Iodomalonic Acid as an Anti-Inhibitor in the Resorcinol Inhibited Briggs−Rauscher Reaction

Thuy Lawson,[†] János Fülöp,[†] Maria Wittmann,*[,†] Zoltán Noszticzius,[†] Norbert Muntean,[‡] Gabriella Szabó,[‡] and Lavinia Onel[§]

Center for Complex and Nonlinear Systems and the Department of Physics, Budapest University of Technology and Economics, H-1521 Budapest, Hungary, Department of Physical Chemistry, Babeş-Bolyai University, RO-400028 Cluj-Napoca, Romania, and Faculty of Chemistry, Al.I.Cuza University, RO-700506 Iaşi, Romania

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It was found that the inhibitory effect of resorcinol is less pronounced if it is added in a later stage of the Briggs−Rauscher reaction, which indicates that an accumulating intermediate—most probably iodomalonic acid—can suppress the inhibition. In fact, when iodomalonic acid was added to the reaction mixture, the inhibitory period was shortened considerably even at micromolar levels of the iodomalonic acid concentration. Moreover, iodomalonic acid can accelerate the rate of the reaction when applied in the same low concentrations, suggesting that it can be an autocatalytic intermediate of the Briggs−Rauscher reaction.

Introduction

The Briggs−Rauscher (BR) reaction, one of the few reactions showing long-lived oscillations under batch conditions, was discovered by Briggs and Rauscher.[1] Its classical version is the oscillatory oxidation and iodination of malonic acid (MA) by hydrogen peroxide and iodate catalyzed by Mn^{2+} ions in an acidic medium. The reaction was studied by many research groups, including the ones led by Noyes, Furrow, Cervellati, and Sørensen,[2−10] just to mention a few. Oscillations can be demonstrated by vivid color changes in the presence of a starch indicator, and usually they are monitored by recording platinum or iodide selective electrode potentials.

Several chemical models[2−7,10−12] have been constructed to explain the observed oscillations of the iodine species. All of these models are based mostly on the reactions of inorganic species, and the only role attributed to the organic substrate is to act as an iodine sink:

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

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

where IMA stands for iodomalonic acid.

Other reactions of IMA in the BR are usually neglected. The only exception is a work by Vukojevic et al.[6] They assumed an overall process with the following stoichiometry:

$$2\ \mathrm{IMA} + \mathrm{H_2O_2} \rightarrow \mathrm{I_2} + \mathrm{U}$$

where U stands for unidentified products.

Recently, however, it was discovered[13] that a periodic CO_2 and CO evolution occurs in the BR reaction. This observation makes it clear that the organic substrate is not only iodinated but also oxidized. It was found[14] that the source of CO_2 and CO is IMA. Moreover, it was suggested[14] that CO_2 and CO are decarboxylation and decarbonylation products of organic free radicals formed from IMA.

IMA can participate also in other reactions. For example, in a previous work[15] we found that IMA can disproportionate to diiodomalonic acid (I_2MA) and MA. This ability of IMA to transfer I(+1) to another molecule also suggests that IMA might play a more active role in the BR mechanism than was suspected previously.

Another phenomenon where IMA might play a role is the inhibition of the BR reaction. It is known[9,16] that when a phenolic antioxidant is added to the BR reaction the oscillations can be suppressed for a while or even completely, depending on the concentration of the inhibitor. The inhibition time can be used to determine the concentration of the antioxidant as well. To study this phenomenon, in a previous work[15] we added resorcinol to the classical BR reaction. We found a complete inhibition of the CO_2 and CO evolution in the inhibitory period. It is quite possible that IMA is able to iodinate resorcinol by an I(+1) transfer. If this working hypothesis is true, then the inhibitory effect of resorcinol in the BR could be attributed to its reaction with IMA, which eliminates IMA by transforming it back to MA.

