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Comparison of Several Substrates in the Briggs−Rauscher Oscillating System

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Acetone, methylmalonic acid, malonic acid, iodomalonic acid, and phenylmalonic acid are compared under identical conditions in the Briggs−Rauscher oscillating system. Each of these five substrates consumes iodine to form an iodo product and produces iodide at the same time. The rates of iodine consumption have been measured for each of the substrates individually. To a first approximation, all of the substrates behave in a similar manner when compared at concentrations which react with iodine at similar rates. A skeleton model for the oscillatory system cannot quantitatively predict variations of the oscillatory period with concentration for any one of the substrates. Several reactions and processes are discussed which must be part of a complete description of the oscillator but which make only marginal improvements when compared to the skeleton model: reduction of iodate ion and iodine by hydroperoxy radical, reduction of iodate by the substrate enol, second-order reduction of iodate by iodide, net oxidation of iodine by hydrogen peroxide, continuous HOIO production, and decomposition of the iodo products.

Introduction

The Briggs−Rauscher oscillating system provides a visually spectacular demonstration of an oscillatory mixture.[1−3] The system is composed of an acid (such as perchloric, sulfuric, or phosphoric), iodate ion, hydrogen peroxide, a metal catalyst (Mn(II) or Ce(IV)), and an organic substrate to react with iodine. Iodine is alternately produced and then consumed. Addition of starch causes a sharper color change when iodine is produced. A skeleton mechanism has been proposed[4,5] which is able to model some of the basic features of the system. The model has some serious deficiencies. In the model the ratio between maximum and minimum concentrations is many-fold too high for both iodine and iodide concentrations.[4] The dependence of period on concentration is incorrect[6] for most species. Decomposition of iodo products is not accounted for.[7]

In this study we concentrate on the substrate dependence. Oscillatory systems with each of the substrates acetone (Ac), methylmalonic acid (MeMA), malonic acid (MA), and phenylmalonic acid (PhMA) have been reported previously.[8−11] Some differences have been noted. The iodomalonic acid oscillator is reported here for the first time. The reaction of iodine with each of the five substrates has been studied individually. In this study, the initial concentrations of all other components are held constant so the effect of different substrates can be compared directly. Suggestions are made to modify the skeleton model to try to improve the correspondence between model and experiment.

Although it was not the original intent to study manganese dependence here, two sets of data are included, one at "high" $[Mn^{2+}] = 0.010$ M, and the other at "low" $[Mn^{2+}] = 0.0020$ M. In a separate study, oscillatory mixtures with no manganese are reported.[12]

Experimental Procedures

All reagents were reagent grade unless noted. Water was double distilled. Hydrogen peroxide was "stabilizer free" from Fisher. MA (Sigma, 99%) and MeMA (Aldrich, 96%) were recrystallized from 30:70 ethyl acetate−chloroform. PhMA (Aldrich, 96%, 2 g) was dissolved in ethyl acetate (15 mL) and then filtered. Toluene (20 mL) was added. The mixture was allowed to evaporate, and PhMA was filtered off. This procedure avoided heating, which caused some decarboxylation.

Absorbance was measured in a Coleman-Hitachi Model 124 or on a Hewlett-Packard Model 8451A spectrophotometer, both equipped with thermostated cell compartments. One centimeter cuvettes were used. The temperature was regulated to +0.2 °C. Iodide ion was measured with an Orion iodide ion electrode, vs a silver−silver chloride double-junction electrode with sodium sulfate in the outer junction. Electrode measurements were done in a thermostated beaker. The last reagent was added with a thermostated rapid delivery buret. The apparatus was completely covered with metal foil to exclude light.

Perchloric acid was analyzed by titration vs sodium carbonate. Hydrogen peroxide was standardized daily by iodometric analysis.

IMA (iodomalonic acid) was prepared as the potassium salt, K_2IMA.[13] IMeMA (iodomethylmalonic acid) was prepared by an analogous method as K_2IMeMA.

All runs were carried out in the batch mode. Oscillating solutions were prepared from stock solutions using pipets or burets, except for MA, MeMA, K_2IMA, K_2IMeMA, and PhMA, which were sometimes added as solutions but usually were weighed and added as solids. Unless stated otherwise, the order of addition was $HClO_4$, KIO_3, $MnSO_4$, substrates, and H_2O_2.

Observations were made using the iodide ion electrode or spectrophotometer. Absorbance measurements for iodine determination were made at 460 nm. The absorbance measurements were much more succeptable to interference from oxygen evolution. This could be minimized by special attention to cleanliness of the cuvets. The absorbance measurements were also affected by lack of stirring and probably by the light beam itself. These solutions are all photosensitive to some degree. Supersaturation of the solutions with oxygen had a marked effect on the behavior and could sometimes stop the oscillations. A tap on the cuvette or removal and inversion of the cuvette and then replacement just after the iodine production phase were sufficient to release the supersaturation and get regular oscillations.

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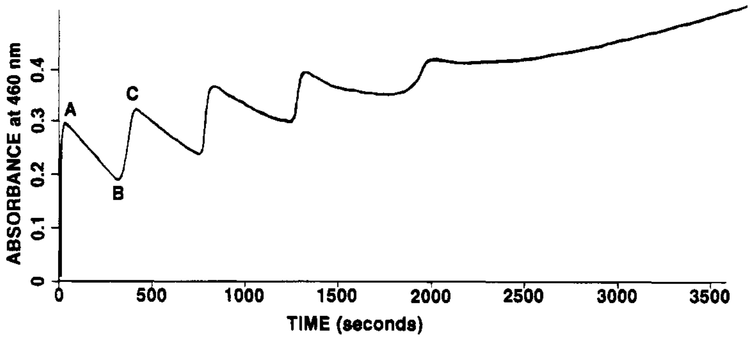

Figure 1. Absorbance at 460 nm vs time for a MeMA oscillator. Concentrations: $[HClO_4]_0 = 0.100$ M; $[KIO_3]_0 = 0.0200$ M; $[MnSO_4] = 0.0020$ M; $[H_2O_2]_0 = 1.50$ M; [MeMA] = 0.0060 M; all at 25 °C.

Skeleton Mechanism

The skeleton mechanism with slight modifications has been investigated by Turanyi[14] using principal-component analysis of the rate sensitivity matrix. The reactions are given here:

$$H^+ + I^- + HOI \rightarrow I_2 + H_2O \tag{I1}$$

$$I_2 + H_2O \rightarrow H^+ + I^- + HOI \tag{I−1}$$

$$H^+ + I^- + HOIO \rightarrow 2HOI \tag{I2}$$

$$2H^+ + I^- + IO_3^- \rightarrow HOIO + HOI \tag{I3}$$

$$H^+ + IO_3^- + HOIO \rightarrow 2IO_2^\bullet + H_2O \tag{I5}$$

$$2IO_2^\bullet + H_2O \rightarrow H^+ + IO_3^- + HOIO \tag{I−5}$$

$$2HOO^\bullet \rightarrow H_2O_2 + O_2 \tag{O2}$$

$$HOI + H_2O_2 \rightarrow H^+ + I^- + O_2 + H_2O \tag{D1}$$

$$H_2O + Mn^{2+} + IO_2^\bullet \rightarrow HOIO + Mn(OH)^{2+} \tag{M1}$$

$$Mn(OH)^{2+} + H_2O_2 \rightarrow HOO^\bullet + Mn^{2+} + H_2O \tag{M2}$$

$$RH \rightarrow enol \tag{C3}$$

$$enol \rightarrow RH \tag{C−3}$$

$$enol + I_2 \rightarrow RI + H^+ + I^- \tag{C4}$$

The notation follows that used previously.[4,14] Two steps were found to be mechanistically unimportant.[14] (They were step (I−3) and step (I4), disproportionation of HOIO.) Steps (O2) and ((M2) are also mechanistically unimportant, since they are the sole reactions of species $HOO^\bullet$ and $Mn(OH)^{2+}$ within the mechanism. Rate constants for reactions I5, I−5, and M1 have not been measured independently.

