowly. Two additional hypotheses are required to understand these features:

i) The iodination of IMA should be considerably faster than that of MA (that would be an analogous behavior with the one observed when brominating BrMA, which is also a faster process than the bromination of MA[35]). As a consequence, at the end of iodination the product is not pure IMA but it is a mixture of MA, IMA, and I_2MA.

ii) I_2MA can react with MA to reach equilibrium in the MA−IMA−I_2MA mixture, and the equilibrium I_2MA concentration should be significantly lower than the initial I_2MA content of the reaction mixture right at the end of iodination.

To test the above two hypotheses, we performed experiments by adding malonic acid to the reaction mixtures of parts a and b of Figure 2 after waiting about 5000 s after the end of the iodination. The results of these experiments are shown in parts a and b of Figure 3. As it can be seen, both experiments justified our hypotheses: addition of MA drove the CO_2 evolution rate to a very low level, indicating that addition of MA influenced the

$$I_2MA + MA \leftrightarrow 2\ IMA \qquad (R2)$$

equilibrium in the expected way, driving the I_2MA concentration in the reactor to a very low level. It is rather probable that the positively charged iodonium ion (I^+) or its hydrated form or hypoiodous acid (in general: I(+1)) plays a role in the above process. I^+ transfer between double bonds was already reported.[36]

From our experiments, the rate constants k_2 and k_{-2} can be estimated in the following way. The equilibrium constant $K = k_2/k_{-2}$ can be determined from the quasi steady state CO_2 current $I_{CO_2} \approx 3.2$ nmol/s of part a of Figure 2, which corresponds to about 35 μmol I_2MA in the reactor. On the basis of component balances, the amount of MA should be also 35 μmol, and the amount of IMA can be calculated as $750 - 2 \times 35 = 680$ μmol. From these values $K \approx 380$.

k_2 can be estimated from the exponential decay of the CO_2 evolution starting after the injection of malonic acid, indicated by an arrow in part b of Figure 3. In that case, the rate constant k of the exponential decay (which is about 4.3×10^{-3} s^{-1} according to part b of Figure 3) can be approximated as,

$$k \approx k_1 + k_2[MA] \qquad (6)$$

where [MA] is the malonic acid concentration after the injection (about 0.068 M here). The above estimation yields $k_2 \approx 6.2 \times 10^{-2}$ M^{-1}s^{-1} and $k_{-2} \approx 1.6 \times 10^{-4}$ M^{-1}s^{-1}.

Evidence for I(+1) Dissociation from I_2MA: The I_2MA−Ascorbic Acid Reaction. In the previous paragraph, we discussed experiments proving a reaction between I_2MA and MA. A possible mechanism for such a reaction is the following scheme

$$I_2MA \leftrightarrow I(+1) + IMA \qquad (R2a)$$

$$I(+1) + MA \leftrightarrow IMA \qquad (R2b)$$

that is, we can assume I(+1) as an intermediate. (I(+1) stands for the sum of all iodine species in the +1 oxidation state. The question whether it is mostly HOI or H_2OI^+ or free iodonium ion is not studied here.) If some free I(+1) species can dissociate from I_2MA then that species should react also with reducing agents like ascorbic acid. In fact, the experiments shown in Figure 4 lived up to that expectation.

As Figure 4 shows I_{CO_2} sharply decreased after each addition of ascorbic acid, indicating a fast drop of the I_2MA concentration.

Complete Inhibition of the CO and CO_2 Evolution in the Briggs−Rauscher Reaction by Resorcinol. In the previous paragraphs we could see that decarboxylation of I_2MA can be a significant CO_2 source. It is also known that an intense CO and CO_2 evolution can be observed in the BR reaction.[26] That gas evolution has both an oscillatory and a nonoscillatory component. It was a logical hypothesis to assume that at least a part of the nonoscillatory CO_2 evolution is due to the decarboxylation of the I_2MA accumulating in the course of the BR reaction. Thus, we speculated that the accumulated I_2MA could be determined if we suppressed the oscillations and measured I_{CO_2} after that. Cervellati and co-workers[17] reported that, for example, resorcinol can inhibit the oscillations in the BR reaction, thus we applied that inhibitor. The experimental results are shown in Figure 5.

