Phenylmalonic Acid Reaction with Iodine and Behavior in a Briggs–Rauscher Oscillator

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Phenylmalonic acid (PhMA) reacts via an enol mechanism with aqueous iodine to form rather reactive iodophenylmalonic acid. The rate at 25 °C in 0.1 M acid can be described by $-d[I_2]/dt$ (M s^{-1}) = $126[I_2][\mathrm{PhMA}]/(1 + (3.8 \times 10^4)[I_2])$. This iodo product can undergo hydrolysis, decarboxylation, and oxidation. Oxidants that oxidize iodide to iodine also regenerate iodine quantitatively from iodophenylmalonic acid, seemingly via an attack by HOI. When manganous ion and hydrogen peroxide are present, iodophenylmalonic acid reacts fairly rapidly by a different mechanism, giving up iodide ions. In a mixture with acidic iodate, hydrogen peroxide, and manganous ions, PhMA can serve as a substrate for a Briggs–Rauscher-type oscillating reaction. The iodo product is much less stable than the iodo product with typical Briggs–Rauscher substrates such as malonic acid or acetone, and any proposed oscillatory mechanism must be able to account for fairly rapid decomposition and iodine regeneration.

I. Introduction

The Briggs–Rauscher oscillating system[1] containing hydrogen peroxide, acid, iodate, manganous or cerous ion catalyst, an organic substrate, (and starch) produces striking visual oscillations in either a batch or flow system as iodine is alternately produced and then consumed. (See ref 2 and references cited therein.) The organic substrate was originally malonic acid (MA), but acetone,[3] methylmalonic acid (MMA),[4] acetylacetone,[5] ethyl acetoacetate, and diethyl malonate[6] oscillators have also been reported. In a skeleton model of the system[7,8] malonic acid was assumed to be a sink for the iodine. Cooke[9] found that under certain circumstances iodomalonic acid (or diiodomalonic acid) could act as a source of iodine in what he termed a "double barreled oscillator", in an oscillator with both malonic acid and acetone present. Others have used the term consecutive or sequential oscillations to describe similar behavior.[10] Further studies with mixed substrate oscillators have shown that phenylmalonic acid–acetone and phenylmalonic acid–MMA mixtures also produce "consecutive oscillations" where two separate oscillatory trains occur.[11] Since phenylmalonic acid (PhMA) forms a particularly unstable iodo product (compared to the other substrates above), this work was undertaken to characterize the reactions of PhMA with iodine and the product, iodophenylmalonic acid (IPhMA), with those reagents found in an oscillatory mixture. The half-life of IPhMA is on the order of a minute or so under oscillating conditions, and iodine is regenerated as a product. Thus PhMA is only a temporary sink for iodine. We will first report investigations of iodination of PhMA in acidic mixtures containing iodate or other oxidant and then report the effect of various reagents on iodine regeneration from IPhMA; finally we report some features of the single-substrate PhMA oscillatory system.

II. Experimental Conditions

Reagent grade chemicals were used except as noted. PhMA was recrystallized from methylene chloride–ethyl acetate solvent. Water was double distilled. Hydrogen peroxide was "stabilizer-free" from Fisher. Solid iodine was stirred with water for several hours. The solution was filtered through Pyrex wool and stored in a glass-stoppered bottle protected from light. Absorbance measurements were carried out in a Coleman-Hitashi Model 124 spectrophotometer or a Hewlett-Packard HP8451A spectrophotometer, both with thermostated cell compartments. The temperature was controlled to 25 + 0.2 °C. Potential measurements were done with an Orion iodide electrode with a double-junction silver–silver chloride reference using sodium sulfate in the outer junction.

III. Reaction of PhMA with Halogens

By analogy with other compounds with active methylene hydrogens, halogenation of PhMA is expected to proceed through an enol mechanism according to the scheme (illustrated with iodine)

$$\mathrm{PhMA} \rightleftharpoons \mathrm{PhMA(enol)} \qquad (1)$$

$$I_2 + \mathrm{PhMA(enol)} \rightleftharpoons H^+ + I^- + \mathrm{IPhMA} \qquad (2)$$

The sum of reactions 1 and 2 is

$$I_2 + \mathrm{PhMA} \rightleftharpoons H^+ + I^- + \mathrm{IPhMA} \qquad (3)$$

The reaction with iodine is highly reversible, so that little reaction takes place in acidic solution unless iodide ion is rapidly removed. The extent of the reaction can be determined by simultaneous measurement of absorbance at 353 and 460 nm, to give initial $[I_2]$, final $[I_2]$, and final $[I_3^-]$. (Absorptivities (M^{-1} cm^{-1}) used were for $[I_2]$, $\epsilon(353\text{ nm}) = 18$, $\epsilon(460\text{ nm}) = 746$; for $[I_3^-]$, $\epsilon(353\text{ nm}) = 26400$, $\epsilon(460\text{ nm}) = 975$.) The overall equilibrium constant of reaction 3 is calculated to be approximately 0.0045.

Reaction 3 reaches a steady state which slowly shifts because of the decomposition of IPhMA.

$$\mathrm{IPhMA} + H_2O \rightarrow \mathrm{PhTA\ (phenyltartronic\ acid)} + H^+ + I^- \qquad (4)$$

Hydrolysis predominates over decarboxylation under the conditions studied, and kinetic runs were followed at 460 and 353 nm to monitor iodine and triiodide (Figure 1). At 353 nm, there is a minor contribution due to IPhMA and possibly other organic products. By use of a numerical integration routine,[12,13] k_4 was determined to be approximately 5×10^{-5} s^{-1}. (The forward constants for reaction 3 were determined with an oxidant present, as described below.)