Involvement of Organic Substrate

In the skeleton mechanism, the organic substrate acts only as a sink for iodine and a source of iodide ion. There is no provision for further interaction with components of the solution, although there is evidence that the substrate or iodo product is further involved.[7,15,16] Also in the Belusov−Zhabotinskii oscillator there is extensive involvement of substrate.[17] This work will explore some of the features in the Briggs−Rauscher oscillator which are substrate dependent.

Iodine Consumption. The iodination of each of the substrates follows an enol mechanism, steps C3, C−3, and C4. Rates have been studied in nonoscillating solutions, usually in the presence of IO_3^- to remove I^- formed in C4. The rate law, under conditions where reaction C−4 can be neglected, is of the form

$$-d[RH]/dt = k_a[RH][I_2]/(1 + k_b[I_2])$$

where $k_a = k_{C3}k_{C4}/k_{C-3}$ and $k_b = k_{C4}/k_{C-3}$.

TABLE 1: Rate Constants for Iodination

substrate	k_a, M^{-1} s^{-1}	k_b, M^{-1} s^{-1}	k_{C-4}, M^{-2} s^{-1}	ref
acetone	0.30	1×10^5		8
MeMA	16	1×10^5	1.5×10^2	18
MA	40	1×10^4	2.0×10^2	9
IMA	35	1×10^3		19
PhMA	125	3.8×10^4	2.86×10^4	11

Enol formation is typically catalyzed by acids and/or bases. The rate constants here reflect the values in 0.1 M $HClO_4$.

Table 1 summarizes rate constants for each of the substrates. In mixtures of substrate, acid, I_2, and IO_3^-, a factor of 0.4 relates iodine removal and substrate removal because of the stoichiometric relationship

$$5RH + 2I_2 + H^+ + IO_3^- \rightarrow 5RI + 5H_2O \tag{P1}$$

since I^- is rapidly reoxidized by IO_3^-.

Representative Run for an Oscillating Mixture. Figure 1 shows a plot of absorbance vs time for a representative run. This run is one where substrate concentration [MeMA] was relatively low, and peak heights and periods are obviously not constant. At higher substrate concentrations, these features were much more uniform. In general, periods and frequencies (1/period) were measured during the early part of the run after any induction period. In runs with low substrate concentration, the periods were measured between the first two peaks with a consistent waveform. With higher substrate concentrations where the periods were shorter, the periods were taken from an average of the first few peaks.

The rate of iodine consumption ($-\Delta[I_2]/\Delta t$) in the oscillating mixtures was measured from the first or second absorbance maximum (point A in Figure 1) to the next minimum (point B). The rate of iodine production was measured from the minimum (B) to the next maximum (C). This approach is arbitrary, since the curves are not strictly linear, but does represent some average over the cycle. When curves deviated from sawtooth shape, slopes were taken over the initial linear portion of the first consumption phase and over the most linear portion of the first production phase.

In general, there is reasonable agreement between $-\Delta[I_2]/\Delta t$ calculated from slopes of absorbance vs time in the oscillators and $-d[I_2]/dt$ calculated from the rate laws above. As an example, from the run in Figure 1, observed initial consumption $= -\Delta[I_2]/\Delta t = \Delta\text{absorbance}/(746\Delta t) = 0.60 \times 10^{-6}$ M s^{-1}, where 746 M^{-1} cm^{-1} is the specific absorptivity for I_2 at 460

TABLE 2: Iodine Consumption/Production Rates for Several Oscillators[a]

subst	concn (M)	initial freq (min^{-1})	[I_2] low (M × 10^4)	[I_2] high (M × 10^4)	$-\Delta[I_2]/\Delta t$ obsd consumption (M s^{-1} × 10^6)	$-d[I_2]/dt$ calcd consumption (M s^{-1} × 10^6)	$\Delta[I_2]/\Delta t$ obsd production (M s^{-1} × 10^6)
					(A) [$MnSO_4$] = 0.0100 M		
Ac	0.37	0.24	4.5	5.1	0.27	0.44	2.1
Ac	0.69	0.27	3.6	4.5	0.62	0.83	1.1
Ac	1.38	0.48	2.1	3.8	1.2	1.7	6.8
Ac	2.23	0.71	1.6	3.3	2.5	2.7	12
Ac	2.76	1.0	1.3	2.7	3.4	3.3	8.9
MeMA	0.006	0.15	3.9	5.0	0.16	0.38	4.4
MeMA	0.010	0.16	2.4	4.0	0.60	0.64	2.7
MeMA	0.020	0.30	1.7	3.8	1.2	1.3	8.6
MeMA	0.037	0.56	1.1	3.1	2.0	2.4	7.4
MeMA	0.060	0.91	1.1	2.1	2.5	3.8	10
MeMA	0.120	1.7	0.7	2.2	8.0	7.7	22
MeMA	0.240	3.3	0.8	2.0	13	14	29
MA	0.0106	1.7	0.2	1.7	5.3	9	29
MA	0.015	2.5	0.2	1.9	12	12	25
MA	0.025	3.0	0.1	1.6	17	16	34
MA	0.048	5.6	0.4	1.1	12−20	32	41
IMA	0.0032[b]						
IMA	0.010[b]						
IMA	0.014[b]						
PhMA	0.0012[c]						
PhMA	0.0042[d]		1.7	5.9	5	5.2	20
PhMA	0.010	0.74	0.9	4.8	8.5	11	38
PhMA	0.0151	1.33	0.4	4.0	12	16	40
PhMA	0.0202	2.5	0.3	2.8	14	23	44
PhMA	0.0251	3.7	0.3	2.5	20	27	49
					(B) [$MnSO_4$] = 0.0020 M		
Ac	0.27	0.085	4.7	5.8	0.21	0.32	0.34
Ac	0.27	0.074	5.2	6.0	0.16	0.32	
Ac	0.55	0.17	3.6	4.7	0.51	0.64	2.3
Ac	1.38	0.34	1.6	3.5	1.4	1.6	7.3
Ac	2.23	0.69	1.1	2.8	2.8	2.5	11
Ac	2.76	1.00	0.9	2.4	3.3	3.1	13
MeMA	0.0060	0.10	4.2	5.6	0.31	0.38	1.5
MeMA	0.0100	0.16	2.8	4.5	0.61	0.62	1.9
MeMA	0.020	0.42	1.2	3.5	1.1	1.2	5.5
MeMA	0.041	0.53	0.54	2.6	2.5	2.5	6.2
MeMA	0.0677	0.77	0.32	2.1	3.8	4.0	6.3
MA	0.0062	0.92	0.35	1.7	5	5.0	8.8
MA	0.0108	1.5	0.01	1.0	6.8	5.8	9.0
MA	0.0155	2.0	0.3	1.0	6	9.5	5
MA	0.0260	3.3	0.21	0.58	3.4	12	6.7
MA	0.039	6.0	0.36	0.6	4.8	20	4.8
IMA	0.014	6	0.13	0.33	3.4	2.2	5.3
PhMA	0.0049	2.0	0.21	0.64	2.4	3.9	6.7
PhMA	0.0075	4.5	0.11	0.40	5.0	4.7	6.3
PhMA	0.010	8.0	0.24	0.39	3.4	7.0	4.5

[a] [$HClO_4$]$_0$ = 0.10 M; [H_2O_2]$_0$ = 1.5 M; [KIO_3]$_0$ = 0.020 M; temperature = 25 °C in all solutions. Frequency is that of the first few maxima. [I_2] high was observed from the first or second peak. [I_2] low was found from the following minimum. [b] Increase in [I_2], no oscillations. [c] Small fluctuations in increasing [I_2]. [d] Only one maximum, two minima in [I_2].

nm. From constants in Table 1 where [RH] = [MeMA] = 0.010 M and [I_2] = 0.000 32 M (average during consumption from Figure 1), calculated consumption, $-d[I_2]/dt$, is (0.4)(16 M^{-1} s^{-1})(0.010 M)(0.000 32 M)/((1 + 1 × 10^{-5} M^{-1} s^{-1} (0.000 32 M)) = 0.64 × 10^{-6} M s^{-1}. This assumes reaction P1 for I_2 + substrate. See Table 2 for additional results. The best agreement for observed and calculated consumption is with Ac or MeMA as substrate.

