

Experimental and Mechanistic Investigation of an Iodomalonic Acid-Based Briggs–Rauscher Oscillator and its Perturbations by Resorcinol

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Classic Briggs–Rauscher oscillators use malonic acid (MA) as a substrate. The first organic product is iodomalonic acid. Iodomalonic acid (IMA) can serve as a substrate also; thus, the first product in that case is diiodomalonic acid (I₂MA). Nonoscillating iodination kinetics can be followed by absorbance at 462 nm in acidic KIO₃ so long as IMA is in substantial excess over [I₂]. At 25 °C, simulations lead to the two most important rate laws, and related rate constant estimates are reported. I₂MA eventually decomposes by unknown processes, but I₂, O₂, H₂O₂, and Mn²⁺ speed up that decomposition, liberating most of the iodine back to the solution. Resorcinol is an effective inhibitor of oscillations both in MA oscillators and in IMA oscillators. Response of an IMA oscillator to varying amounts of resorcinol is shown herein and is similar to that for MA-based oscillators. The inhibitory effect of resorcinol is diminished by addition of IMA to a MA-based oscillator. The iodination reaction between IMA and resorcinol is too slow (0.043 M⁻¹ s⁻¹) to account for the decreased inhibitory effectiveness of resorcinol. Rather, the decomposition of I₂MA is responsible for the inhibition decrease.

Introduction

Very recently the chemistry of monoiodomalonic acid (IMA) in the Briggs–Rauscher (BR) oscillator¹ and in its subsystems has attracted renewed interest because new experimental evidence showed that IMA could be an intermediate of the classic malonic acid (MA)-based BR oscillator.^{2,3} Indeed, except for an early paper by Vanag,⁴ all the mechanisms proposed for the MA-based oscillating reaction considered IMA as an end product of this reaction (oxidation and iodination of MA by acidic iodate in the presence of H₂O₂ catalyzed by Mn(II) ion).^{5–8}

The fact that IMA can serve as a substrate for an oscillator⁹ shows that IMA cannot be the final product of the reaction. Since the initial iodination product of IMA is diiodomalonic acid (I₂MA), the unperturbed IMA oscillator opens a window to the later stages of the MA-based oscillator, where initially the only product would be IMA. We intend to show that I₂MA reacts rapidly in an acidic-IO₃⁻-Mn²⁺-H₂O₂ environment, returning I⁻ and I₂ to the solution, thereby strongly affecting oscillations, and causing the IMA-based oscillator to “end” in a state of high [I⁻] and high [I₂].

Ultimately, a model for the MA- or IMA-based oscillator will need rate constants for iodination of IMA and decomposition of I₂MA. A preliminary investigation is reported here.

Further comparison of MA-based and IMA-based oscillators is based on the effect of resorcinol on each. Inhibition of the oscillatory regime of a MA-based BR oscillator by addition of resorcinol and other substituted diphenols was found and investigated in detail by Cervellati et al.^{10,11} They ascribed these inhibitory effects to the scavenging action of a phenolic –OH group against hydroperoxyl radicals HOO[•], an important intermediate in the BR reaction.¹² We report here further experimental and mechanistic investigation on an unperturbed

IMA-based BR oscillator and comparison of an IMA oscillator perturbed by resorcinol. Lawson et al.² reported that in a MA-based BR oscillator perturbed by resorcinol (Re), (1,3-dihydroxybenzene), IMA could act as an “anti-inhibitor”, that is, diminish or even eliminate the inhibitory effect of resorcinol. We will show that IMA acts as an anti-inhibitor because it is iodinated to I₂MA, which then breaks down to form I₂ and I⁻, rather than react with resorcinol directly.