As Figure 5 shows during the inhibitory regime, both CO and CO_2 evolution rates were practically zero (below the measurability level). In other words, the I_2MA produced in the first 157 s of the BR reaction is below the detection limit of our technique (which is about 0.2 nmol CO_2 /s).

Whereas CO and CO_2 evolution was completely suppressed by resorcinol (at least within the experimental error) some other nonradical reactions should proceed during the inhibitory regime. This is indicated by the fact that the highest peak of the gas evolution after the inhibitory period is nearly two times lower than the highest peak in the case of the uninhibited BR reaction. The missing reactants are probably consumed by some nonradical reactions during the inhibition.

Implications for the Mechanism of the Briggs−Rauscher Oscillator

Here, we discuss briefly what type of conclusions can be drawn from our results for the BR reaction. While we think that these conclusions are logical and most probably correct, it is also obvious that further experiments are needed to prove them. Thus, the main aim of the questions and the possible answers discussed in this paragraph is to initiate further research in this field.

On the Possibility of I(+1) Reservoir Compounds. Our experiments prove that I(+1) can be transferred from I_2MA to MA. As it was shown, I_2MA can react also with ascorbic acid, indicating that I(+1) in I_2MA is available for other reactions as well. It is reasonable to assume that I(+1) in IMA behaves similarly like in I_2MA. I(+1) may dissociate from I_2MA and IMA in the form of HOI or H_2OI^+or I^+ (or in all three forms), and this free I(+1) is able to react with various other chemical species, not only with malonic and ascorbic acids.

Formation of IMA in the Briggs−Rauscher reaction was proven by spectrophotometry more than 20 years ago.[28] Usually, it is not considered to be an active intermediate, however. In most mechanistic schemes of the BR reaction (review of these schemes e.g. in ref 12), IMA is an inert end product of the reaction. The only exception is the mechanism of Vukojević, Sørensen, and Hynne,[12] where they assume the following reaction between IMA and H_2O_2:

$$2\,\mathrm{IMA} + \mathrm{H_2O_2} \rightarrow \mathrm{I_2} + \mathrm{U} \qquad \mathrm{(Q12)}$$

Here, (Q12) is the 12th reaction in their model "Q", and U denotes an unknown product.

If I(+1) can dissociate from IMA, then the role of IMA as an I(+) reservoir can be significant because I(+1) plays an important role in the mechanism of the BR reaction by removing $\mathrm{I^-}$ in reaction (Q3):

$$\mathrm{HOI} + \mathrm{I^-} + \mathrm{H^+} \rightarrow \mathrm{I_2} + \mathrm{H_2O} \qquad \mathrm{(Q3)}$$

IMA and $\mathrm{I_2MA}$ are probably not the only organic iodocompounds that can act as I(+1) reservoirs. A few years ago Furrow, Cervellati, and Amandori[16] have discovered some new substrates for the BR reaction. Among these were acrylic and crotonic acids, the double bond in which can react with I(+1) in a similar way like the double bond in the enol form of malonic and iodomalonic acids. Thus, it is possible that hydroxyiodinated[16] acrylic and crotonic acids can also act as I(+1) reservoirs.

What Are the $\mathrm{CO_2}$ and CO Generating Reactions in the BR Reaction? As we concluded from the experiment shown in Figure 5, the contribution of $\mathrm{I_2MA}$ decomposition to the $\mathrm{CO_2}$ and CO production observed in the BR reaction[26] is negligible. Thus, we have to find other $\mathrm{CO_2}$ and CO sources. Possible candidates are the oxidation reactions of MA and IMA by inorganic free radicals and maybe by manganese(III). Experiments are in progress to check these possibilities.