Cooke[8] has shown that the time period for acetone oscillators is proportional to 1/[Ac] over a wide range of concentrations. This is equivalent to the frequency of oscillations being proportional to [Ac]. If the same relation holds for other substrates, a plot of some scaled concentration vs frequency should yield a universal straight line for all substrates. The scaling factor for MeMA, for example, has been chosen as the ratio of acetone to MeMA in two oscillating systems which have the same frequency. Plots of scaled concentration vs frequency are shown in Figure 2A (high [Mn^{2+}]) and 2B (low [Mn^{2+}]). The plots are very similar. It is obvious that the straight line relation is not universal for different substrates but that the plot does give a method of comparison between different oscillators. Since the line is not straight (and may not extrapolate through the origin) for the separate substrates, the scaling factors are only approximate. The points for Ac and MeMA fit the relationship best; points for MA and PhMA seem to have different slopes, reflecting greater complexity for reactions with those substrates. [Mn^{2+}] has little effect on the initial frequencies at the concentrations of Ac, MeMA, and MA used here. IMA solutions did not oscillate at high [Mn^{2+}], and PhMA solutions required a different scaling factor when [Mn^{2+}] was changed.

Using the scaling factors found for Figure 2, initial iodine concentration ranges are displayed in Figure 3 for each of the substrates. The concentration ranges were taken as described above, from peak to peak for the first consistent waveforms. Though the individual ranges are subject to uncertainty, it is evident that the substrates fit fairly well on the same curve in each plot, except for PhMA in Figure 3A, where the maxima in [I_2] are much higher. One can generalize that the different substrates cause oscillations of the same frequency when the

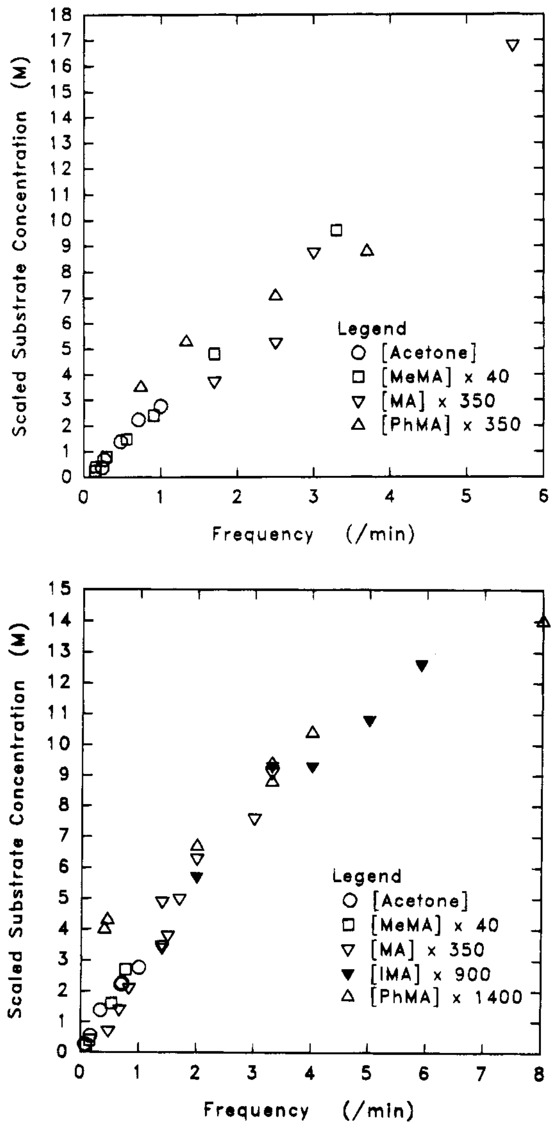

Figure 2. (A, top) Scaled concentrations of substrate vs frequency of oscillator. Concentrations: $[HClO_4]_0 = 0.100$ M; $[KIO_3]_0 = 0.0200$ M; $[MnSO_4] = 0.0100$ M; $[H_2O_2]_0 = 1.50$ M; all at 25 °C. (B, bottom) Scaled concentrations of substrate vs frequency of oscillator. Same as Figure 2A except $[MnSO_4] = 0.0020$ M, and scaling factor for PhMA.

iodine concentrations are comparable, especially when $[Mn^{2+}]$ is low (Figure 3B).

With conditions similar to those used here, the oscillatory period is usually dominated by the iodine consumption phase. That is, typically 70–80% of the time is taken by iodine consumption. The scaling factors should be related to the k's in Table 1, especially to k_a/k_b. For acetone and MeMA, $[I_2]$ is high enough so that the rate of substrate consumption is nearly independent of $[I_2]$ for the entire oscillatory period. The scaling factor for MeMA, 40, is in the same neighborhood as the ratio of k_a/k_b's for the two compounds.

Most of the acetone oscillators consume iodine at a slightly slower rate than expected from the rate law above. This is partly because of a side reaction between acetone and hydrogen peroxide, leading to formation of acetone–hydrogen peroxide adducts. (The adducts can be explosion hazards, so mixtures containing both reagents should never be allowed to dry out.) Though the rate of reaction is "slow" (the half-life is on the order of 10–15 min), appreciable reaction can take place in just a few minutes. If the oscillatory period is comparable, iodine consumption will be slowed because of conversion of acetone to peroxy product. The conversions of acetone and hydrogen peroxide to 2-hydroxy, 2-hydroperoxypropane (HP1), and 2,2-bis(hydroperoxy)propane (HP2) have been studied.[20,21] An adaptation of a mechanism to handle adduct formation in acetone oscillators is presented in the Appendix.

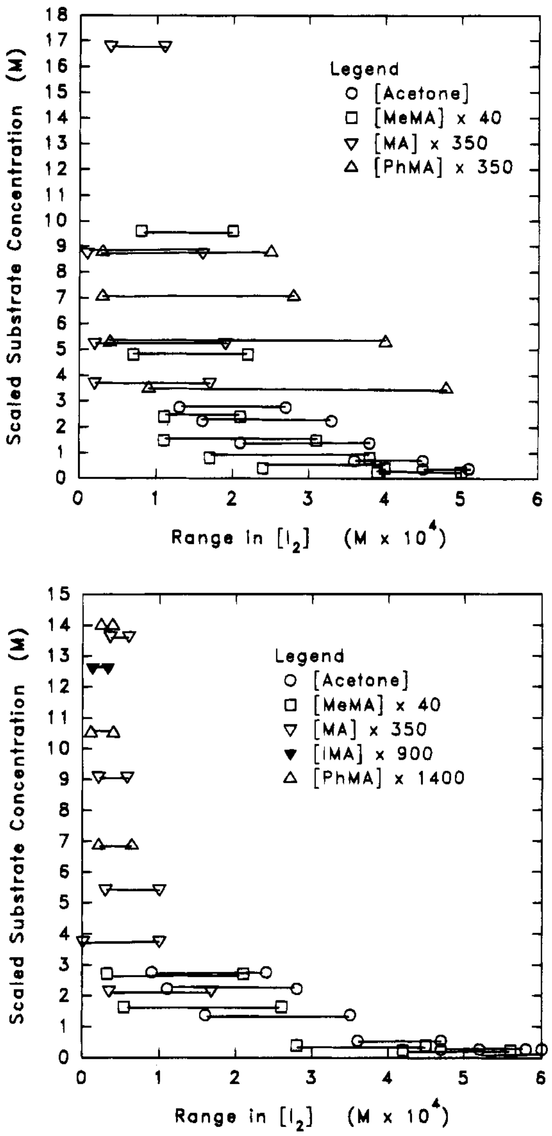

Figure 3. (A, top) Scaled concentration of substrate vs [iodine] range in oscillator. Concentrations: $[HClO_4]_0 = 0.100$ M; $[KIO_3]_0 = 0.0200$ M; $[MnSO_4] = 0.0100$ M; $[H_2O_2]_0 = 1.50$ M; all at 25 °C. (B, bottom) Scaled concentration of substrate vs [iodine] range in oscillator. Same as Figure 3A except $[MnSO_4] = 0.0020$ M, and scaling factor for PhMA.