All the above speculations suggest that IMA might be a kinetically important intermediate of the BR reaction. The aim of the present paper is to check these hypotheses with various experiments. To this end we performed three different series of experiments. In the first series we added resorcinol to the BR reaction at different times. As IMA accumulates in the initial phase of the BR reaction, we expected that a later addition of resorcinol during this phase will have less effect because according to our hypothesis the inhibition is due to a removal of IMA by resorcinol. In the second series of experiments, we added IMA to a BR system inhibited by resorcinol. The aim of these experiments was to show that the addition of IMA is able to shorten or even eliminate completely the inhibitory effect of resorcinol. Finally, we added IMA to an unperturbed BR system to study whether IMA can really accelerate the reaction.

* To whom correspondence should be addressed. E-mail: wittmann@eik.bme.hu.
[†] Budapest University of Technology and Economics.
[‡] Babeş-Bolyai University.
[§] Al.I.Cuza University.

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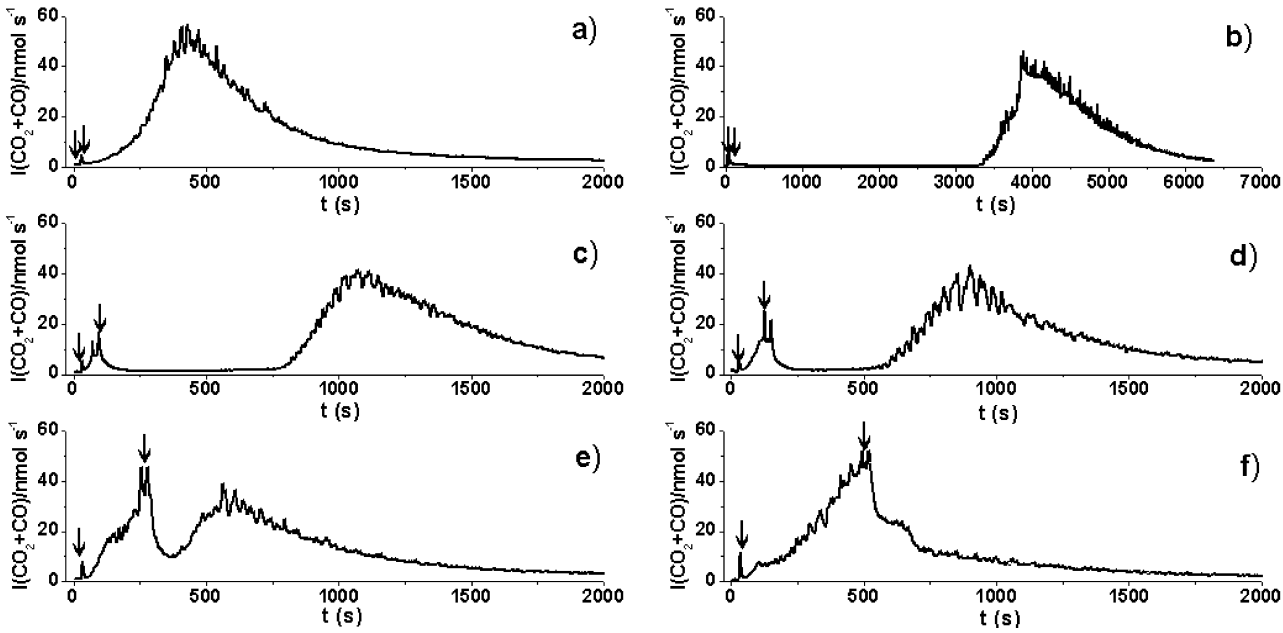

Figure 1. Inhibitory effect of resorcinol applying different injection times. (a) Standard BR reaction; its composition is given in the Experimental Section. (b−f) At the times indicated by arrows in the figures, 0.3 mL of 50 μM resorcinol solution was added. The resulting initial concentration of resorcinol in the BR solution was 6.5 μM. The time of injection was (b) 30 s, (c) 60 s, (d) 2 min, (e) 4 min, and (f) 8 min.

