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Iodine-Production Subsystem of the Briggs–Rauscher Oscillating Reaction. Effect of Crotonic Acid

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the overlaying Mo layer.

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The system H_2O_2 , IO_3^- , H^+ , Mn^{2+} is a subsystem (no malonic acid) of the Briggs-Rauscher oscillator. As H_2O_2 disproportionates, iodine is initially produced and then after a long time is reoxidized to iodate. The initial rate of iodate reduction is highly dependent on $[H_2O_2]$ and $[Mn^{2+}]$. When crotonic acid is present in the subsystem to prevent I_2 from forming, the rate of iodate reduction is highly dependent on $[IO_3^-]$ and $[Mn^{2+}]$, and disproportionation of H_2O_2 is greatly reduced. With addition of iodine-oxidation steps, the skeleton model of Noyes and Furrow, and of DeKepper and Epstein, which predicts oscillations in the full Briggs-Rauscher system, reproduces behavior of the subsystem with and without crotonic acid. The scheme also reproduces oxidation of I_2 by H_2O_2 in the H_2O_2 , IO_3^- , H^+ , I_2 system, though O_2 evolution in the model is too high.

Introduction

The Briggs-Rauscher oscillating system¹ (H_2O_2 , IO_3^- , H^+ , Mn²⁺, malonic acid, starch) undergoes striking color changes as I_2 is alternately produced and then consumed. Furrow and Noyes² and DeKepper and Epstein³ have recently independently proposed nearly identical mechanisms based on I₂ production during a mode of high radical concentration, and a mode of I₂ consumption involving nonradical species.

In the absence of malonic acid or other iodine-consuming substrate, I_2 is initially rapidly produced. The subsystem H_2O_2 , IO_3^{-} , H^+ , Mn^{2+} has been studied by Cooke⁴ and by Furrow and Noyes.^{2a,b} This paper discusses mainly this iodine-producing (IP) subsystem, and the effect off crotonic acid (CA, trans-2-butenoic acid) on the IP subsystem.

The overall reaction leading to iodine production may be considered as the manganous ion catalyzed reduction of IO_3^- by H_2O_2 .

$$5H_2O_2 + 2IO_3^- + 2H^+ \xrightarrow{Mn^{2+}} 5O_2 + I_2 + 6H_2O$$
 (A

This reaction is accompanied by considerable catalytic decomposition of H_2O_2

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{B}$$

which is in fact the predominant reaction. Spectrophotometric studies of the IP subsystem are complicated by oxygen bubbles, sometimes by mild autocatalytic behavior, by occasional induction periods, especially at low acid, and by the reoxidation of I_2 by H_2O_2 . As Cooke⁴ has stated, at long times (several hours) the iodine is completely reoxidized to iodate, leaving reaction B as the sole net reaction.

In order to eliminate the reoxidation of iodine, another component was added to the IP subsystem to prevent I_2 from forming. CA reacts quickly with HOI, a precurser of I_2 in the IP subsystem, to form a stable iodohydrin.⁵ No visible I_2 is formed, and the catalytic decomposition of H_2O_2 is lowered considerably. The rate of reduction of iodate by H_2O_2 can be followed by monitoring oxygen evolution. The overall reaction with CA present is

$$CH_{3}CH = CHCOOH + IO_{3}^{-} + H^{+} + 2H_{2}O_{2} \xrightarrow{\text{MM}^{-}} CH_{3}CH(OH)CHICOOH + 2H_{2}O + 2O_{2} (C)$$

16.2+

This paper will show that the very strong influence which CA has on the rate of iodate reduction can be explained qualitatively by using the same model which leads to oscillations in the complete oscillating system.

Experimental Section

CA was recrystallized 3 times from hot water. KIO₃ was also recrystallized from water before use. Fisher stabilizer-free H_2O_2 was used. Other reagents were reagent grade. All solutions were made with triple-distilled water.

Oxygen volumes were measured in a thermostated gas buret. Solutions were saturated with oxygen before use, as was the water in the gas buret. Usually H_2O_2 was added last from a thermostated buret. The gas volume was corrected for the volume of solution added.

Rapid stirring is essential to prevent supersaturation. A submersible magnetic stirrer with a 1-in. spin bar provided adequate stirring with 60 mL of solution in a 125-mL flask.6

Briggs, T. S.; Rauscher, W. C. J. Chem. Educ. 1973, 50, 496.
 (a) Furrow, S. D.; Noyes, R. M. J. Am. Chem. Soc. 1982, 104, 38-42.
 (b) Ibid. 1982, 104, 42-5. (c) Noyes, R. M.; Furrow, S. D. Ibid. 1982, 104,

^{45 - 8}

⁽³⁾ DeKepper, P.; Epstein, I. R. J. Am. Chem. Soc. 1982, 104, 49-55. (4) Cooke, D. O. Int. J. Chem. Kinet. 1980, 12, 683-98.

⁽⁵⁾ Furrow, S. D. Int. J. Chem. Kinet., in press.

⁽⁶⁾ Kenneth Smith of the University of Oregon kindly shared his design for a submersible stirrer which would prevent supersaturation.



Figure 1. [I₂] and O₂ evolution vs. time for the system H₂O₂, IO₃⁻, H⁺, Mn²⁺. Initial conditions: $[H_2O_2]_0$, 0.10 M; $[IO_3^{-}]_0$, 0.015 M; $[H^+]_0$, 0.10 M; $[Mn^{2+}]$, 0.0020 M; ionic strength 0.31; *T*, 25.0 °C.

Mixtures were measured by buret or pipet to give the calculated total volume. Ionic strength was adjusted with NaClO₄.