Iodine Production. For most of the conditions investigated, the last column in Table 2 shows increasing rate of iodine production with increasing substrate concentration. The rates in the table represent observed rates, derived as described above. For example, from Figure 1, observed initial production = $\Delta[I_2]/\Delta t = \Delta\text{absorbance}/(746\ \Delta t)$, $= 2.7 \times 10^{-6}$ M s^{-1}. The observed I_2 production is a net rate, equal to total I_2 production minus I_2 consumed during the same time via steps C3, C−3, and C4. The total I_2 production must therefore be the sum of the net (observed) production and the consumption (calculated): the sum of the last two columns. The total iodine production is shown in Figure 4 as a function of the scaled concentration. Although there are variations within each group, the trends are obvious. There is a strong correlation between substrate concentration and rate of iodine production. This feature of enhanced iodine production is missing from the skeleton mechanism.

The increase in iodine production with substrate is also related to the $[I_2]$ maxima in Table 2. If I_2 production was not

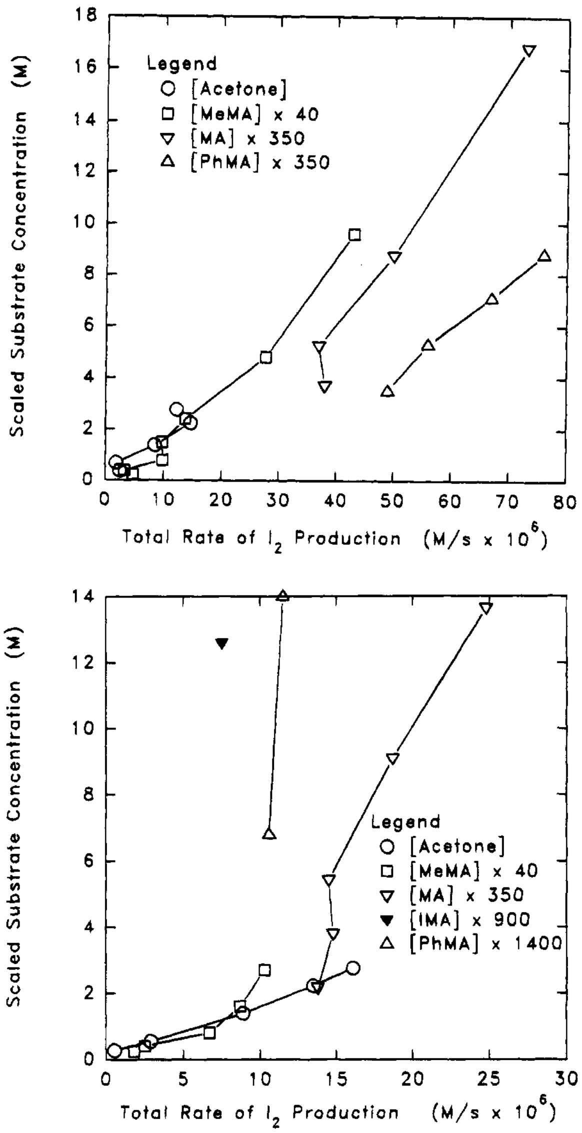

Figure 4. (A, top) Scaled concentration of substrate vs rate of [iodine] production in oscillator. Concentrations: $[HClO_4]_0 = 0.100$ M; $[KIO_3]_0 = 0.0200$ M; $[MnSO_4] = 0.0100$ M; $[H_2O_2]_0 = 1.50$ M; all at 25 °C. (B, bottom) Scaled concentration of substrate vs rate of [iodine] production in oscillator. Same as Figure 4A except $[MnSO_4] = 0.0020$ M, and scaling factor for PhMA.

enhanced, those I_2 maxima would drop off much more sharply at high substrate concentrations. For example, experimentally increasing [MeMA] from 0.0060 to 0.24 M lowers maximum $[I_2]$ (labeled "I_2 high" in Table 2) from 5.0×10^{-4} to 2.0×10^{-4} M. Using the modified skeleton model over the same range of [MeMA], maximum $[I_2]$ drops by a factor of 27. Some process not included in the skeleton model keeps the rate of I_2 production high when substrate concentration is high.

A possible point of intervention for the substrate is in the autocatalytic formation of HOIO. In the skeleton model, Mn^{2+} serves that function:

$$H^+ + IO_3^- + HOIO \rightleftharpoons 2IO_2^\bullet + H_2O \qquad (I5)$$

$$\{H_2O + Mn^{2+} + IO_2^\bullet \rightarrow HOIO + Mn(OH)^{2+}\} \times 2 \qquad (M1)$$

followed by regeneration of the metal ion catalyst and destruction of $HOO^\bullet$:

$$\{Mn(OH)^{2+} + H_2O_2 \rightarrow HOO^\bullet + Mn^{2+} + H_2O\} \times 2 \qquad (M2)$$

$$2HOO^\bullet \rightarrow H_2O_2 + O_2 \qquad (O2)$$

This sequence results in the autocatalytic process

$$H_2O_2 + H^+ + IO_3^- + HOIO \rightleftharpoons 2HOIO + H_2O + O_2 \qquad (P2)$$

Knowledge of organic reactions in these mixtures is limited; involvement of the substrate in reduction of $IO_2^\bullet$ is a possibility. Inclusion of a possible hydrogen atom abstraction process

$$RH + IO_2^\bullet \rightarrow R^\bullet + HOIO \qquad (S1)$$

in the simulation allows a much wider correspondence of $[I_2]$ maxima with substrate concentration. ($R^\bullet$ is assumed to disproportionate or lead to inert products.) (The designation S1 refers to a suggested reaction.)

Attempts were made to find evidence of reaction S1 in subsystems of the oscillator or in concentration regions away from the oscillatory region. Two subsystems tried were

$$H^+ + MeMA + IO_3^- \rightarrow IMeMA + \text{oxidized organic products} \qquad (P3)$$

$$(5 + 2n)H_2O_2 + 2IO_3^- + 2H^+ \xrightarrow{Mn^{2+}} I_2 + (6 + 2n)H_2O + (5 + n)O_2 \qquad (P4)$$

The first, P3, is addressed further in the next section. The reaction is relatively slow. The catalyzed reduction of iodate by H_2O_2 accompanied by H_2O_2 decomposition, reaction P4, is much faster. Presumably in the oscillator I_2 is produced by P4 (and some P3), and consumed by C4. If P4 is "perturbed" by addition of MeMA with nonoscillating conditions, will MeMA have an accelerating effect in iodate reduction? Table 3 shows the results of several runs. The rate of iodate reduction was compared by either following increasing absorbance at 460 nm (for $[I_2]$), or near 280 nm (for [IMeMA]). In each of the conditions studied, the rate of iodate reduction in the full (nonoscillating) system (column 5) was comparable to or less than the sum of the rates in the subsystems (column 1 + column 4). The addition of MeMA to the acidic H_2O_2, IO_3^-, Mn^{2+} subsystem did not increase the rate of iodate reduction. This would seem to rule out reaction S1 as the source of the increase in the oscillators. An effect that does not show in the table, however, is that the presence of MeMA causes the rate of iodate reduction to be maintained. The rate of I_2 production in the P4 subsystem drops off sharply within the first minute of observation.

Direct Oxidation of Substrate by Iodate. Another property of the oscillator possibly related to the substrate dependence is the switch from iodine consumption to iodine production when $[I_2]$ is still relatively high. Refer to Figure 1 and Table 2. Within the simulated mechanism, a small amount of "extra" HOIO is sufficient to change the iodine consumption mode to iodine production, so long as substrate concentration is low. When substrate concentration is high, however, the rate of iodide production is so large during iodine consumption that much higher levels of HOIO are needed to drive $[I^-]$ below the critical amount needed to allow autocatalytic rise in [HOIO]. One component of the solution which has an increasing concentration during $[I_2]$ consumption is the enol. (Since the enol reacts with I_2 via reaction C4, [enol] is higher when $[I_2]$ is low, so [enol] increases as $[I_2]$ decreases.) Is it possible that direct reaction of iodate with enol can produce HOIO (or $IO_2^\bullet$) fast enough to switch the mode?