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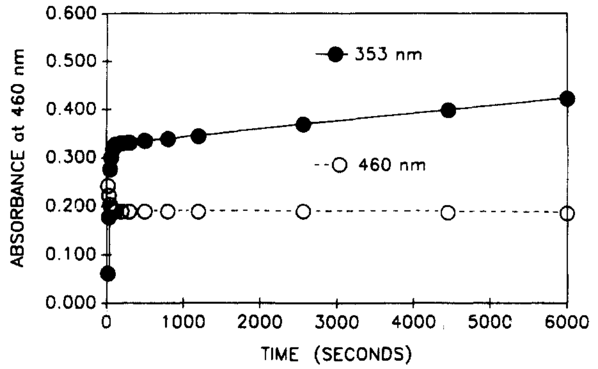

Figure 1. Phenylmalonic acid–iodine system (no oxidant). Absorbance at 460 (I_2) and at 353 nm (I_3^-) vs time. $[PhMA]_0 = 0.000\,50$ M, $[I_2]_0 = 0.000\,33$ M, $[HClO_4] = 0.10$ M.

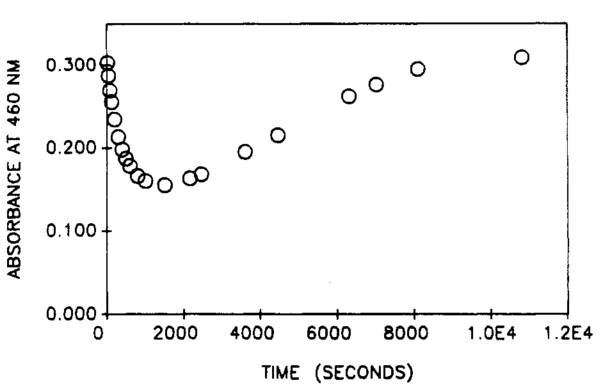

Figure 2. Phenylmalonic acid–iodine–hydrogen peroxide system. Absorbance at 460 nm vs time. $[PhMA]_0 = 0.000\,70$ M, $[I_2]_0 = 0.000\,40$ M, $[H_2O_2]_0 = 1.0$ M, $[HClO_4] = 0.10$ M.

Reaction of PhMA with Bromine. We hoped to learn about the very unstable iodine intermediates through study of the bromine analogues. Bromophenylmalonic acid (BrPhMA) is sufficiently stable so that a 1:1 mole ratio mixture of bromine and PhMA in aqueous solution reacts to completion. BrPhMA can be isolated.[14] In 0.1 M $HClO_4$ solution, it undergoes slow hydrolysis to phenyltartronic acid (PhTA) and apparent simultaneous decarboxylation to bromophenylacetic acid with a combined first-order rate constant of approximately $0.000\,067$ s^{-1}.

Several kinetic runs were made with bromine and PhMA to try to confirm the magnitude of the iodination rate constants. If enolization were rate-determining, then rates of bromination and iodination would be identical. There is a complication in that bromine continues to disappear slowly after PhMA should have all reacted.

With Br_2 in excess, mandelic acid and benzoic acid were both isolated after the mixture stood overnight. Some bromine is consumed in oxidation of one of the intermediates. (Neither phenyltartronic acid, mandelic acid, bromophenylacetic acid, nor phenylacetic acid undergoes appreciable oxidation by bromine under these conditions.) Bromine is consumed by BrPhMA. The pathway to benzoic acid has not been resolved.

Measurement of these rate constants is discussed in Appendix A. Although rate constants for analogous iodine compounds are typically higher for both hydrolysis and for decarboxylation, the hydrolysis constants found here were slightly higher for BrPhMA than for IPhMA.

The rate of the first bromination was the same as the rate of iodination, within the precision of the measurements. Consumption of additional bromine, beyond the first bromination step, was slow but not negligible compared to bromine consumption by the enol.

Reaction of PhMA + Iodine + Oxidant. Reaction 3 can be forced to the right by rapid removal of iodide ion with an appropriate oxidant. With each of the oxidants, not only was the iodide oxidized, but the product, IPhMA, was also affected by the oxidizing medium. The starting materials, I_2 and PhMA, do not react appreciably with any of the oxidants under the conditions studied. Three different oxidants were used: hydrogen peroxide, iodate ion, and nitrous acid. Each will be discussed in turn.

Reaction of PhMA with Iodine and Hydrogen Peroxide. Hydrogen peroxide is capable of removing iodide by oxidation to iodine:[15]

$$H_2O_2 + I^- + H^+ \rightarrow HOI + H_2O \tag{5}$$

The two equilibria also apply:

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^- \tag{6}$$

and

$$I_2 + I^- \rightleftharpoons I_3^- \tag{7}$$

Our results for rates of iodide oxidation in solutions containing iodine were slightly higher than those previously reported[15] and could be accounted for quantitatively with addition of a term for oxidation of triiodide with hydrogen peroxide (Appendix B).

$$H_2O_2 + I_3^- + H^+ \rightarrow HOI + I_2 + H_2O \tag{8}$$

Figure 2 shows the course of a typical reaction with I_2, PhMA, and H_2O_2. The initial drop in iodine concentration is relatively rapid, as IPhMA is formed. A minimum in iodine concentration is reached as iodide builds up and the reverse reaction (−3) becomes important as well as some reaction accounting for iodine regeneration. Reaction steps 1, 2, and 4–8 were used to attempt to model the process under these conditions. The mechanism requires some step(s) to provide an increase in speed of iodine regeneration even though IPhMA concentration decreases. Since [HOI] increases toward the end of the reaction, the following process was included:

$$IPhMA + HOI \rightarrow I_2 + P \tag{9}$$

where P represents organic product, possibly initially PhTA. The iodine is returned quantitatively. The apparent rate constant, however, depends on H_2O_2 concentration. The effect is nonlinear (Table I). With k_9 regarded as an adjustable parameter, absorbance curves at 460 nm (iodine concentration) could be fit very well for the entire range of any one experiment. Effect of acidity was not studied and $[H^+]$ was not included in the rate law. The value of k_9 is the effective value in 0.10 M acid. The mechanism for iodine regeneration has not been clarified further because a different and much faster mechanism applies with manganese ion present (section IV). Reaction 9 is accompanied by decomposition of hydrogen peroxide and by further oxidation of organic product. Benzoic acid precipitated from a reaction mixture in which PhMA, H_2O_2, and solid I_2 stood in aqueous solution for 3 days. The amount of PhMA converted to benzoic acid was near 30%, based on the amount precipitated out and the amount remaining in the saturated solution.