Materials and Methods

IMA was prepared and purified as dipotassium salt as reported by Conrad and Reinbach¹³ and Mahon and Smith.¹⁴ The purity of the synthesized compound was checked by UV–vis and NMR spectroscopy. I₂MA was prepared using stoichiometric amounts of iodine, malonic acid and iodic acid in 90% formic acid. Commercial chemicals were malonic acid (Merck >99%), sublimed iodine (Carlo Erba, >99%) further purified by double sublimation, manganese(II) sulfate monohydrate (Merck; >99%), NaIO₃ (Merck; >99.5%), and resorcinol (1,3-benzenediol, SigmaUltra; >99%). HClO₄ (Merck; 70–72%) and H₂O₂ (Merck; 35–36.5%) were of analytical grade. Iodic acid (Alfa Aesar; 99.5%) and formic acid (Fisher; 90% solution) were used without further purification. Perchloric acid was analyzed by titration versus a standard 0.1 M NaOH solution (from Merck). H₂O₂ was standardized daily by manganometric analysis. Oscillations in the BR mixtures were followed potentiometrically by recording the potential of the solution with a bright-Pt electrode (Hamilton, model P/N 238 945) - reference electrode (double-junction Ag/AgCl electrode, Ingold, model 373–90-WTE-ISE-S7).

Electrodes were connected to a pH multimeter (Eutech Instr., model Cyberscan pH2100) controlled by an IBM-compatible PC. The accuracy of the multimeter was ±1 mV. A suitable data-acquisition program furnished by Eutech Instr. was used. BR mixtures for resorcinol inhibition were prepared by mixing

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TABLE 1: IMA Oscillators with Initial I₂MA

[IMA] (M)	[I ₂ MA] (M)	No. of oscillations	time (s) from mixing to transition to state II
0.0062	0	12	450
0.0062	0.0026	3	180
0.0062	0.0030	3	160
0.0062	0.0040	0	90
0.0052	0.0010	3	180
0.0042	0.0020	2	100
0.0036	0.0025	0	30

the appropriate amounts of stock solutions of reagents using pipets or burets in a 100 mL beaker to a total volume of 30 mL. The order of addition was: IMA (as dipotassium monoiodomalonic), MnSO₄, HClO₄, NaIO₃, and H₂O₂. Oscillations started after the addition of H₂O₂. All solutions and reaction mixtures were maintained at constant temperature by means of a suitable thermostating system (accuracy ±0.1 °C). Inhibitory effects by resorcinol were studied by adding 1.0 mL of suitably diluted solution of resorcinol to 30 mL of an active BR mixture after the first oscillation.

Spectrophotometric data were acquired with a Shimadzu model 1501 with a thermostatted cell compartment at 25 °C. NMR spectroscopy was performed at ambient temperature on a 300 MHz Bruker Avance Microbay spectrometer equipped with a 5 mm H–X ATM broadband probe and a deuterium lock channel. The excitation field strength for ¹H spectra was 18.5 kHz.

Results and Discussion

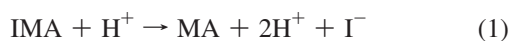
Vanag⁴ has characterized the end state of MA-based batch BR oscillators as either state (I) (low [I[−]] and [I₂]), or state (II) (high [I[−]] and [I₂]), in correspondence with steady states found in flow reactors. The attained state depends largely on the ratio of [MA]₀ to [IO₃[−]]₀. High ratios (>approximately 2:1) tend toward state (I). MA-based oscillators with lower ratios end at state (II) following an autocatalytic production of I[−] and I₂. With IMA-based oscillators, the end state seems always to be state (II).

With IMA-based oscillators having some initial I₂MA (generated in situ by slow addition of KI solution, added before H₂O₂), the number of oscillations is either reduced or none are seen, and there is immediate transition to state (II). Examples are shown in Table 1 for the specific system [HClO₄] = 0.10 M, [KIO₃] = 0.020 M, [MnSO₄] = 0.0020 M, [H₂O₂] = 1.50 M.

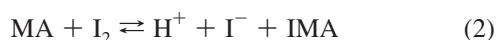
The higher the [I₂MA] or the higher the ratio of [I₂MA] to [IMA], the fewer number of oscillations and shorter time before transition to state (II). These facts suggest that attainment of state (II) is due mainly to the decomposition of I₂MA.

Reactions of Mono- and Di-iodomalonic Acid. Several possible reactions of IMA and I₂MA that could occur in the unperturbed oscillator have been studied:

IMA in Acid Solution. IMA is fairly stable in neutral solution, but in acid it slowly releases I[−], which can be followed with an I[−] sensitive electrode. (What appears to be a reaction of IMA could be actually due to I₂MA. See IMA Disproportionation, below).



The I[−] reacts with IMA by the reverse of reaction 2



This equilibrium proceeds via the enolic form of malonic acid.¹⁵ The I[−] and I₂ form triiodide.