Each of the substrates does react directly with iodate in 0.1 M acid solution. Several runs are summarized in Table 4.

TABLE 3: Comparison of Rates of Iodate Reduction[a]

rate, P3 $d[IO_3^-]/dt$ (M s^{-1})	$[H_2O_2]_0$ (M)	$[Mn^{2+}]$ (M)	initial rate, P4 $d[IO_3^-]/dt$ (M s^{-1})	rate, P4 + MeMA $d[IO_3^-]/dt$ (M s^{-1})
2×10^{-7}	0.057	0.0050	3.6×10^{-6}	3.4×10^{-6}
2×10^{-7}	0.113	0.0010	7.5×10^{-7}	6×10^{-7}
2×10^{-7}	0.57	0.0010	3.3×10^{-6}	3.6×10^{-6}

[a] $[HClO_4]_0 = 0.10$ M; $[KIO_3]_0 = 0.010$ M; $[MeMA]_0 = 0.10$ M in columns 1 and 5; temperature = 25 °C in all solutions. Column 1, P3 contains $HClO_4$, KIO_3, and MeMA. Measured absorbance at 286 nm. Column 4, P4 contains $HClO_4$, KIO_3, H_2O_2, and Mn^{2+}. Measured absorbance at 460 nm. Column 5, P4 + MeMA. Measured absorbance at 290 nm.

TABLE 4: Rates of Substrate Reaction with Iodate[a]

substrate	[substrate] (M)	$[IO_3^-]_0$ (M)	absorptivity (M^{-1} cm^{-1})	wavelength	k' (M^{-1} s^{-1})
acetone	0.69	0.020	320	300	4×10^{-7}
MeMA	0.020	0.020	339	286	1.5×10^{-4}
MeMA	0.110	0.020	339	286	1.9×10^{-4}
MeMA	0.220	0.020	339	286	2.0×10^{-4}
MeMA	0.10	0.0050	339	286	1.9×10^{-4}
MeMA	0.20	0.040	339	286	1.4×10^{-4}
MeMA	0.23	0.011	339	286	1.6×10^{-4}
MA	0.0300	0.030	300	286	$<2 \times 10^{-6}$
PhMA	0.0020	0.020	700	280	1.8×10^{-4}
PhMA	0.0041	0.010	700	280	1.6×10^{-4}
PhMA	0.0219	0.020	700	280	1.3×10^{-4}

[a] $[HClO_4]_0 = 0.10$ M; temperature = 25 °C in all solutions. k' in column 6 from assumed rate law: $d[RI]/dt = -d[IO_3^-]/dt = k'[IO_3^-][RH]$.

Increase of absorbance in the UV (typically from 280 to 300 nm) is consistent with formation of the iodo product, and the rate is close to first order in both iodate ion and substrate. The rate is too slow to distinguish whether or not iodate reacts initially directly with the substrate or with the enol form. Identity of organic oxidation products is not known. A possibility is

$$\text{enol} + IO_3^- + H^+ \rightarrow HOIO + ROH \qquad (S2)$$

The rate of this reaction (assumed to be rate determining and measured in solutions without Mn^{2+} or H_2O_2) is too slow to account for switching from iodine consumption to production. The rate for MeMA$-IO_3^-$ or PhMA$-IO_3^-$ is about an order of magnitude too slow. The rate for MA or acetone with IO_3^- is about three orders of magnitude too slow. Although the reaction mode has not yet been identified to account for "high" $[I_2]$ minimum in Figure 1, enol involvement has the correct concentration dependence to cause a switch with a relatively small decrease in $[I_2]$.

Reactions of Iodo Products

Iodination of enols in aqueous solution is usually reversible to some extent. (Reactions C4 and −C4). Other (unknown) decomposition routes can lead to formation of I_2. The stability of iodo compounds varies with structure. Iodoacetic acid is available commercially. K_2IMA and K_2IMeMA (but not the pure acids) have been isolated. We have not been able to isolate K_2IPhMA.

The stability of the iodo products among these substrates is inversely related to the rate of formation from iodine and substrate. Iodoacetone, IAc, forms slowly and is fairly stable; there is no evidence that decomposition takes place during the initial stages of oscillatory behavior. The other iodo products are unstable enough that the oscillations are affected by the presence of the iodo compounds. IMA and IMeMA have a small effect at first, but I_2MA and IPhMA contribute in a major way to I_2 formation.

IMA is stable enough in solution that it can act as a substrate for an oscillator, at least when $[Mn^{2+}]$ is low. See Figure 5 for an example. At high $[Mn^{2+}]$, iodine forms rapidly and no oscillations are observed. The second iodination product, I_2-MA, is much less stable toward decomposition. This conclusion has been reached by other workers.[7]

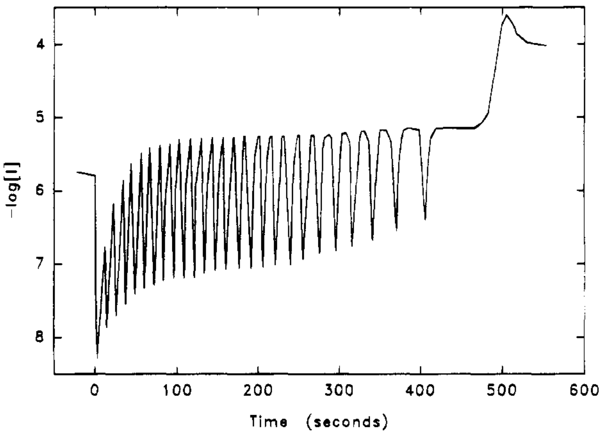

Figure 5. Oscillator with IMA as substrate. $[HClO_4]_0 = 0.100$ M; $[H_2O_2]_0 = 1.49$ M; $[KIO_3]_0 = 0.020$ M; $[Mn^{2+}] = 0.0020$ M; $[IMA]_0 = 0.012$ M; temperature 25 °C.

The maximum $[I_2]$ decreases slowly with time for acetone oscillators. For concentration ranges reported in this study, the decrease is mostly due to decreasing $[IO_3^-]$ as the oscillations proceed. For oscillators with other substrates, the maximum $[I_2]$ often increases, unless substrate concentration is very high. This increase is due to decomposition of iodo product. The effect is clearly seen in Figure 1 with low [MeMA].

Iodine Regeneration, Nonoscillatory Mixtures. A comparison of the lability of the iodo substrates can be made by forming the iodo-substrate in situ, then waiting for iodine regeneration. In order to form a reasonable amount of iodo substrate by reaction with iodine, iodide must be removed. In the oscillatory systems, iodide removal is accomplished by oxidation with iodate or other oxyiodine species. For forming iodo substrate in nonoscillating mixtures, H_2O_2 oxidation was used. The reactions were

$$RH + I_2 \rightarrow RI + H^+ + I^- \qquad (C3 + C4)$$

$$H_2O_2 + H^+ + I^- \rightarrow HOI + H_2O \qquad (U1)$$

TABLE 5: Comparison of I_2 Regeneration from RI[a]

substrate	[substrate] (M)	[$MnSO_4$] (M)	[I_2]$_0$ (M)	time to I_2 min (min)	time to I_2 max (min)
acetone	0.010	0.0050	0.000 52	78	*b*
MeMA	0.0011	0.0050	0.000 52	120	670
MeMA	0.0049	0.0050	0.000 48	35	≫700
MA	0.0010	0.0050	0.000 52	11	70
MA	0.00050	0.0020	0.000 50	10	50
IMA	0.0015	0.0020	0.0	*c*	50
IMA	0.0015	0.0020	0.000 37	*c*	35
IMA	0.0029	0.0020	0.000 48	*c*	23
PhMA	0.00050	0.0054	0.000 40	4.0	43
PhMA	0.0010	0.0010	0.000 40	5	40
PhMA	0.0010	0.0030	0.000 39	3	30
PhMA	0.0010	0.0054	0.000 40	3.3	33
PhMA	0.0020	0.0054	0.000 40	4.0	43

[a] [$HClO_4$]$_0$ = 0.10 M; [H_2O_2]$_0$ = 1.0 M; temperature = 25 °C in all solutions. These are nonoscillating mixtures with no IO_3^- present. [b] No increase in [I_2] in 1200 min. [c] Iodine concentration increased from the beginning.