Reaction 3 is the major reaction governing iodine consumption, (with reactions −6 and 5 consuming iodide). It is difficult to determine the forward rate constants (1) and (2) precisely because of iodine production as IPhMA builds up in concentration. That is, the rate of iodine regeneration must be known in order to determine that the rate of iodine consumption (and vice versa). Under conditions where the reverse reaction (−2) and iodine regeneration are minimized (excess peroxide and excess PhMA), the rate-determining step reduces to

$$-d[I_2]/dt = 0.5k_\alpha[I_2][PhMA]/(1 + k_\beta[I_2])$$

assuming a steady-state concentration for the enol, where $k_\alpha = k_1k_2/k_{-1} = 126$ and $k_\beta = k_2/k_{-1} = 3.8 \times 10^4$. The factor 0.5 is a stoichiometric factor from the sum of 2 × (3) + (5) + (−6). (Although two I_2's react, one I_2 is formed from oxidation of two I^-'s.) In the experimentally accessible region, however, the rate law would be nearly

$$-d[I_2]/dt = 0.5(k_\alpha/k_\beta)[PhMA]$$

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TABLE I: Phenylmalonic Acid–Iodine–Hydrogen Peroxide[a]

$[H_2O_2]_0$, M	$[PhMA]_0$, M × 10^3	$[I_2]_0$, M × 10^4	time to min abs, s	ratio $[I_2]_{min}$ to $[I_2]_0$	time[b] for 50% I_2 regeneration, s	k_9, M^{-1} s^{-1} × 10^6	σ[c] × 10^3
0.10	1.0	4.0	5000	0.45	28000	0.10	0.7
0.30	1.0	4.0	3100	0.31	16000	0.21	0.6
1.0	0.70	4.2	1500	0.50	8000	0.40	0.3
1.0	1.4	4.1	3100	0.15	11000	0.30	0.5

[a] $[HClO_4]$ was 0.10 M and temperature was 25 °C for all runs. [b] Time (from beginning) for 50% regeneration from $[I_2]_{min}$ to $[I_2]_{final}$. [c] σ is the average deviation ($\sum$|absorbance expt − absorbance calcd|)/n over the entire measurement set.

TABLE II: Rate Constants Used for Numerical Simulation

reaction	rate law	reference
1	$(0.0033\ s^{-1})[PhMA]$	this work
−1	$(1.00\ s^{-1})[PhMA(enol)]$	arbitrary, this work
2	$(3.8 \times 10^4\ M^{-1}\ s^{-1})[I_2][PhMA(enol)]$	this work
−2	$(2.86 \times 10^4\ M^{-2}\ s^{-1})[H^+][I^-][IPhMA]$	this work
4	$(5 \times 10^{-5}\ s^{-1})[IPhMA]$	this work
5	$(0.028\ M^{-1}\ s^{-1})[H_2O_2][I^-]$ at $[H^+] = 0.10$ M	15
6	$(0.020\ M^{-1}\ s^{-1})[H_2O_2][I_3^-]$ at $[H^+] = 0.10$ M	this work
7	$0.0018[I_2]/[H^+]$	see ref 16
−7	$(3.6 \times 10^9\ M^{-1}\ s^{-1})[HOI][I^-]$	see ref 16
12	$(1.4 \times 10^3\ M^{-3}\ s^{-1})[H^+]^2[I^-][IO_3^-]$	17
13	$(4.0 \times 10^8\ M^{-4}\ s^{-1})[H^+]^2[I^-]^2[IO_3^-]$	this work; see ref 18
14	$(3.7 \times 10^{10}\ M^{-4}\ s^{-1})[HNO_2]^2[H^+][I^-]^2$	19
17	$(0.015\ M^{-1}\ s^{-1})[H_2O_2][IPhMA]$	this work
−17	$(0.05\ s^{-1})[IPhMA - H_2O_2]$	arbitrary, this work
18	$(50\ M^{-1}\ s^{-1})[IPhMA - H_2O_2][Mn^{2+}]$	this work

except for curvature introduced by iodine regeneration.

Experimentally, then, the ratio of the empirical constants k_α/k_β may be determined with some confidence and can be found by looking at initial rates with low initial $[I_2]$. The individual constants k_α and k_β are less precise because iodine regeneration is never negligible.

For the model, k_{-1} was arbitrarily chosen and then k_1 and k_2 were chosen for the best fit to the data. k_{-2} was determined from the value of the equilibrium constant, $0.0045 = k_1k_2/(k_{-1}k_{-2})$. See Table II for all values used in modeling.

PhMA + Iodine + Iodate. In the presence of iodate, the (initial) overall reaction is

$$2I_2 + 5PhMA + IO_3^- + H^+ \rightarrow 5IPhMA + 3H_2O \quad (10)$$

As reaction 10 proceeds, however, IPhMA reacts further, regenerating iodine and forming the hydroxy derivative, phenyltartronic acid (PhTA), and other organic products. At longer times, therefore, the overall process can be written as

$$2I_2 + 5PhMA + 2IO_3^- + 2H^+ \rightarrow 5PhTA + 3I_2 + H_2O \quad (11)$$

Several typical absorbance vs time curves are shown in Figure 3 and initial conditions are given in Table III. With excess iodate present, the ratio of [PhMA] used to final $[I_2]$ is 5:1, showing that whatever the final organic product, further oxidation by iodate is not involved; otherwise the reduced iodate would end up eventually as extra I_2.