In a spectrophotometer I₂ can be followed at 462 nm and I₃[−] at 353 nm. The reaction with acid was found to be slow.³ Reaction 1 is too slow to be of significance in the oscillating systems.

IMA Disproportionation. IMA cannot be studied in isolation from I₂MA, since some I₂MA will always be present.¹⁶

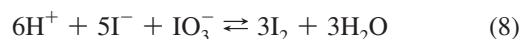


I₂MA Decarboxylation. If no other reaction took precedence, diiodoacetic acid (I₂AA) would be formed.¹⁶



Not much I₂AA is observed, however, at the end of MA or IMA oscillations.³ Onel et al.¹⁶ have shown that this decarboxylation is *not* responsible for the bulk of CO₂ produced during oscillations. The major organic end product from the oscillators is oxalic acid along with CO₂. With IMA-based oscillators, solid I₂ and I[−] are present (state II), sometimes with a delay after oscillations cease.

Iodination of IMA. Presumably the enolic form of IMA is an intermediate in this reaction. In the presence of IO₃[−] to remove I[−], the kinetics of this reaction may be followed spectrophotometrically.



The above reactions are predominant only when IMA is in large excess over I₂ or if [IO₃[−]] is high enough to keep I[−] low. In fact, as soon as I₂MA forms, it begins to decompose, returning some I₂ into the solution. Caution is necessary because IMA and I₂MA are both photosensitive. Further reactions are necessary to describe I₂MA decomposition. To date, attempts to model that decomposition have been unsuccessful.

When there is a substantial excess of IMA over I₂MA formed, it is possible to model the initial stages of iodination of IMA, using reactions 2–7, with component parts of reaction 8, and neglecting I₂MA decomposition. We have examined iodination at two acidities in the presence of KIO₃ to keep [I[−]] low and allow the iodination to proceed to near completion. Reactions and assumed rate constants are shown in Table 2.

Absorbance at 462 nm was followed versus time with intermittent readings to minimize exposure to light. The COPASI²² simulation program was used for integration of the rate equations and for determination of the parameters *k*₆, *k*_{−6}, and *k*_{−7}. The value for *k*₇ was arbitrarily assumed as 2 × 10⁶ M^{−1}s^{−1}. This is close to the value assumed for bromination of MA enol.²³ Rates for iodination and bromination have been reported to be nearly the same.²⁴ Extinction coefficients used at 462 nm were 746 M^{−1} cm^{−1} for I₂, and 975 M^{−1} cm^{−1} for I₃[−].²⁵ For five runs at [HClO₄] = 0.028M, [IMA] from 0.0041

TABLE 2: Reactions and Rate Constants used for Simulation of IMA Iodination

number	reaction	rate law	ref
2A	$MA \rightarrow MA\text{-enol}$	$0.0039 [MA]$	17
-2A	$MA\text{-enol} \rightarrow MA$	$91 [MA\text{-enol}]$	17
2B	$MA\text{-enol} + I_2 \rightarrow IMA + H^+ + I^-$	$9.1 \times 10^5 [MA\text{-enol}][I_2]$	17
-2B	$IMA + H^+ + I^- \rightarrow MA\text{-enol} + I_2$	282	17
3	$I_2 + I^- \rightarrow I_3^-$	$6.08 \times 10^9 [I_2] [I^-]$	18
-3	$I_3^- \rightarrow I_2 + I^-$	$8.5 \times 10^6 [I_3^-]$	19
4	$2IMA \rightarrow MA + I_2MA$	$0.062 [IMA]^2$	16
-4	$MA + I_2MA \rightarrow 2IMA$	$0.00016 [MA][I_2MA]$	16
5	$I_2MA \rightarrow I_2AA + CO_2$	$8 \times 10^{-5} [I_2MA]$	16
6	$IMA \rightarrow IMA\text{-enol}$	$k_6 [IMA]$	This work
-6	$IMA\text{-enol} \rightarrow IMA$	$k_{-6} [IMA\text{-enol}]$	This work
7	$IMA\text{-enol} + I_2 \rightarrow I_2MA + H^+ + I^-$	$k_7 [IMA\text{-enol}][I_2]$	This work
-7	$I_2MA + H^+ + I^- \rightarrow IMA\text{-enol} + I_2$	$k'_{-7} [I_2MA][H^+][I^-]$	This work
8A	$2H^+ + I^- + IO_3^- \rightarrow HOIO + HOI$	$1200 [H^+]^2 [I^-] [IO_3^-]$	20
8B	$2H^+ + 2 I^- + IO_3^- \rightarrow 2HOI + OI^-$	$4.2 \times 10^8 [H^+]^2 [I^-]^2 [IO_3^-]$	20
8C	$H^+ + OI^- \rightarrow HOI$	$1 \times 10^{10} [H^+][OI^-]$	diffusion controlled
8E	$H^+ + I^- + HOIO \rightarrow 2HOI$	$5 \times 10^9 [I^-] [HOIO]$	21
8F	$H^+ + I^- + HOI \rightarrow I_2 + H_2O$	$3.67 \times 10^9 [I^-] [HOI]$	21
-8F	$I_2 + H_2O \rightarrow H^+ + I^- + HOI$	$0.0018 [I_2]/[H^+]$	21
8G	$H^+ + OH^- \rightarrow H_2O$	$1 \times 10^{10} [H^+][OH^-]$	diffusion controlled