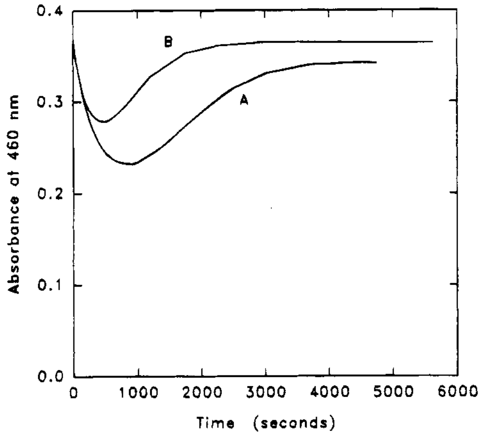

Figure 6. Influence of [Mn^{2+}] on reaction of MA with I_2 in the presence of H_2O_2. Curve A: [Mn^{2+}] = 0.0 M. Curve B: [Mn^{2+}] = 0.0020 M. Both curves: [$HClO_4$]$_0$ = 0.100 M; [H_2O_2]$_0$ = 1.00 M; [MA]$_0$ = 0.00050 M; [I_2]$_0$ = 0.000 50 M; temperature 25 °C.

$$H^+ + I^- + HOI \rightleftharpoons I_2 + H_2O \qquad (I1, I-1)$$

The net process is $2RH + I_2 + H_2O_2 \rightarrow 2RI + 2H_2O$.

These iodosubstrates are fairly stable in dilute acid solution or in the presence of Mn^{2+}. I_2 is not regenerated within 1 or 2 h. With high H_2O_2, I_2 is regenerated. In the presence of both Mn^{2+} and H_2O_2, I_2 is regenerated even faster. Absorbance vs time measurements on mixtures containing acid, iodine, substrate, $MnSO_4$, and H_2O_2 typically show first a decrease in absorbance and then a rise to approximately the same value as the initial absorbance, showing that little or no organic iodine remains. Two runs with MA are shown in Figure 6. The run with manganese ion reacts more quickly and I_2 regeneration is more nearly complete. Table 5 shows a comparison of the behavior of several substrates under similar conditions. The acetone data are not strictly comparable with the others because of much higher initial concentration and partial conversion of acetone to peroxy adducts. The iodine−acetone reaction is much slower than that of iodine with the other substrates, so to get a reasonable reaction rate, acetone concentration was higher. Even if iodoacetone products were decomposing, the rate was slow enough so that no I_2 reappeared over many hours. In the oscillatory mixtures, acetone concentrations were typically 2 orders of magnitude higher than in Table 5, and iodine regeneration can be neglected. The table clearly shows that iodo compounds of MA and PhMA are completely decomposed to noniodinated products in a time scale of approximately 1 h, whereas iodo compounds of acetone and MeMA are stable over a much longer period. (Similar regeneration of I_2 from IPhMA has been reported previously.[11])

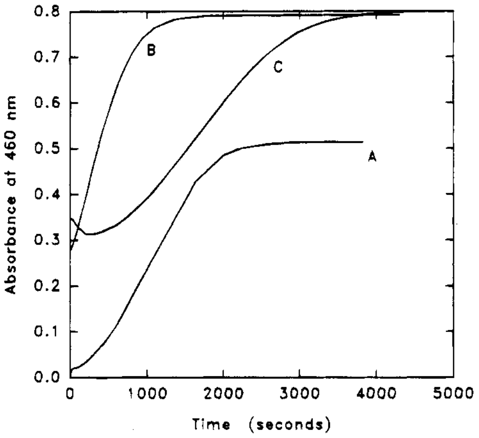

Figure 7. Influence of [Mn^{2+}] and [I_2] on decomposition of IMA in the presence of H_2O_2. Curve A: [Mn^{2+}] = 0.0020 M; [I_2]$_0$ = 0.0 M. Curve B: [Mn^{2+}] = 0.0020 M; [I_2]$_0$ = 0.000 36 M. Curve C: [Mn^{2+}] = 0.0 M; [I_2]$_0$ = 0.000 47 M. All curves: [$HClO_4$]$_0$ = 0.100 M; [H_2O_2]$_0$ = 1.00 M; [K_2IMA]$_0$ = 0.001 50 M; temperature 25 °C.

The rate of iodine regeneration in mixtures described above is approximately half-order in H_2O_2 and $MnSO_4$ and between half and first order in RI.

The mixtures with IMA had no minimum absorbance when $MnSO_4$ was in the mixture from the beginning. I_2 increased as soon as all components were added. The rate of iodine formation was greater when initial iodine was present. See Figure 7.

Iodine is also regenerated in mixtures of substrate plus iodine plus iodate (no H_2O_2 or $MnSO_4$).

A mechanism consistent with the above observations (generating reaction rates with one-half order in all initial reactants) assumes reaction with HOI:

$$HOI + RI \rightarrow I_2 + ROH \qquad (S3)$$

The HOI is generated by reaction I−1. At low [H_2O_2], (or at low [IO_3^-] where IO_3^- is used to oxidize I^-), the formation of triiodide can be significant:

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (I6 \text{ and } I-6)$$

The mechanism with HOI does not address the function of Mn^{2+} (Ce^{+3} is also effective). A radical mechanism is certainly a possibility, although O_2 evolution is low (not measured, but bubbles are not observed during absorbance measurements). We suggest that metal ion and iodosubstrate rapidly form a complex which is more reactive than the uncomplexed iodo substrate.

Iodine Regeneration, Oscillatory Mixtures. In mixtures such as the above which also contain IO_3^-, oscillations are possible. Iodine (and/or iodide) is regenerated from iodo substrate in these oscillatory mixtures by some mechanism other than the reaction with HOI, that is, more rapidly than can be accounted for by reaction S3. With MA or IMA substrates, after oscillations have ended, the mixture nearly always "kicks out" iodine, frequently exceeding the solubility and forming solid I_2. (Note the sharp rise in [I^-] near 600 s in Figure 5, which corresponds to rapid [I_2] formation.) This decomposition occurs suddenly, is autocatalytic, and "starts" from a situation where [I^-] is relatively high. Neither HOI not HOIO is present in sufficient amount to cause the reaction directly or from forming radicals. (Reaction I5 is considered to be a source of radicals in the Briggs–Rauscher mechanism.)[4]

For simulation purposes in oscillatory mixtures we have represented the regeneration process as an autocatalytic decomposition process, with dependencies on manganese ion, iodate ion, etc., omitted. This is clearly a gross approximation of the true process and is not intended to represent an elementary step. Neither the oxidation state of the iodine nor the identity of the organic product(s) has been established. For substrate RH we used

$$H_2O + RI + I_2 \rightarrow {}^3/_2 I_2 + ROH \qquad (S4)$$

where ROH represents a hydrolysis product, or oxidation product, or decarboxylation product. As stated above, the rate is faster than in nonoscillating mixtures. The functional relationship to species concentrations has not been determined, but the iodo compound and manganese ion are definitely involved. Experimentally, oscillations with PhMA last for only relatively few excursions. An empirical rate constant of approximately 0.003 M^{-1} s^{-1} for reaction S4 is of the correct order of magnitude to allow several oscillations then a cessation, followed later by rapid I_2 and I^- production.

The process represented by reaction S4 is a fair representation within the model of some of the features of the Briggs–Rauscher oscillators with PhMA as the substrate. When the substrate is MA, the process is more complex since both IMA and I_2MA will be formed and subsequently decompose. We have not tried to represent the process with a single reaction and reaction rate. Vanag[7] has found an exponential rate constant of 0.2–0.3 s^{-1} represents the autocatalytic decomposition with different conditions including much higher [Mn^{2+}].

The C–I bond in IMA, I_2MA, and IPhMA is much weaker than the C–I bond in iodinated hydrocarbons. The iodination, reaction C4, is highly reversible. In addition, the iodo compounds are subject to hydrolysis and decarboxylation, thus many iodinated and noniodinated organic species are possible intermediates and products. It is not surprising that in active oscillatory mixtures that regeneration can be rather rapid when the substrate is MA or PhMA.