Experimental Section

Chemicals. Malonic acid (Fluka, puriss.), $NaIO_3$ (Fluka, puriss. p.a.; ≥99.5%), KI (Riedel-deHaën, puriss. p.a.), resorcinol (Sigma-Aldrich, ReagentPlus, 99%), H_2SO_4 (97%, Merck, p.a.), $MnSO_4$*$4H_2O$ (Reanal, a.lt.), and H_2O_2 (Fluka, puriss. p.a. ACS; ≥30%) were used as received. All solutions were prepared with doubly distilled water.

Preparation of Iodomalonic Acid. Iodomalonic acid was prepared by the method of Noszticzius et al.[17] The resulting solution contains also some MA to increase the stability of IMA which would dissociate in a pure solution.[15] Stock solution "IMA" was prepared in the following way: first 6 mL of 1 M MA, 1.2 mL of 5 M H_2SO_4, and 5 mL of 0.2 M $NaIO_3$ were mixed in a 25 mL beaker, and then 5 mL of 0.4 M KI solution was added dropwise from a buret into the solution under continuous stirring. After each drop of the KI solution, we waited several seconds until the brown color of iodine disappeared. As a result a 1:1 mixture of MA and IMA was obtained with [IMA] = [MA] = [H_2SO_4] = 174 mM. (Beside these components the mixture also contains sodium and potassium hydrogen sulfate in the same total concentration [$NaHSO_4$] + [$KHSO_4$] = 174 mM.) This solution was prepared each day freshly and kept in the refrigerator if not used immediately. As in most cases IMA was applied in minute concentrations in the BR, this solution was further diluted to the following concentrations: IMA(1) 8.7 μM; IMA(2) 87 μM; IMA(3) 870 μM; IMA(4) 40 mM; IMA(5) 0.1 M.

Recipe for the Briggs−Rauscher Reaction Used in Our Experiments−Our "Standard" BR Reaction (Figure 1a). One milliliter of a 0.16 M $NaIO_3$ solution, 1 mL of solution containing 26 mM $MnSO_4$ and 0.2 M MA, and 1 mL of 0.1 M H_2SO_4 were mixed in a beaker. An amount of 1.5 mL of this mixture was put into the reactor, and the reaction was started by injecting 0.5 mL of 2.64 M H_2O_2. The initial concentrations of the BR reaction were [$NaIO_3$] = 0.04 M, [MA] = 50 mM, [$Mn(SO_4)$] = 6.5 mM, [H_2O_2] = 0.66 M, and [H_2SO_4] = 25 mM.

Briggs−Rauscher Reaction with IMA + MA Mixed Substrates. IMA was applied in concentrations from 1.1 μM to 25 mM while the total substrate concentration was kept constant, i.e., [IMA] + [MA] = 50 mM in all cases. All other concentrations were the same as for the standard BR. In the experiments depicted in Figures 2 and 3, in the cases of (b), (c), and (d) 1 mL of 0.16 M $NaIO_3$, 1 mL of 26 mM $MnSO_4$ containing also 0.2 M MA, 0.2 mL of 0.5 M H_2SO_4, and 0.3 mL of distilled water were mixed with 0.5 mL of IMA(1) or IMA(2) or IMA(3) solution ([IMA] = [MA] = 8.7, 87, 870 μM), respectively. In case of Figures 2e and 3e, 0.5 mL of 0.32 M $NaIO_3$, 0.5 mL of 52 mM $MnSO_4$, 0.4 mL of 0.4 M MA, 0.5 mL of IMA(4) solution ([IMA] = [MA] = 40 mM), 0.4 mL of 0.2 M H_2SO_4, and 0.7 mL of distilled water were mixed, while in case of Figures 2f and 3f 1 mL of 0.16 M $NaIO_3$, 1 mL of 26 mM $MnSO_4$, and 1 mL of IMA(5) solution ([IMA] = [MA] = 0.1 M) were mixed. In all cases 1.5 mL of the total 3 mL was poured in the reactor, and the reaction was started by the injection of 0.5 mL of 2.64 M H_2O_2. The resulting concentrations can be found in the figure captions.

Resorcinol Solution. First a 0.1 M solution of resorcinol in distilled water was prepared which was diluted in four steps to reach the desired 50 μM concentration. An amount of 0.3 mL of this solution was injected into the reactor by a syringe. The resulting concentration of resorcinol in the BR solution was 6.5 μM. The time of addition is varied in Figure 1, while in Figure 2 resorcinol was always injected 60 s after the start of the BR reaction.