PhMA itself undergoes slow decarboxylation, about 0.25% per hour at 25 °C.[20] Undoubtedly, IPhMA also decarboxylates readily. On the time scale of these experiments (3–4 h), a minor amount of gas was detected, so decarboxylation is not a major pathway under the above conditions. When attempts were made to extract and purify the hydroxy product, only the decarboxylation product, mandelic acid, was recovered. (PhTA reportedly decarboxylates on heating to 60–80 °C.[21] We show in the Appendixes that the first-order rate constant for decarboxylation of PhTA in 0.10 M $HClO_4$ at 25 °C is approximately 1.7×10^{-5} s^{-1}, or 6% per hour.

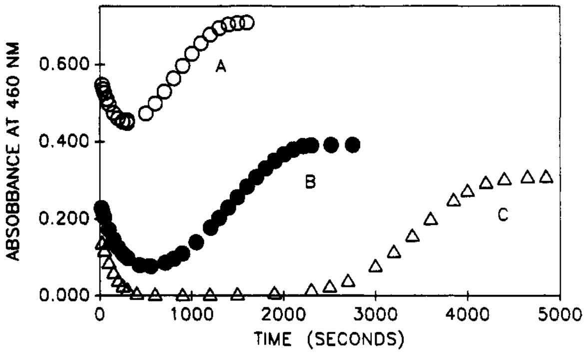

Figure 3. Phenylmalonic acid–iodine–iodate system. Absorbance at 460 nm vs time. $[PhMA]_0 = 0.0010$ M, $[IO_3^-]_0 = 0.030$ M, $[HClO_4] = 0.19$ M, (A) $[I_2]_0 = 7.6 \times 10^{-4}$ M, (B) $[I_2]_0 = 3.3 \times 10^{-4}$ M, (C) $[I_2]_0 = 2.2 \times 10^{-4}$ M.

The following additional steps (as well as (1), (2), (4), (6), (7), and (9)) were assumed in the reaction:

$$IO_3^- + I^- + 2H^+ \rightarrow HOI + HOIO \quad (12)$$

$$IO_3^- + 2I^- + 2H^+ \rightarrow 3HOI \quad (13)$$

Reaction 13 is a composite reaction which, along with (12), is rate determining for the Dushman reaction[18,22] ($IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$).

Again with k_9 regarded as adjustable (as was done with H_2O_2 oxidant), absorbance curves at 460 nm could be modeled rather well for any one run. The values for k_9 clearly depend on iodate concentration; ionic strength also plays a role. Values of k_9 were low in runs with higher ratios of substrate to iodine, where the minimum in iodine concentration was very low. For the set of calculations reported in Table III, the acid ionization of HIO_3 ($K_a = 0.18$) was included in the model. As above, specific steps for involvement of iodate in step 9 have not been included.

Since IPhMA is extremely light sensitive,[23] some radical involvement is a possibility. Reactions showed no difference in rate under oxygen or argon atmosphere. Direct addition of I(I) (in sulfuric acid)[24] to solutions containing IPhMA (generated in situ) showed a very fast I_2 production, consistent with reaction 9.

Reaction of PhMA + Iodine + Nitrous Acid. Another alternative for rapid iodide removal is use of nitrous acid.[25] In an attempt to avoid the complications of the reaction of IPhMA with iodate, several runs were made in the presence of nitrite ion, which forms HNO_2 in acidic solution. Iodine is again regenerated, essentially quantitatively. The absorbance curves are similar to Figure 2, where hydrogen peroxide was used as oxidant for iodide. The reaction of nitrite with iodide is reported[19] to be

$$2HNO_2 + 2I^- + 2H^+ \rightarrow I_2 + 2NO + 2H_2O \quad (14)$$

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TABLE III: Phenylmalonic Acid-Iodine-Iodate[a]

$[IO_3^-]_0$, M	$[PhMA]_0$, M × 10^3	$[I_2]_0$, M × 10^4	time to min abs, s	ratio $[I_2]_{min}$ to $[I_2]_0$	time[b] for 50% I_2 regeneration, s	k_0, M^{-1} s^{-1} × 10^6	σ^d × 10^3
0.100[c]	2.00	2.35	500	0.03	3000	1.05	12
0.0625	1.51	4.48	400	0.40	950	0.83	11
0.0625[c]	1.44	4.07	400	0.40	1020	0.90	7
0.030	0.99	7.52	300	0.80	1000	0.50	16
0.030	1.00	3.21	550	0.32	1400	0.63	7
0.030	1.00	2.11	700	0.02	3400	0.38	14
0.030	0.87	3.41	650	0.50	1300	0.60	7
0.020	2.03	4.38	1100	0.02	4500	0.28	19
0.020[c]	1.45	4.10	850	0.11	2500	0.40	13
0.020	0.50	4.54	400	0.73	1050	0.44	3
0.0050[c]	1.44	4.16	1100	0.12	4700	0.29	14
0.0010[c]	1.51	4.16	1300	0.22	9500	0.29	8
0.00038[c]	1.92	7.20	1200	0.42	5700	0.24	12

[a] $[HClO_4]$ was 0.10 M and temperature was 25 °C for all runs. [b] Time (from beginning) for 50% regeneration from $[I_2]_{min}$ to $[I_2]_{final}$. [c] Ionic strength was adjusted to 0.625. [d] σ is the average deviation ($\sum$|absorbance expt − absorbance calcd|)/n over the entire measurement set.