Addition of Initial IMeMA. Several runs were made with iodinated material initially present. IMA can potentially either react with more iodine or regenerate iodine, so we focus here instead on adding IMeMA to MeMA oscillators where a second iodination is not possible.

Solid IMeMA (as the potassium salt) was an initial component of several runs with MeMA substrate. As shown in Figure 8 and Table 6, the lifetime of the run is shortened the more the initial [IMeMA]. Initial iodine concentration is higher, periods are longer, rates of [I_2] consumption are lower as [IMeMA] increases. After oscillations cease, [I_2] rises exponentially, approximately following a rate law d[I_2]/dt = 0.000 28 s^{-1} [I_2] for the conditions in Table 6, until I_2 eventually precipitates out.

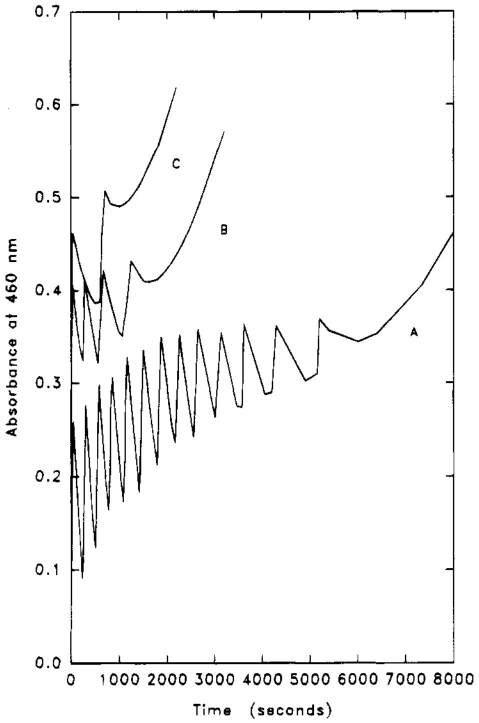

Figure 8. Influence of IMeMA on a MeMA oscillator. Curve A: $[IMeMA]_0$ = 0.0 M. Curve B: $[IMeMA]_0$ = 0.0044 M. Curve C: $[IMeMA]_0$ = 0.0083 M. All curves: $[HClO_4]_0$ = 0.100 M; $[H_2O_2]_0$ = 1.50 M; $[IO_3^-]_0$ = 0.020 M; $[MnSO_4]_0$ = 0.010 M; $[MeMA]_0$ = 0.020 M; temperature 25 °C.

TABLE 6: MeMA Oscillators with Initial IMeMA[a]

[MeMA] (M)	[IMeMA] (M)	no. of oscillations	period (min)	$[H_2O_2]_0$ (M)
0.0110	0.0	5+	8	1.50
0.0110	0.0059	1		1.50
0.0112	0.0110	0		1.50
0.020	0.0	13	3.1	1.50
0.020	0.0044	4	4.0	1.50
0.020	0.0083	2	10.7	1.50
0.040	0.0	28	1.9	1.00
0.040	0.012	11	5.0	1.00
0.040	0.018	7	6.7	1.00
0.040	0.027	4	8.1	1.00

[a] $[HClO_4]_0$ = 0.100 M; $[KIO_3]_0$ = 0.0200 M; $[MnSO_4]$ = 0.0100 M; all at 25 °C. Period is from the initial portion of the reaction.

Hydrogen Peroxide Reactions with Iodine Species

Continuous HOIO Production. In the original skeleton mechanism, [I_2] decreases during iodine consumption to values far lower than observed experimentally. No changes in rate constants have been successful in modifying that pattern appreciably. There must be some other route to switching from iodine consumption to iodine production. This problem was discussed above under "Direct Oxidation of Substrate by Iodate". A possibility for raising the threshold [I_2] level is the reaction

$$H^+ + IO_3^- + H_2O_2 \rightarrow HOIO + O_2 \qquad (D2)$$

This reaction was studied by Liebhafsky[22] at higher temperatures. A rate law, $-d[IO_3^-]/dt = 1.1 \times 10^{-6}$ M^{-1} s^{-1} [IO_3^-] [H_2O_2] can be calculated at 25 °C at [H^+] = 0.1 M from his data. Inclusion of this reaction raises minimum [I_2] at very low substrate concentration, but the constant is too low to bring about an earlier switch from I_2 consumption to I_2 production over a large range in substrate concentration. Also the above rate law does not accurately reflect reaction rates in acidic iodate–hydrogen peroxide mixtures at room temperature. For these reasons, we believe reaction D2 plays a minor role in the Briggs–Rauscher oscillators.

Oxidation of Iodine by Hydrogen Peroxide. Since at low $[I^-]$, iodine can be oxidized by H_2O_2, it is possible that this process occurs in this oscillator. (In the Bray–Liebhafsky oscillator,[2,23] oxidation must account for *all* iodine consumption.) A process such as $HOI + H_2O_2 \rightarrow HOIO + H_2O$ could be an important part of an autocatalytic process which could drive $[I^-]$ low while allowing $[I_2]$ to remain fairly high. The scheme devised by Schmitz[24] for iodine oxidation in the B–L oscillator is attractive for this purpose. This scheme is a nonradical process, beginning with dimerization of HOI, followed by rapid oxidation of the dimer by H_2O_2. The initial dimerization is rate determining.

Addition of a process to accomplish I_2 oxidation was incorporated into the model, and I_2 was enhanced somewhat at high substrate concentration. No substantial improvement in the modeling was seen, however. Since most iodine is believed to be consumed through reaction with organic substrate rather than by oxidation, and rates of I_2 consumption in Table 2 can be predicted without considering oxidation, this process also seems to play a minor role in these oscillators.

Reduction of Iodate and Iodine by Hydroperoxyl Radical

The reaction

$$H^+ + IO_3^- + HOO^\bullet \rightarrow IO_2^\bullet + O_2 + H_2O \qquad (D3)$$

was considered earlier[4] but was removed from the skeleton mechanism because there was no direct evidence for its existence. We consider now two kinds of evidence.

Franz[25] has reported that BR oscillations are stopped by addition of superoxide dismutase (SOD). We concur with that observation and find that lesser amounts of SOD disrupt oscillations temporarily. SOD also decreases the rate of iodine production in the nonoscillatory system H^+, IO_3^-, Mn^{2+}, H_2O_2. Though SOD may not exclusively remove $HOO^\bullet$ radicals from further reaction, the inhibiting effect strongly suggests involvement of $HOO^\bullet$ in the process.

Further evidence for involvement of $HOO^\bullet$ comes from addition of potassium superoxide to acidic solutions containing iodate. The fast reaction $H^+ + O_2^{-\bullet} \rightarrow HOO^\bullet$ is accompanied by formation of small amounts of I_2. The formation of I_2 is more pronounced if Mn^{2+} is also present. Reaction D3 must compete with disproportionation of $HOO^\bullet$.

Inclusion of reaction D3 in the model may result in shifting the major reductant of iodate ion from HOIO (reaction I5) to $HOO^\bullet$ by reaction D3.

Reduction of other iodine species (HOIO, $IO_2^\bullet$, HOI, I_2) by $HOO^\bullet$ is also possible. $HOO^\bullet$ produced as above in acidic solutions of I_2 causes an increase in I^- and I_3^- indicating initial 1-equiv reduction of I_2 to form $I^\bullet$. We have tried adding the reactions

$$HOO^\bullet + I_2 \rightarrow I^\bullet + H^+ + I^- + O_2 \qquad (D4)$$

$$H_2O_2 + I^\bullet \rightarrow H^+ + I^- + HOO^\bullet \qquad (D5)$$

(Others have suggested that H_2O_2 oxidizes $I^\bullet$ to form $HO^\bullet$ and HOI.)

Competition for $HOO^\bullet$ between I_2 and IO_3^- causes a sharper transition between iodine consumption and production when reaction D4 is included in the model. The ratio between the rates of reactions D3 and D4 can be important in determining the ratio of iodine maxima between solutions of low and high substrate concentration.