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.[13,15,18] Briefly, CO_2 and CO were stripped from the reaction mixture by a N_2 gas flow and were mixed with H_2. Then CO_2 and CO were converted to methane in a catalytic reactor, and the produced CH_4 was measured by a flame ionization detector (FID). A CO_2 or CO injection caused a FID current pulse after a 30 s delay at the applied gas flow rates. Arrows indicating the injection time in the figures point to times corrected with that time delay (e.g., an arrow points to 130 s if the injection is made at 100 s). Other details of our CO_2/CO measuring apparatus and method can be found in ref 18. The H_2 flow rate was 40 mL/min and the N_2 flow rate was 80 mL/min in the present experiments. Moreover,

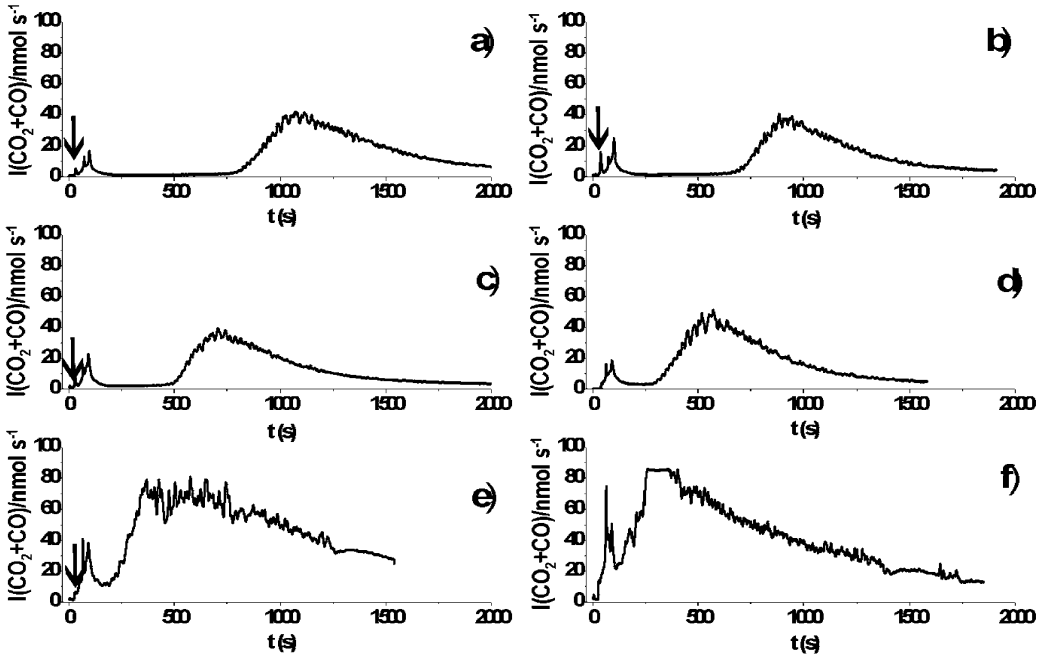

Figure 2. Anti-inhibitory effect of IMA. Figure 2a is a reference; it is the same as Figure 1c. In experiments depicted in (b−f) an increasing amount of IMA was added at time zero to our standard BR system keeping the total concentration of the organic substrates constant: (b) [MA] = 50 mM, [IMA] = 1.1 μM; (c) [MA] = 50 mM, [IMA] = 11 μM; (d) [MA] = 50 mM, [IMA] = 0.11 mM; (e) [MA] = 45 mM, [IMA] = 5 mM; (f) [MA] = 25 mM, [IMA] = 25 mM. In all cases 60 s after the start of the BR reaction 0.3 mL of 50 μM resorcinol was injected to the BR solution.