How Can Resorcinol Stop All Radical Reactions in a BR System? As Figure 5 shows, resorcinol as a radical scavenger is not only able to stop oscillations but also drives the $\mathrm{CO_2}$ and CO production below the detection limit. If we assume that $\mathrm{CO_2}$ and CO are generated by inorganic free radicals, then resorcinol should stop all these reactions for a long time. (Manganese(III) is also a product of inorganic free radicals, thus its any ability to produce $\mathrm{CO_2}$ and CO should also depend on the presence of these radicals.)

The fact that resorcinol can stop all radical reactions is somewhat surprising regarding its low concentration (10^{-5} M). In the mechanistic schemes of the BR reaction,[12] $\mathrm{HIO_2}$ molecules and $\mathrm{IO_2^\bullet}$ radicals are the autocatalytic species. $\mathrm{IO_2^\bullet}$ is formed in the following steps:

$$2\mathrm{H^+} + \mathrm{I^-} + \mathrm{IO_3^-} \rightarrow \mathrm{I_2} + \mathrm{HIO_2} \qquad \mathrm{(Q1)}$$

$$\mathrm{HIO_2} + \mathrm{IO_3^-} + \mathrm{H^+} \rightarrow 2\mathrm{IO_2^\bullet} + \mathrm{H_2O} \qquad \mathrm{(Q4)}$$

and to complete the autocatalytic cycle, $\mathrm{IO_2^\bullet}$ oxidizes $\mathrm{Mn^{2+}}$ to get back $\mathrm{HIO_2}$ again:

$$\mathrm{IO_2^\bullet} + \mathrm{Mn^{2+}} + \mathrm{H_2O} \rightarrow \mathrm{HIO_2} + \mathrm{Mn(OH)^{2+}} \qquad \mathrm{(Q6)}$$

Furrow, Cervellati, and Amandori[16] (FCA) suggested a second autocatalytic cycle also starting with $\mathrm{HIO_2}$, but in their additional cycle this species reacts with $\mathrm{H_2O_2}$ to produce $2\mathrm{HOO^\bullet}$ radicals according to reaction (FCA11):

$$\mathrm{HIO_2} + 2\,\mathrm{H_2O_2} + \mathrm{Mn^{2+}} \rightarrow 2\,\mathrm{HOO^\bullet} + \mathrm{HOI} + \mathrm{Mn^{2+}} + \mathrm{H_2O} \qquad \mathrm{(FCA11)}$$

Then, the protonated superoxide radical reacts with acidic iodate to give $\mathrm{IO_2^\bullet}$ radicals in (FCA12) (that reaction is also a part of model Q), which are reduced to $\mathrm{HIO_2}$ in reaction (FCA13) completing the autocatalytic cycle:

$$\mathrm{H^+} + \mathrm{IO_3^-} + \mathrm{HOO^\bullet} \rightarrow \mathrm{IO_2^\bullet} + \mathrm{H_2O} + \mathrm{O_2} \qquad \mathrm{(FCA12)}$$

$$\mathrm{IO_2^\bullet} + \mathrm{H_2O_2} \rightarrow \mathrm{HIO_2} + \mathrm{HOO^\bullet} \qquad \mathrm{(FCA13)}$$

With (FCA12) and (FCA13), $\mathrm{HIO_2}$ will be produced in a chain reaction, and this chain reaction will be amplified by the autocatalysis when one $\mathrm{HIO_2}$ generates two chain initiating superoxide radicals in (FCA11). According to FCA, inhibition of BR oscillations by resorcinol and other phenolic compounds can be explained by their ability to scavange the superoxide radicals in reaction (IN):

$$\mathrm{Ar(OH)_2} + \mathrm{HOO^\bullet} \rightarrow \mathrm{Ar(OH)O^\bullet} + \mathrm{H_2O_2} \qquad \mathrm{(IN)}$$

as it was suggested by Cervellati et al.,[20] where $\mathrm{Ar(OH)_2}$ indicates a generic diphenol.