Higher Order Reduction of Iodate by Iodide

The rate law for reduction of iodate by iodide contains both a first-order term and a second-order term in iodide.[25] The second-order term is detectable only for iodide concentrations of approximately 10^{-6} M or higher. Inclusion of the higher order term has not resulted in a noticable improvement in iodine range for the model oscillator.

Modification of the Skeleton Mechanism

As mentioned before, the skeleton mechanism for the Briggs–Rauscher mechanism can qualitatively represent this system. Analysis by Sorensen's group[27] indicates that the dynamics of the mechanism are fairly reasonable. Our modeling attempts were based on revisions or additions to Turyani's[14] model. The modifications mentioned above have been added to the skeleton mechanism and tried, individually and in combination, without a major breakthrough in prediction capability. It is possible to match $[I_2]$ and oscillation period for a single run by using unknown rate constants as adjustable parameters, but the correspondence is lost when initial concentration variables are changed, even when changes are limited to substrate concentrations. The correspondence between model and theory is also seen to be weak in regard to oxygen evolution.

Conclusions

The initial behavior of the B–R oscillator in the batch mode is rather similar with different substrates when relative rates of iodine consumption are accounted for, even though the relative stability of iodo products is greatly different. It seems that substantial improvement of the model must await further modification in the iodine–peroxide–(manganous ion) subset of reactions, in involvement of substrate in the iodine production mode, and iodoorganic decomposition. There is evidence for involvement of hydroperoxyl radical in reduction of iodate. Organic reactions are important when substrate concentration is low, in later stages of the oscillatory reactions, and in the behavior after the oscillation mode ends. Iodine production from organic iodo compounds is more important for PhMA, IMA, and MA substrates than for acetone and MeMA.

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Appendix

Acetone–Hydrogen Peroxide Adduct Formation. Our estimation of the rate from changes in absorbance at 310 nm is consistent with the reported process (HP1 = 2-hydroxy–2-hydroperoxypropane, HP2 = 2,2-bis(hydroperoxy)propane):

$$H_2O_2 + \text{acetone} \rightleftharpoons \text{HP1} \qquad (A1)$$

$$k_{A1} = 2.9\ M^{-2}\ s^{-1}\ [H^+][H_2O_2][Ac] \qquad (\text{ref } 20)$$

$$k_{-A1} = 33.8\ M^{-1}\ s^{-1}\ [H^+][HP1] \qquad (\text{ref } 21)$$

$$H^+ + \text{HP1} \rightleftharpoons \text{P1}^+ + H_2O \qquad (A2)$$

$$k_{A2} = 3.4\ M^{-1}\ s^{-1}\ [H^+][HP1] \qquad (\text{ref } 20)$$

$$k_{-A2} = 5100\ \mathrm{s}^{-1}\ [\mathrm{P1}^+]$$

$$\mathrm{P1}^+ + \mathrm{H_2O_2} \rightleftharpoons \mathrm{HP2} + \mathrm{H}^+ \qquad (A3)$$

$$K_{23} = k_{A2}k_{A3}/k_{A-2}k_{A-3} = [\mathrm{HP2}]/([\mathrm{HP1}][\mathrm{H_2O_2}]) = 170/55.5 \qquad (\text{ref } 21)$$

$$k_{A3} = 29\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}\ [\mathrm{P1}^+][\mathrm{H_2O_2}]$$

$$k_{-A3} = 0.0055\ \mathrm{s}^{-1}\ [\mathrm{HP2}][\mathrm{H}^+]$$

Our value for equilibrium constant $K = [\mathrm{HP2}]/([\mathrm{H_2O_2}]^2[\mathrm{Ac}])$ was in agreement with the reported value (0.3).

Our value for K came from allowing room concentrations of H_2O_2 and acetone to come to equilibrium. We then estimated the equilibrium [Ac] by mixing an equilibrium sample with I_2 solution at the same acidity, and determining the rate of acetone + iodine in the presence of hydrogen peroxide. For that combination the reaction is

$$2\mathrm{CH_3COCH_3} + \mathrm{H_2O_2} + \mathrm{I_2} \rightarrow 2\mathrm{CH_3COCH_2I} + 2\mathrm{H_2O}$$

The acetone−peroxide mixture was allowed to stand for 2−3 h before mixing with iodine. The rate of iodination was nearly independent of all concentrations except that of acetone, so the concentration of uncombined acetone could be estimated, just after the addition of iodine solution, since the rate law for acetone iodination is known. The dilution of [Ac] can be accounted for, and the shift of equilibrium due to dilution is slow. Reaction of the hydroperoxy product with other components in the solution seemed to be negligible, although they may be reactive in the full oscillatory system.

The estimated values for k_{-A2} and k_{-A3} were derived from changes in absorbance at 310 nm. The value for k_{-A2} is closely related to the forward approach to equilibrium. After equilibrium was reached (2−4 h), the solution was suddenly diluted by a known factor (with 0.10 M $HClO_4$); the new approach to equilibrium is related to k_{-A3}. k_{A3} was adjusted so the overall equilibrium constant was equal to 0.3.

No claim is made for high accuracy in these estimated constants. The constants are consistent with observed behavior and serve to calculate changes in acetone and H_2O_2 concentrations due to adduct formation in oscillating mixtures. Higher adducts have been reported[21] which have been neglected here. For a mixture with $[H_2O_2] = 1.5$ M and [Ac] = 1.0 M, the constants above predict a lowering of $[H_2O_2]$ and [Ac], each by about 10% in the first minute, and another 10% in about 10 min.

References and Notes

(1) Briggs, T. S.; Rauscher, W. C. *J. Chem. Educ.* **1973**, *50*, 496.
(2) Furrow, S. D. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; John Wiley and Sons: NY, 1985; p 171.
(3) Shakashiri, B. *Chemical Demonstrations*; University of Wisconsin Press: Madison, WI, 1985; Vol. 2.
(4) Noyes, R. M.; Furrow, S. D. *J. Am. Chem. Soc.* **1982**, *104*, 45.
(5) DeKepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 49.
(6) Edelson, D. *J. Phys. Chem.* **1983**, *87*, 1204.
(7) Vanag, V. K. *J. Chem. Biochem. Kinet.* **1993**, *2 (2)*, 9.
(8) Cooke, D. O. *Int. J. Chem. Kinet.* **1980**, *12*, 683.
(9) Furrow, S. D. *J. Phys. Chem.* **1981**, *85*, 2026.
(10) Cooke, D. O. *Int. J. Chem. Kinet.* **1982**, *14*, 1047.
(11) Furrow, S. D. *J. Phys. Chem.* **1989**, *93*, 2817.
(12) Furrow, S. D. *J. Phys. Chem.*, to be submitted.
(13) Koros, E.; Varga, M. *J. Phys. Chem.* **1982**, *86*, 4839.
(14) Turyani, T. *React. Kinet. Catal. Lett.* **1991**, *45*, 235.
(15) Vanag, V. K.; Alfimov, M. V. *J. Phys. Chem.* **1993**, *97*, 1878.
(16) Vanag, V. K.; Alfimov, M. V. *J. Phys. Chem.* **1993**, *97*, 1884.
(17) Gyorgyi, L.; Turanyi, T.; Field, R. J. *J. Phys. Chem.* **1990**, *94*, 7162.
(18) Furrow, S. D. *Int. J. Chem. Kinet.* **1979**, *11*, 131.
(19) Furrow, S. D., unpublished results.
(20) Sauer, M. C. V.; Edwards, J. O. *J. Phys. Chem.* **1971**, *75*, 3004.
(21) Sauer, M. C. V.; Edwards, J. O. *J. Phys. Chem.* **1972**, *76*, 1283.
(22) Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 896.
(23) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262.
(24) Schmitz, G. *J. Chim. Phys.* **1987**, *84*, 957.
(25) Franz, D. A. *J. Chem. Educ.* **1991**, *68*, 57.
(26) Liebhafsky, H. A.; Roe, G. M. *Int. J. Chem. Kinet.* **1979**, *11*, 693.
(27) Vukojevic, V.; Sorensen, P. Graee; Hynne, F. *J. Phys. Chem.* **1993**, *97*, 4091.

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