TABLE IV: Phenylmalonic Acid-Iodine-Nitrous Acid[a]

$[HNO_2]_0$, M	$[PhMA]_0$, M × 10^3	$[I_2]_0$, M × 10^4	time to min abs, s	ratio $[I_2]_{min}$ to $[I_2]_0$	time[b] for 50% I_2 regeneration, s
0.010	1.0	3.9	1000	0.18	
0.010	1.0	4.5	1000	0.27	8000
0.010	1.0	6.7	850	0.50	4300
0.010	1.0	7.0	1000	0.51	5800
0.010	1.5	2.8	500	0.03	9000
0.010	1.5	4.0	1000	0.03	
0.010	2.5	4.3	900	0.02	
0.020	2.5	4.3	900	0.02	
0.050	0.15	4.0	700	0.87	4000
0.050	1.5	4.0	400	0.10	4550

[a] $[HClO_4]$ was added to $NaNO_2$ to give excess acid 0.10 M in all solutions. Temperature was 25 °C. [b] Time (from beginning) for 50% regeneration from $[I_2]_{min}$ to $[I_2]_{final}$.

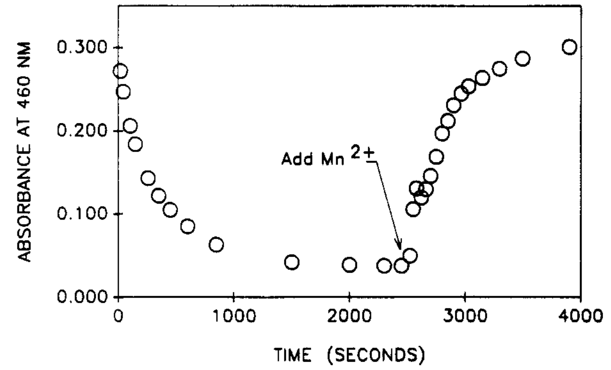

Figure 4. Addition of $MnSO_4$ to phenylmalonic acid-iodine-hydrogen peroxide system. Absorbance at 460 nm. $[PhMA]_0$ = 0.0015 M, $[I_2]_0$ = 0.00040 M, $[H_2O_2]_0$ = 1.00 M, $[HClO_4]_0$ = 0.10 M, $[MnSO_4]$ = 0.0054 M.

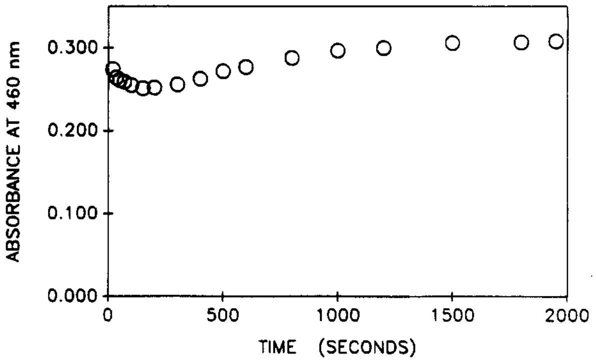

Figure 5. Phenylmalonic acid-iodine-hydrogen peroxide-manganous sulfate system. Absorbance at 460 nm vs time. $[PhMA]_0$ = 0.0010 M, $[I_2]_0$ = 0.00040 M, $[H_2O_2]_0$ = 1.00 M, $[HClO_4]$ = 0.10 M.

The sum of 2 × reaction 1, 2 × reaction 2, + reaction 14 results in

$$I_2 + 2PhMA + 2HNO_2 \rightarrow 2IPhMA + 2NO + 2H_2O \quad (15)$$

for the iodine consumption process, and the sum of reaction 6 × 2, reaction 9 × 2, plus reaction 14 leads to

$$2IPhMA + 2HNO_2 \rightarrow I_2 + 2PhTA + 2NO \quad (16)$$

for the iodine regeneration process.

Adjustment of the apparent constant k_9 was not as successful as with hydrogen peroxide or iodate as oxidant. Results are given in Table IV. Systemmatic deviations of up to 10% between calculated $[I_2]$ and experimental $[I_2]$ were observed using a value of 2 × 10^5 M^{-1} s^{-1} for k_9. The disagreement clearly shows lack of knowledge of the mechanism of iodine regeneration. The measurements are still consistent with the assumption of a direct reaction of HOI with IPhMA, reaction 9, but reactions of HOI with other intermediates are also important.

IV. Reaction of IPhMA in the Presence of Manganous Ion and Hydrogen Peroxide

In the oscillatory mixture, iodine regeneration appears to be much faster than in a mixture without H_2O_2 and Mn^{2+}. To assess this reaction, IPhMA was prepared in solution with a small excess of IO_3^-. Manganous ion and H_2O_2 were then added. Neither reagent alone causes much reaction. With both, however, I_2 is immediately regenerated rapidly at first, then more slowly (Figure 4). Iodide concentration is increased as shown by spectrophotometric measurements at 353 nm (for I_3^-) or by iodide electrode measurements. The concentration of HOI would be so low that regeneration by step 9 would be out of the question. Some other mechanism must be involved. Also, Mn^{2+} ion has a minor effect on iodine regeneration in solutions with I_2, PhMA, and excess iodate (no H_2O_2). The presence of Mn^{2+} and H_2O_2 is necessary for rapid I_2 regeneration.

Iodophenylmalonic acid was also generated in a solution with hydrogen peroxide and manganese ion already present (in the section above, manganese ion was added after some iodo product

TABLE V: Phenylmalonic Acid-Iodine-Hydrogen Peroxide, Addition of $MnSO_4$ at Minimum Absorbance[a]

$[PhMA]_0$, M × 10^3	$[I_2]_0$, M × 10^4	$[H_2O_2]_0$, M	$[MnSO_4]$,[b] M	time of addn, s	ratio $[I_2]_{min}$ to $[I_2]_0$	time[c] for 50% I_2 regeneration, s
0.50	4.0	1.00	0.0054	1500	0.63	75
1.0	4.0	0.40	0.0054	2700	0.36	200
1.0	4.1	1.00	0.0012	2000	0.29	300
1.0	4.0	1.00	0.0053	2000	0.27	125
1.5	4.0	1.00	0.0054	2600	0.09	200

[a] $[HClO_4]$ was 0.10 M and temperature was 25 °C for all runs. [b] $[MnSO_4]$ is after addition; other concentrations are before addition of $MnSO_4$. The concentration was diluted by less than 5% by $MnSO_4$. [c] Time from $MnSO_4$ addition.