to 0.0088 M, $[KIO_3]$ between 0.0083 and 0.020 M, and $[I_2]$ near 0.0005 M, the k values are as follows: $k_6 = 0.0039 \pm 0.003$ s^{-1} , $k_{-6} = 176 \pm 20$ s^{-1} , $k'_{-7} = 2500 \pm 2500$ $M^{-2}s^{-1}$, where k'_{-7} is an apparent rate constant, being a composite constant including unknown decomposition processes as explained below. For any one run, the value of k'_{-7} had a covariance of only a few percent, but k'_{-7} values for the individual runs varied from 500 to 5000 $M^{-2} s^{-1}$. The reason for the high uncertainty ascribed to k'_{-7} is that k'_{-7} is mainly dependent on $[I_2]$ at the “end” of a run. The end time is arbitrary, and in reality is the time of a broad minimum in $[I_2]$ absorbance. Eventually the absorbance increases again due to unknown decomposition processes of I_2MA referred to above. Thus, in the absence of specific decomposition reactions, those effects show up in k'_{-7} .

The same methods were used for $[HClO_4] = 0.10$ M for 11 runs with $[IMA]$ from 0.0012 to 0.0036 M, $[KIO_3]$ between 0.0050 and 0.010 M, and $[I_2]$ from 0.0003 to 0.0006 M. Although each individual run could be fitted within a standard deviation in absorbance (experimental vs calculated) of ~ 0.002 (see Figure 1), the covariances in k_6 , k_{-6} , and k'_{-7} were high, some well over 100%. Accordingly, k_6 values for all the runs were averaged to 0.014 ± 0.004 s^{-1} ; that value was fixed and values for k_{-6} and k'_{-7} were redetermined for

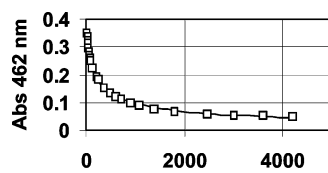


Figure 1. Iodination of IMA: $[HClO_4] = 0.10$ M, $[KIO_3] = 0.010$ M, $[IMA] = 0.0012$ M, and $[I_2] = 0.00051$ M. Squares, experimental; solid line, calculated from best fit to k_{-6} (570 s^{-1}) and k'_{-7} (60 700 $M^{-2} s^{-1}$) with k_6 fixed at 0.014 s^{-1} and k_7 fixed at 2×10^6 $M^{-1}s^{-1}$. Mean standard deviation: 0.004.

each run. Values for k_{-6} were fixed at the average, 520 $M^{-1} s^{-1}$, and values for k'_{-7} were determined once again. By this time, the standard deviations in absorbance ranged from 0.003 to 0.012, but the values for k'_{-7} again show a great variation among the individual runs. A reasonable average value was found to be 50 000 $M^{-2} s^{-1}$.