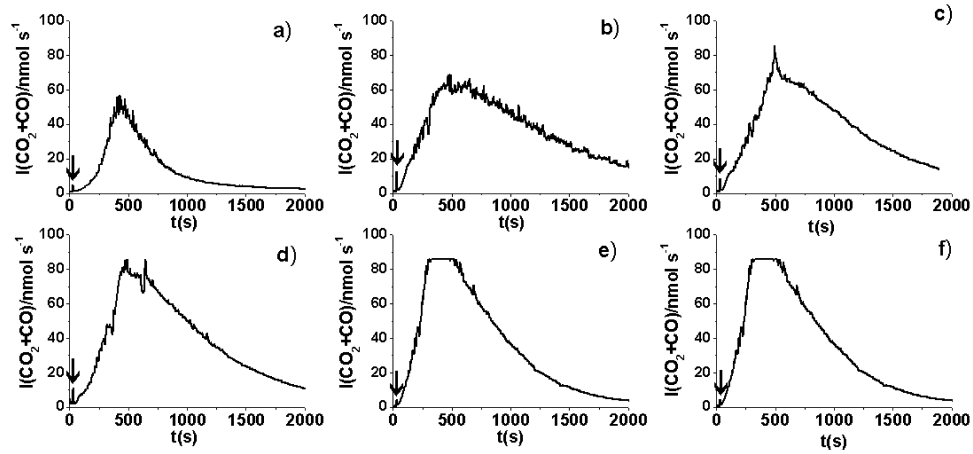

Figure 3. Effect of iodomalonic acid on the BR reaction. (a) Standard BR reaction; (b−f) the same BR reaction but with IMA + MA mixed substrate. Concentrations are the same as in Figures 2b−f, but no resorcinol was added.

the N_2 flow was split: only 16% of the 80 mL/min was mixed with H_2; otherwise, the signal would have been too high. The reactor was stirred with a magnetic stirring bar. The stirring rate was 500 rpm. In our previous papers the stirring rate was 1200 rpm. The 500 rpm applied in the present experiments made the CO_2/CO evolution faster and the signal higher in the initial period of the BR reaction. This is because the stirring rate affects the transport of iodine from the liquid to the gas phase, and this way it can affect the iodine concentration in the reactor and consequently also the reaction rate.

Results and Discussion

In the first series of experiments, it was investigated whether the inhibitory effect of resorcinol depends on the time when it is added to the BR system. In Figure 1 a standard oscillatory BR system (Figure 1a) is compared with those which are perturbed by resorcinol (Figures 1b−f). The amount of the added resorcinol was the same, but the time of addition was varied from 30 s to 8 min. Experiments were started by injecting the H_2O_2 solution into the reactor that already contained all other components of the BR reaction (indicated by the first arrow in Figure 1). Observe that at the beginning of each curve a small peak can be seen at around 30 s. This peak is due to the CO_2 dissolved in the H_2O_2 solution, which CO_2 needs about 30 s to reach the FID through the tubings with the N_2 stream. So, this peak indicates the starting time of the reaction. A similar small peak appears on each curve when resorcinol is added.

In the standard BR reaction (Figure 1a), the CO_2/CO evolution reaches its maximum at about 450 s, and then it decreases first rapidly and then after ~900 s more gradually toward zero. In Figure 1b resorcinol is injected practically at the beginning of the BR reaction (at 30 s). This suppresses the gas evolution for more than 3000 s. Note that in Figure 1b the time scale goes up to 7000 s, while in all other figures it ends at 2000 s.

By adding the resorcinol later, its inhibitory effect decreases. When resorcinol is added in a relatively early stage of the

reaction (at 60 s like in Figure 1c or 120 s like in Figure 1d), the gradual increase in the CO_2 evolution suddenly stops and drops to zero, but the course of the reaction when the inhibition is over is qualitatively similar to the original one with the maximum shifted to approximately 1100 or 900 s. However, when resorcinol is added after 4 or 8 min (Figures 1e and 1f, respectively), the decrease in the gas evolution starts only about 1 min after the addition of resorcinol, and it does not drop to zero. This series of experiments clearly shows that resorcinol has the stronger effect the sooner it is added.