TABLE VI: Phenylmalonic Acid-Iodine-Hydrogen Peroxide-Manganese Sulfate[a]

$[H_2O_2]_0$, M	$[PhMA]_0$, M × 10^3	$[I_2]_0$, M × 10^4	$[MnSO]_4$, M × 10^3	time to min abs, s	ratio $[I_2]_{min}$ to $[I_2]_0$	time[b] for 50% I_2 regeneration, s
1.00	0.50	4.0	1.0	220	0.90	650
1.00	0.50	4.0	5.4	160	0.93	450
0.040	1.0	4.0	5.4	240	0.76	5000
0.40	1.0	4.0	5.4	200	0.81	1100
1.00	1.0	4.0	0.40	500	0.69	1700
1.00	1.0	4.0	1.0	280	0.77	950
1.00	1.0	4.0	3.0	220	0.83	700
1.00	1.0	4.0	5.4	230	0.83	600
1.00	1.0	4.0	10.8	160	0.83	600
1.00	1.5	4.0	1.0	400	0.68	1200
1.00	2.0	4.0	5.4	230	0.69	820
1.00	4.0	4.0	5.4	280	0.51	2750

[a] $[HClO_4]$ was 0.10 M and temperature was 25 °C in all solutions. [b] Time (from beginning) for 50% regeneration from $[I_2]_{min}$ to $[I_2]_{final}$.

had formed). In these solutions, I_2 regeneration was nearly as rapid as I_2 consumption, so the net effect was only a small observed drop in absorbance (Figure 5 and Table VI). The rate of iodine release is dependent on manganese ion concentration and to a lesser extent on hydrogen peroxide concentration. The mechanism for iodine release is unknown but may well involve free radicals. In the HP8451A spectrophotometer where illumination is intermittant, absorbance due to iodine was not smoothly increasing during iodine release. That effect was not seen in the Coleman instrument with steady illumination. The participation of iodate ions can be ruled out completely in this mixture. No iodate was present initially, and final $[I_2]$ equals initial $[I_2]$. (Reaction of iodate with iodous acid was postulated as a source of radicals in the Briggs-Rauscher mixture.)

The process can be modeled empirically with a sequence involving complex or adduct formation

$$IPhMA + H_2O_2 \rightleftharpoons IPhMA\text{-}H_2O_2 \qquad (17)$$

$$IPhMA\text{-}H_2O_2 + Mn^{2+} \rightarrow I^- + P + Q + Mn^{2+} \qquad (18)$$

where P represents organic products (including CO_2), and Q represents peroxide decomposition products. Mn^{2+} appears on both sides of process 18 but may pass through Mn^{3+}. The constants for processes 17 and 18 have been adjusted to give the correct dependence on Mn^{2+} and H_2O_2 concentrations. (The rate increases with increasing $[H_2O_2]$ and increases at first with increasing $[Mn^{2+}]$, but at higher concentrations, further increases in $[Mn^{2+}]$ have little effect.) Though Mn^{2+} might be suspected of complexing with an organic acid, no effect for Mn^{2+} was found on the position of equilibrium for reaction 3. Adding to suspicion of free radical involvement is oxygen evolution from the hydrogen peroxide and the fact that ferrous ion or cerium(III) ion can replace Mn^{2+} as an effective catalyst in reaction 18. (These are all one-electron reductants.)

Cooke[26] has suggested involvement of OH radicals, formed from reduction of hydrogen peroxide, in the release of iodine from iodomalonic acid. That step could presumably operate even at relatively high iodide concentration. The role of manganese ion and hydrogen peroxide in radical initiation is still not clear.

V. PhMA Oscillators

PhMA can also act as an effective substrate to produce oscillations in a mixture similar to the Briggs-Rauscher mixture. The PhMA oscillatory mixture is not as "robust" as mixtures with many other substrates, especially at $[H^+] = 0.10$ M. A train of absorbance oscillations is shown in Figure 6. All components were in solution except H_2O_2, which was added to start the reaction. Figure 7 shows a typical train of oscillations measured with an iodide-sensitive electrode vs a Ag-AgCl reference with a sodium sulfate salt bridge. Only a few peaks are observed, and the mixture frequently "dies" in a high iodine state. No induction period has been observed.

At lower acid concentration, longer lasting oscillators are produced that run for 10 min or so.

The skeleton mechanism for the Briggs-Rauscher oscillator,[7,8] when "enhanced" with appropriate reactions from above, still generates oscillations with the iodination constants for malonic acid, methylmalonic acid, or acetone (with no iodine regeneration included). When PhMA constants are substituted and iodine regeneration is included, however, the mechanism has failed to generate oscillations. In the model, IPhMA forms and then decomposes, but not enough PhMA is left to continue oscillations. The model needs a faster way to dispose of rapidly accumulating iodide ions. The fault may lie with the choice of a process to represent the IPhMA decomposition (reactions 17 and 18). The skeleton model for the Briggs-Rauscher oscillator may also be the source of the problem. The range of iodine and iodide concentrations in the skeleton model is much too large, for example.[7] In the model $[I_2]$ changes by 2 or 3 orders of magnitude during consumption. Experimentally the change is typically less than 1 order of magnitude.

VI. Comparison with Other Oscillators

The best characterized systems are those containing MA, acetone,[3] and MMA.[4] The systems exhibit mostly the same general dependencies of period length on concentrations. The oscillatory period is increased by increasing iodate concentration; the period is decreased by increasing manganous ion or substrate. The period is not strongly affected by hydrogen peroxide concentration. Higher acid concentration increases the period of MA or MMA oscillators but decreases the period of acetone oscillators. The MA oscillator frequently "dies" in a condition with high iodine concentration. Acetone and MMA oscillators stop oscillating in a low iodine condition.