The three values, k_6 , k_{-6} , and k'_{-7} are all higher at the higher acidity. The values for k'_{-7} are especially uncertain, probably partly because of the iodination of IMA being reversible, and in addition I_2MA is subject to decomposition by other as yet unknown means. At long times and at lower $[KIO_3]$, the absorbance increases as shown in Figure 2. This behavior cannot be explained with reactions 2–8. When $[I_2]_0$ to $[IMA]_0$ is greater than approximately 0.5, the absorbance minimum appears much sooner.

I₂MA in Acid Solution. This decomposition of diiodomalonic acid was found to be slow. Other reactions are more important. This decomposition may be the source of I^- when starting with just IMA and acid, because of reaction 4.



Effect of Oxygen and Nitrogen on the System IMA–I₂–KIO₃(H⁺). The decomposition of I_2MA in the presence of I_2 was found to be autocatalytic (faster with more initial

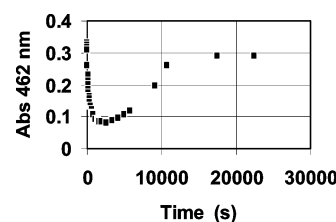


Figure 2. Long-term iodination and decomposition of IMA: $[HClO_4] = 0.10$ M, $[KIO_3] = 0.0050$ M, $[IMA] = 0.0012$ M, and $[I_2] = 0.00052$ M.

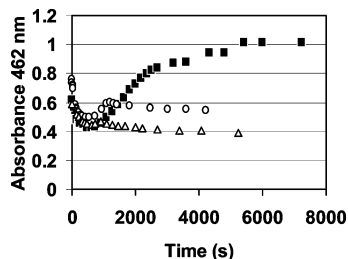
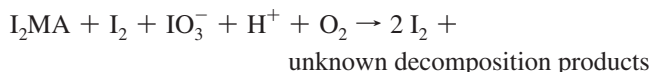


Figure 3. Effect of oxygen on iodination and decomposition of IMA. $[\text{HClO}_4] = 0.10 \text{ M}$, $[\text{KIO}_3] = 0.0050 \text{ M}$, $[\text{IMA}] = 0.0012 \text{ M}$, and $[\text{I}_2] = 0.0010 \text{ M}$. Open diamonds, saturated with N_2 ; open circles, air saturation; black squares, O_2 saturation.

iodine) and O_2 is involved. The decomposition often stops abruptly, probably when dissolved O_2 is used up. Radicals are probably involved in the reaction.



This system with high ratio of $[\text{I}_2]_0$ to $[\text{IMA}]_0$ (so that I_2MA was produced in large relative amounts) was studied (a) in saturated O_2 solution, (b) in equilibrium with air, and (c) in deaerated condition with a stream of N_2 . The absorbance of I_2 at 462 nm was followed for over 4000 s. The results are reported in Figure 3.

As can be seen from the figure, oxygen plays an important role in the decomposition of IMA/ I_2MA . First IMA is iodinated to I_2MA , with the decreasing absorbance reaching a minimum. Then I_2MA decomposes with a regular increase of I_2 absorbance. This is particularly evident when the mixture is saturated with oxygen; the S-shaped curve is an indication of an autocatalytic reaction. The behavior of $\text{Abs}(\text{I}_2)$ versus time for the mixture in equilibrium with the atmosphere is similar to the situation with O_2 saturation initially. After the increase of I_2 following the minimum there is an abrupt change to a slow regular decrease. The behavior in the deaerated mixture shows an initial decrease of iodine until a minimum followed by a little increase (possibly due to some residual oxygen) and a continuous slow decrease past 5000 s.

Effect of H_2O_2 and Mn^{2+} on I_2MA (H^+). The reaction $\text{I}_2\text{MA} + \text{H}^+ + \text{Mn}^{2+} + \text{H}_2\text{O}_2$ yields mainly I_2 , $\text{H}_2\text{C}_2\text{O}_4$, CO_2 , and smaller amounts of I_2AA (see Figure 4 in ref 3). It is much faster than any of the above reactions and is responsible for producing increasing amounts of I_2 and I^- , eventually leading to state II when oscillations cease. This reaction, probably combined with the reaction above involving iodate and I_2 , is responsible for the autocatalytic increase in I_2 and I^- reported by Vanag.⁴

Comparison of Unperturbed and Perturbed IMA-Based Oscillators. In Figure 4a the recording of the oscillatory behavior of the potential versus time of a typical IMA-based BR mixture is reported. 1.00 mL of doubly distilled water was added after the first oscillation. Figure 4b shows the perturbation provoked by the addition of 1.00 mL of a suitably diluted aqueous solution of resorcinol. It can be seen that the perturbation consists in an immediate quenching of the oscillations that resume after a time (inhibition time, t_{inhib}).