Our hypothesis to explain this trend was that in the course of the reaction some intermediate accumulates that destroys the effect of resorcinol. As our candidate for this intermediate was iodomalonic acid, in the next series of experiments we added IMA to the BR reaction in increasing concentration. The concentration of IMA was chosen so that the total substrate concentration remained constant; i.e., [IMA] + [MA] = 50 mM in all cases. The lowest concentration of IMA was 1.1 μM, which is ~6 times smaller than the concentration of resorcinol (6.5 μM), while the highest was 25 mM, which was limited as otherwise the disproportionation of IMA would be disturbing. The reaction was started by adding H_2O_2 to a mixture of IMA and MA with the other BR components. Resorcinol was added always at the same time, 60 s after the start of the reaction.

Figure 2 shows the results of these experiments. Figure 2a is identical with Figure 1c; the experiment containing no IMA is repeated here to show how long the oscillations and the gas evolution are inhibited by the addition of resorcinol at 60 s. Adding IMA to the reactants has an effect even when its concentration is smaller than that of resorcinol, as it can be seen in Figure 2b. With increasing IMA concentration the inhibition time due to resorcinol decreases. At medium IMA concentrations (Figures 2c and 2d), the inhibition period becomes considerably shorter and the course of the reaction follows the one without IMA. However, at higher IMA concentrations (Figures 2e and 2f), the intensity of the gas evolution and also the total quantity of the evolved CO_2/CO greatly increases. By zooming on the first 1−2 min of the curves of the Figures 2e and 2f, it can be seen that an increase in the CO_2 production already occurs at the beginning of the reaction, before the addition of resorcinol.

This observation initiated the next series of experiments depicted in Figure 3. Here no resorcinol was added; the effect of IMA was investigated exclusively. In Figure 3 all the compositions at time zero were the same as in Figure 2. Figures 3a−f show that increasing the initial IMA concentration makes the maximum gas evolution rate higher, and in addition it increases the total amount of the evolved CO_2/CO. It is interesting to note that while the maximum gas evolution rate increases gradually with the increasing IMA concentration, the total CO_2/CO amount is approximately independent of the quantity of IMA.

Conclusions

1. Addition of IMA accelerates the CO_2/CO evolution rate considerably (see Figure 3), proving that iodomalonic acid is an important intermediate of the BR reaction.

2. Iodomalonic acid can counterbalance or even eliminate the inhibitory effect of resorcinol (see Figure 2). Iodomalonic acid is kinetically effective in such experiments even at concentrations lower than that of resorcinol.

3. The inhibitory effect of resorcinol decreases rapidly if it is added to the BR mixture in a later phase of the reaction (see Figure 1). That decrease can be also explained by the counterbalancing effect of IMA which accumulates in the course of the BR reaction.

Summarizing conclusions 1−3, as IMA is produced in the BR reaction and is also able to accelerate the reaction rate, we can state that IMA is a kind of autocatalytic intermediate of the BR reaction.

Open Problems and Hypotheses

1. The inhibitory effect of resorcinol is most probably exerted by its ability to remove IMA. A straightforward possibility is that resorcinol is iodinated by IMA, and this way the latter is transformed back to MA. Experiments are in progress to check this hypothesis.

2. As it is known,[15] IMA can iodinate another IMA suggesting that an iodinating inorganic I(+1) species might be present in a dissociation equilibrium together with IMA. At this stage of the research it is not clear whether IMA itself or an inorganic I(+1) species (like HOI or iodonium ion) is the kinetically important intermediate in the BR reaction. This is another open problem what we are planning to study experimentally.

In this respect it is interesting to mention the work of Noyes and Furrow.[19] They found that phenols are able to inhibit the oxygen evolution even in the $H_2O_2 + IO_3^- + Mn^{2+}$ inorganic subsystem. As phenols are very effective I(+1) scavengers, their result suggests that I(+1) has an important kinetic role. If that is true, then IMA and analogous iodinated compounds play the role of reversible I(+1) reservoirs. (It is known that various organic compounds can serve as BR substrates; see, e.g., Furrow.[20]) All these speculations, however, should be checked by further experiments.

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