Table VII shows oscillatory periods and approximate ranges of concentration for oscillatory conditions for PhMA oscillators. Trends are similar to those with the above-mentioned substrates,

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[26] Cooke, D. O. *React. Kinet. Catal. Lett.* **1985**, *27*, 379.

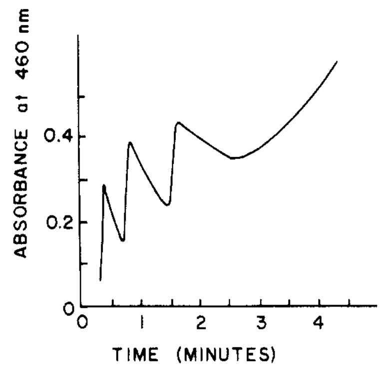

Figure 6. Phenylmalonic acid oscillator. Absorbance at 460 nm vs time. $[H_2O_2]_0 = 2.37$ M, $[KIO_3]_0 = 0.0167$ M, $[HClO_4] = 0.090$ M, $[PhMA]_0 = 0.0144$ M, $[MnSO_4]_0 = 0.0095$ M.

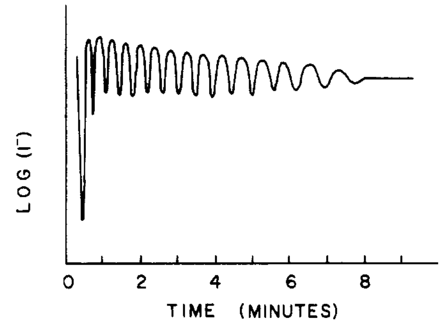

Figure 7. Phenylmalonic acid oscillator, log $[I^-]$ (arbitrary units) vs time. $[H_2O_2]_0 = 1.46$ M, $[KIO_3]_0 = 0.020$ M, $[HClO_4] = 0.048$ M, $[PhMA]_0 = 0.010$ M, $[MnSO_4]_0 = 0.0050$ M.

except for the effect of manganese ion. Increasing manganese increases the period with PhMA present, opposite to the effect when other substrates are used. This effect is certainly due to the effect of manganese ion on iodine regeneration.

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Appendix A. Bromine Reactions

Bromophenylacetic Acid Hydrolysis. Hydrolysis of bromophenylacetic acid (Aldrich) was determined by two methods: by direct spectrophotometry and by spectrophotometry after oxidation of bromide to bromine by bromate. Direct spectrometric measurements showed the greatest absorption loss at 268 nm. Final absorbance readings were taken about 1 week after the initial readings. For the second method, aliquots were delivered at various times into an acidic mixture containing $KBrO_3$. After 10 min, spectrophotometric readings of Br_2 were taken at 396 nm. Both methods gave a first-order rate constant of 1.6×10^{-5} s^{-1}.

Phenyltartronic Acid Decarboxylation. The potassium salt of PhTA was prepared in a manner similar to that for the ammonium salt reported by Lutz.[14] BrPhMA was dissolved in a minimum volume of methanol containing KOH. The potassium salt began to precipitate within a few seconds. It was filtered and washed with ethanol. Weighed amounts were dissolved in 0.10 M $HClO_4$, and the conversion to mandelic acid was followed at 260 nm by spectrophotometry. The first-order rate constant is 1.7×10^{-5} s^{-1} at that acidity at 25 °C. The rate is much higher in solution with no mineral acid ($k = 2 \times 10^{-3}$ s^{-1}), indicating that one of the anionic forms is the active decarboxylating form.

Bromophenylmalonic Acid Reactions. BrPhMA was prepared by reaction of PhMA with bromine water in approximate 1:1 mole ratio. After disappearance of the bromine, the solution was extracted with ether, dried over $MgSO_4$, and allowed to evaporate. When the volume of ether was considerably reduced, toluene was added, and the solution evaporated with an air stream until crystals formed. The product was recrystallized by dissolving in a small volume of ether, adding toluene, and then allowing the solution to evaporate. (Heating to dissolve causes decarboxylation.)

TABLE VII: Effect of Concentrations on Oscillatory Period[a]

Effect of $[IO_2^-]$

$[IO^-_3]_0$, M	period, min	no. of oscillns
$[HClO_4] = 0.0258$ M, $[H_2O_2]_0 = 1.48$ M		
0.010		no oscillns
0.011	0.17	33
0.0125	0.17	45
0.015	0.20	38
0.020	0.24	26
0.030	0.33	11
$[HClO_4] = 0.096$ M, $[H_2O_2] = 1.40$ M		
0.010	0.40	19
0.020	0.20	7

Effect of $[H_2O_2]$

$[H_2O_2]_0$, M	period, min	no. of oscillns
$[HClO_4] = 0.0258$ M		
1.08	0.14	5
1.48	0.24	26
1.80	0.20	14
$[HClO_4] = 0.096$ M		
1.40	0.80	3
1.47	1.0	7
2.43	1.06	3

Effect of $[MnSO_4]$

$[MnSO_4]_0$, M	period, min	no. of oscillns
$[HClO_4] = 0.0258$ M, $[H_2O_2] = 1.48$ M		
0.0025	0.15	5
0.050	0.24	26
0.0075	0.29	15
$[HClO_4] = 0.096$ M, $[H_2O_2] = 1.40$ M		
0.0025	0.16	15
0.0050	0.80	7
0.010	0.15	3

Effect of [PhMA]

$[PhMA]_0$, M	period, min	no. of oscillns
$[HClO_4] = 0.0258$ M, $[H_2O_2] = 1.47$ M		
0.0041	0.44	6
0.0094	0.26	19
0.0159	0.12	8
$[HClO_4] = 0.096$ M, $[H_2O_2] = 1.47$ M		
0.00503	1.2	1
0.00754	1.0	2
0.0101	1.0	3
0.0152	0.26	18
0.0200	0.05	9

Effect of $[HClO_4]$

$[HClO_4]$, M	period, min	no. of oscillns
$[H_2O_2]_0 = 1.46$ M		
0.006		no oscillns
0.012	delay, then 0.26	10
0.024	0.20	27
0.048	0.38	15
0.096	1.0	3
0.192	1.7	1
0.240		no oscillns

[a] Unless otherwise specified, $[KIO_3] = 0.020$ M, $[MnSO_4]_0 = 0.0050$ M, and $[PhMA] = 0.010$ M. Temperature was 25 °C.