It was found that the inhibition time depends linearly on the concentration of the resorcinol added in a certain concentration range. In Figure 5 the straight line t_{inhib} versus $[\text{Re}]$ is shown.

At low resorcinol concentrations the inhibition time approaches the oscillation period. At high concentrations the

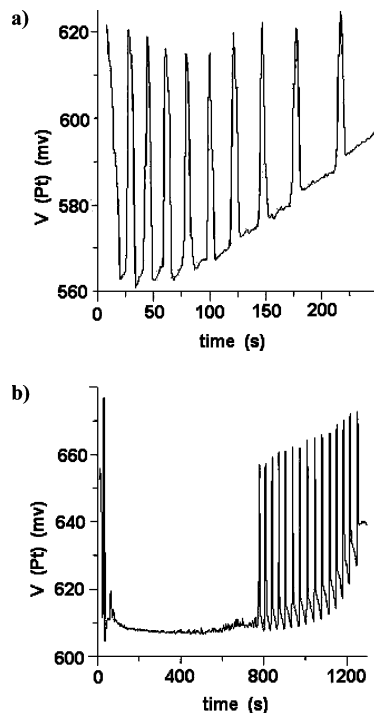


Figure 4. (a) Reference oscillator. Concentrations: $[\text{IMA}] = 0.012 \text{ M}$, $[\text{Mn}^{2+}] = 0.0020 \text{ M}$, $[\text{IO}_3^-] = 0.020 \text{ M}$, $[\text{HClO}_4] = 0.10 \text{ M}$, and $[\text{H}_2\text{O}_2] = 1.20 \text{ M}$. (b) Example of inhibition: 1.0 mL of Re solution added, initial concentration as in panel a, $[\text{Re}] = 4.88 \mu\text{M}$.

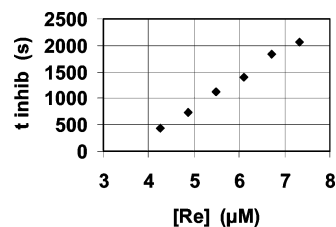
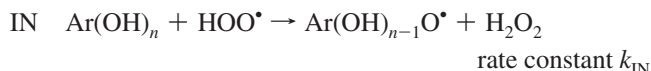


Figure 5. Effect of resorcinol on inhibition times. Initial concentrations as in Figure 4a.

amplitude of the resumed oscillations becomes too low, until up to a given concentration oscillations do not restart. The reaction essentially stops, having lost the ability to produce intermediates.

The reported findings for the perturbed IMA-based oscillator are similar to those reported for the MA-based BR oscillator perturbed by resorcinol,^{9,10} mechanistically interpreted by adding two further steps to the FCA model,^{8–10} i.e.:



where step IN represents the subtraction of hydroperoxyl radicals HOO^\bullet by a generic polyphenol $\text{Ar}(\text{OH})_n$, and DEG represents the possible parallel oxidation and/or iodination overall reactions by the BR reagents or intermediates. Mechanistic calculations on inhibitory effects of a MA-based BR oscillator by ten diphenols¹¹ (including resorcinol) showed that the order of magnitude of k_{IN} values falls in the range $10^5 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$, whereas k_{DEG} values are in the range $0 - 10^{-3} \text{ s}^{-1}$. Even if it is not permissible to compare rate constants from different-order

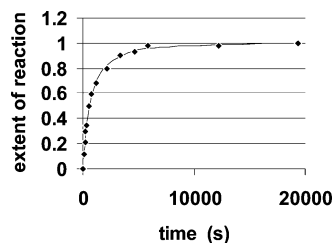
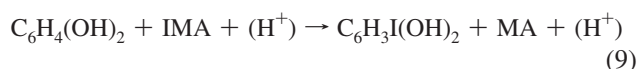


Figure 6. Simulated vs experimental extent of reaction, $[\text{H}_2\text{SO}_4]_0 = 0.10 \text{ M}$, $[\text{K}_2\text{IMA}]_0 = 0.033 \text{ M}$, $[\text{Re}]_0 = 0.039 \text{ M}$, and $[\text{acetic acid}]_0 = 0.020 \text{ M}$ reference, $22 \text{ }^\circ\text{C}$.

rate equations, k_{IN} values are of several orders of magnitude higher than k_{DEG} values, so it was concluded that the scavenging action by diphenols against HOO^\bullet radicals is the main source of the inhibition of oscillations.