The above theory gives a basis for the explanation of the inhibition of the second autocatalytic cycle. If there was an intense generation of $\mathrm{HIO_2}$ in the first autocatalytic cycle, however, then resorcinol would be consumed rather rapidly. This was not the case in our experiments: the inhibitory period lasted nearly two hours. Thus, to prevent the autocatalytic production of $\mathrm{HIO_2}$ and the free radicals, any outer source for $\mathrm{HIO_2}$ should be extinguished. This outer source is the reaction (Q1) of $\mathrm{I^-}$ with iodate. In fact, according to the experiments of Cervellati et al.[17] the $\mathrm{I^-}$ level during the inhibition period is very low. The ion-selective electrode indicates an iodide concentration around 10^{-9} M, which is much below the solubility limit of a AgI electrode. In this case, the electrode measures[37] the concentration of HOI and not of $\mathrm{I^-}$, thus the actual $\mathrm{I^-}$ concentration can be even smaller.

Thus, resorcinol can keep somehow the concentration of $\mathrm{I^-}$ at a low level. Naturally, HOI and I(+1) reservoirs could keep this low iodide via reaction (Q3) rather easily, except some $\mathrm{I^-}$ inflow removes most of the I(+1). Consequently, it is possible that resorcinol can control that minute $\mathrm{I^-}$ inflow. Resorcinol as a radical scavenger cannot react with $\mathrm{I^-}$ ions but it can easily capture free iodine atoms. If $\mathrm{I^\bullet}$ is an intermediate when I(+1) is reduced to $\mathrm{I^-}$, then resorcinol is able to control the $\mathrm{I^-}$ inflow. Thus, we propose the following two-step hypothetical mechanism:

$$\mathrm{HOI} + \mathrm{H_2O_2} \rightarrow \mathrm{I^\bullet} + \mathrm{HOO^\bullet} + \mathrm{H_2O} \qquad \mathrm{(H1)}$$

$$\mathrm{I^\bullet} + \mathrm{H_2O_2} \rightarrow \mathrm{I^-} + \mathrm{HOO^\bullet} + \mathrm{H^+} \qquad \mathrm{(H2)}$$

It is worth to mention that the sum of the above two-step mechanism together with (Q8)

$$2\,\mathrm{HOO^\bullet} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad \mathrm{(Q8)}$$

gives (Q10):

$$\mathrm{HOI} + \mathrm{H_2O_2} \rightarrow \mathrm{I^-} + \mathrm{H^+} + \mathrm{H_2O} \qquad \mathrm{(Q10)}$$

(Q10) plays a role in all known mechanistic schemes[12] of the BR reaction.

As step (H1) requires the simultaneous emergence of two radical species from molecular precursors, most probably it is the rate determining reaction. If the produced $\mathrm{I^\bullet}$ atom is scavenged by resorcinol, then the iodide source is blocked.

A possible mechanism of the iodine atom removal can be its reaction with the $\mathrm{Ar(OH)O^\bullet}$ radical in (H3),

$$\mathrm{I^\bullet} + \mathrm{Ar(OH)O^\bullet} \rightarrow \mathrm{IAr(OH)_2} \qquad \mathrm{(H3)}$$

where $\mathrm{IAr(OH)_2}$ is an iodinated generic diphenol, here iodoresorcinol. In this respect, it is interesting to mention that Weitl[32] was able to perform 2,4-diiodination of resorcinol with nascent iodine. Iodo- and 2,4-diodoresorcinol can participate in reactions analogous to (IN) and (H3), thus these intermediates should still be regarded as radical scavengers. The inhibitiory regime in the BR reaction is over when the added resorcinol is converted mostly to 2,4,6-triiodoresorcinol.

Thus, as we could see, the bottleneck of the whole autocatalytic radical multiplication is the iodine atom production in (H1), which can be blocked by resorcinol and by other phenolic type radical scavengers. To achieve a complete halt of the autocatalytic processes, however, these radical scavengers should also react with $IO_2^\bullet$ radicals. Further experimental work should prove or disprove the above hypotheses.

Acknowledgment. This work was partially supported by OTKA grant K-60867, CNCSIS Romanian grant AT-164, the Bilateral Hungarian-Romanian Science and Technology Foundation RO-31/2005, and the ESF Programme Functional Dynamics. The authors thank István Bitter for helpful discussions.

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JP8064163