BrPhMA oxidizes iodide to iodine rapidly, but bromophenylacetic acid does not. Thus, if either hydrolysis or decarboxylation occurs with BrPhMA, the products are relatively inert to iodide. Samples of BrPhMA in 0.10 M $HClO_4$ were removed at appropriate intervals and mixed with acidic iodide solutions. The resulting iodine was titrated with thiosulfate. The total first-order

TABLE VIII: Iodide plus Iodine plus Hydrogen Peroxide[a]

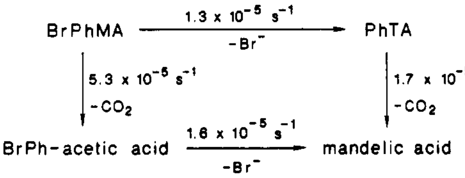
$[H_2O_2]_0$, M	$[I_2]_0$, M × 10^4	$[I^-]_0$, M × 10^5	$[I_3^-]_0$, M × 10^5	σ^b at 460 nm	σ^b at 352 nm	% completion[c]
0.00463	3.3	8.2	1.9	0.003	0.011	92
0.00944	6.5	7.0	3.2	0.005	0.007	93
0.0183	6.5	6.8	3.2	0.002	0.006	94
0.0287	6.5	6.9	3.2	0.006	0.013	99
0.0566	6.5	6.8	3.2	0.005	0.013	99
0.0787	9.4	11.8	7.9	0.002	0.013	93

[a] $[HClO_4]$ was 0.10 M and temperature was 25 °C in all solutions. [b] σ is the average deviation ($\sum$|absorbance expt − absorbance calcd|)/n over the entire measurement set. [c] Based on $[I^-]$.

rate constant for loss of BrPhMA (in 0.10 M $HClO_4$ at 25 °C) by both processes was 0.000 67 s^{-1}.

Formation of bromide ion by hydrolysis for BrPhMA (or bromophenylacetic acid) can be followed with a Ag–AgBr electrode. Since the reactions are parallel or consecutive first-order reactions, closed-form equations relating electrode potential to time can be written. The only undetermined constant is the one for BrPhMA hydrolysis.

The constants can be summarized as follows:



Bromination Reactions. Bromination of the above compounds was followed by spectrophotometry at 396 nm. Mandelic acid and bromophenylacetic acid are relatively inert to aqueous bromine in 0.10 M acid. PhTA reacts slowly, at a rate independent of bromine concentration, but far too slowly to account for the loss of bromine when initial reactants are PhMA and aqueous bromine. We have concluded that BrPhMA reacts directly with bromine by an unknown mechanism, possibly involving a rearrangement or decarbonylation. The rate can be modeled by a first-order constant involving PhMA only ($k = 4.7 \times 10^{-5}$ s^{-1}).

Appendix B. Oxidation of Triiodide Ion by Hydrogen Peroxide

Our results for speed of oxidation of iodide by hydrogen peroxide in the presence of iodine were somewhat higher than predicted.[15] These runs were observed at 460 and 353 nm. All runs were at 25 °C at $[HClO_4] = 0.10$ M and were followed until the initial iodide was diminished by 92–99%. Table VIII shows the initial conditions. For these concentrations, the iodine concentration stayed relatively constant, and most of the change occurred at the triiodide peak at 353 nm. Table VIII shows deviation from experimental values when absorbances were calculated with the constants in Table II for reactions 5–8.

Registry No. PhMA, 2613-89-0; IPhMA, 118725-10-3; BrPh–acetic acid, 4870-65-9; BrPhMA, 70882-17-6; PhTA·K, 118725-11-4; H_2O_2, 7722-84-1; KIO_3, 7758-05-6; HNO_2, 7782-77-6; $MnSO_4$, 7785-87-7.

Three-Dimensional Scroll Ring Dynamics in the Belousov–Zhabotinsky Reagent and in the Two-Variable Oregonator Model

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The long-term motion of scroll rings of chemical activity was monitored in the Belousov–Zhabotinsky reagent. The ring's shrinkage toward extinction follows the mathematically anticipated pattern. Corresponding numerical experiments were run using the two-variable Oregonator model, with results that are not distinguishable from the experiments. By varying pertinent chemical parameters, it was also found that a variety of other phenomena should be observable in the laboratory, including stably persistent drifting scroll rings of unique size and a coiled scroll that unwinds from the inside.

1. Introduction

If a chemical system can be provoked by a small stimulus to execute an immediate large excursion followed by return to nearly the original state, it is called "excitable". A spontaneously oscillatory reaction may be excitable if it is susceptible to such provocation during some phase of its cycle, e.g., during its slow passage by a slightly repelling steady state, as in the original ferroin-catalyzed Belousov–Zhabotinsky reagent.[1] The stimulation, excitation, and recovery processes are scarcely altered if the steady state is made an attractor by slight adjustment of recipe parameters to suppress the spontaneity of self-excitation.[2] The well-stirred Belousov–Zhabotinsky reagent provides a convenient laboratory example of such chemical excitability. Unstirred, it manifests a generic consequence of spatially distributed excitability: the excitation propagates as a traveling pulse of chemical activity. In a two-dimensional thin-layer preparation the pulse occurs as a wave front that propagates like a shock at a speed characteristic of the medium, typically a closed ring expanding away from the point of initial excitation. In three dimensions such a wave front resembles a closed spherical surface.

But activity in excitable media can also be self-organized, independent of any recent stimulus. The wave fronts in this case resemble a spiral in cross section, which emanates from a pivot

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