The similarity between the inhibitory effects by resorcinol on MA-based and IMA-based oscillators suggests that the above interpretation can be also reasonable for the IMA-based oscillator perturbed by resorcinol.

Lawson et al.² claimed that the “anti-inhibitory” effect of IMA on the MA-based oscillator is due to the iodination of resorcinol by IMA:



We then decided to obtain an experimental estimate of the rate constant for this reaction.

Kinetics of the System IMA+Re+H⁺. The kinetics of this system was followed by ¹H NMR spectrometry in a mixture of initial formal composition $[\text{H}_2\text{SO}_4]_0 = 0.10 \text{ M}$, $[\text{K}_2\text{IMA}]_0 = 0.033 \text{ M}$, $[\text{resorcinol}]_0 = 0.039 \text{ M}$, and $[\text{acetic acid}]_0 = 0.020 \text{ M}$ at $22 \text{ }^\circ\text{C}$.

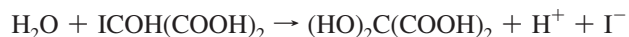
Acetic acid was used as an internal standard. At the times shown in Figure 6, a spectrum was acquired and five peaks were integrated: one for acetic acid, one for malonic acid product, one for iodoresorcinol product (4-iodo-1,3-dihydrobenzene), and two for resorcinol. Each peak was normalized to the acetic acid reference. The extent of reaction was calculated as a fraction between 0 and 1, comparing the normalized peak integral with the total change from beginning to end (0–322.2 min). Those fractions were averaged, giving the values shown in Figure 6.

The COPASI simulation program²² was used to calculate one parameter, the constant in the rate law $d[\text{IMA}]/dt = k[\text{IMA}][\text{resorcinol}]$. The fit is shown in Figure 6, giving a value of $k = 0.043 \text{ M}^{-1} \text{ s}^{-1}$.

Conclusion

IMA-based BR oscillators have many features in common with MA-based BR oscillators. One difference is the formation of I₂MA immediately in the IMA oscillators. In MA-based oscillators, I₂MA is a minor product initially so long as some MA remains unreacted. When the $[\text{MA}]_0/[\text{IO}_3^-]_0$ ratio is greater than 2:1, IMA is the major product, and the system ends oscillations in state (I). With IMA-based oscillators, I₂MA is formed, but begins to decompose and return I₂ immediately to the solution. There must be some hold-up of iodine in some

form, otherwise [I₂] could not oscillate. It appears that the half-life of I₂MA is rather short. Another potential short-term reservoir for iodine could be iodotartaric acid (ITTA). This compound has not been detected directly in solutions, but simulations of oxidation of tartaric acid by I₂, where ITTA is an intermediate, indicate a half-life for ITTA of approximately 100 s.³ ITTA is expected to decompose to mesoxalic acid.



In regards to the IMA-based BR oscillator perturbed by resorcinol, even though more experiments will be needed to obtain a precise value of k_9 , the obtained experimental estimate of $0.043 \text{ M}^{-1} \text{ s}^{-1}$ cannot be too far off. This value is certainly much lower than that of the reaction $\text{C}_6\text{H}_4(\text{OH})_2 + \text{HOO}^\bullet \rightarrow \text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet + \text{H}_2\text{O}_2$ in the IMA-based oscillator. (In the MA-based oscillator the calculated rate constant for this reaction was $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).¹¹ The facts indicate that the anti-inhibitory effect of IMA is due to its iodination to I₂MA and subsequent decomposition to form I₂ and I⁻.

In conclusion, degradation pathways for both IMA and I₂MA must be elucidated and included in the mechanism for BR oscillators. For resorcinol-perturbed oscillators, that degradation pathway will also affect the step DEG in the mechanistic model of both MA-based and IMA-based oscillators, step IN remaining the main step responsible for the inhibitory effects.

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