 H_2O_2 strength was determined by excess iodide with molybdate catalyst, followed by thiosulfate titration.

Total oxidizing power (from both H_2O_2 and IO_3^-) was determined iodometrically. Iodate was determined by precipitation with Ag⁺. Details have been reported previously.⁷

Spectrophotometric measurements were made in a modernized Beckman DU spectrophotometer with thermostated cell compartment. I₂ absorbance was followed in 2-cm cells at 460 nm. The temperature was 25.0 ± 0.05 °C.

Results

IP Subsystem without Crotonic Acid. In order to emphasize the effect of CA, a few results of I_2 production without CA are summarized here. In spite of difficulties with spectrophotometric measurements mentioned in the Introduction, initial slopes of absorbance with time are reproducible to within approximately 20%. The initial rate of reaction A is calculated from the initial slope. Slopes are reported in the supplementary material. (See paragraph at end of text regarding supplementary material.) Figure 1 shows the results from an experiment carried past the maximum in $[I_2]$. A similar figure (at lower $[H_2O_2]$) was reported in ref 2a.

Though not all conditions are varied in the supplementary material, the rate of reaction A is dependent on $[H_2O_2]$ at approximately first order; $[Mn^{2+}]$, up to second order when $[Mn^{2+}]$ is low; $[H^+]$, approximately inverse first order over a short range near 0.10 M; and $[IO_3^-]$, nearly zero order. Cooke⁴ has reported similar results, but with lower $[Mn^{2+}]$ dependence and with a rather complex dependence on $[H^+]$.

The quantity α , defined as moles of H_2O_2 catalytically decomposed divided by moles of H_2O_2 oxidized by IO_3^- , is always high; the overall value varies from around 4 at the beginning (depending on concentration) to infinity at the end.

The maximum $[I_2]$ is increased by the same factors which increase the initial rate. The rate of reoxidation of I_2 (decrease of iodine concentration after the maximum) is increased by increased $[IO_3^-]$.

Initial presence of I_2 does not greatly alter the maximum $[I_2]$. With $[I_2]_{max}$ defined from a solution with no initial $[I_2]$, then for separate experiments initial $d[I_2]/dt$ decreases with increasing initial $[I_2]$ until $d[I_2]/dt$ is near zero when



Figure 2. Rate of O₂ evolution vs. time for the system H₂O₂, IO₃⁻, H⁺, Mn²⁺, crotonic acid. (A) Upper line: $[H_2O_2]_0$, 0.050 M; $[IO_3^{-}]_0$, 0.015 M; $[H^+]_0$, 0.10 M; $[Mn^{2+}]$, 0.002 M; $[crotonic acid]_0$, 0.10 M; ionic strength 0.31; *T*, 25.0°. For comparison with system without CA, see ref 2a. Lower line: same as upper line except $[H_2O_2] = 0.10$ M. Compare with Figure 1 for no CA. (B) $[H_2O_2]_0$, 0.029 M; $[IO_3^{-}]_0$, 0.050 M; other conditions same as A.

initial $[I_2]$ equals $[I_2]_{max}$. (At this $[I_2], d[I_2]/dt$ stays near zero for several minutes before decreasing.) When initial $[I_2]$ exceeds $[I_2]_{max}$, initial $d[I_2]/dt$ is negative.

IP Subsystems with Crontonic Acid. All rates in this section are based on oxygen evolution. Since reaction C is usually accompanied by minor amounts of reaction B, another parameter is needed to separate the contribution from each. In this work after following gas evolution for a given time, aliquots of the solution were analyzed for $IO_3^$ and total I⁻ oxidizing power, allowing calculation of the total amount of H_2O_2 decomposition up to that time. The quantity α can be calculated from either

$$\alpha = \frac{3\Delta[O_2] - 4\Delta[IO_3^-]}{2\Delta[IO_3^-]} \tag{1}$$

or

$$\alpha = \frac{3\Delta[\mathrm{TI}] - 5\Delta[\mathrm{IO}_3^-]}{2\Delta[\mathrm{IO}_3^-]} \tag{2}$$

where $\Delta[O_2]$ and $\Delta[IO_3^-]$ are changes in concentration measured in equiv L⁻¹, and $\Delta[TI]$ is total loss in equiv L⁻¹ based on oxidizing power toward I⁻. The two methods are independent and give a check on the overall α calculated from the beginning of the reaction up to the time of analysis. When overall α is significantly different from zero, some ambiguity is present in separating contributions to reaction C and B at times other than that of analysis, because α changes with time.

In most cases with CA present, an induction period occurs while $d[O_2]/dt$ increases to a maximum. Typical runs are shown in Figure 2A. When IO_3^- is in stoichiometric excess, the induction period is very short. $d[O_2]/dt$ increases rapidly to a high value and then may increase further until H_2O_2 is nearly all consumed (see Figure 2B). Rates quoted here are maximum rates, when the curve is similar to Figure 2A, and the early high rates when the curve corresponds to Figure 2B.

More detailed information on individual runs is given in the supplementary material. The trends with concentration are listed here. The rate, $-d[IO_3^-]/dt$, is approximately first order in $[IO_3^-]$, though the order varies from approximately 0.5 to 1.5 depending on conditions. At $[H_2O_2] = 0.4$ M, the order is indistinguishable from 1 in $[IO_3^-]$ for the entire course of the reaction. The quantity α increases with increasing $[IO_3^-]$, especially when $[IO_3^-]$ is in stoichiometric excess.

The rate of reaction C is affected in a minor way by $[H_2O_2]$. From $[H_2O_2] \simeq 0.03-0.2$ M, increasing $[H_2O_2]$

⁽⁷⁾ Furrow, S. D. J. Phys. Chem. 1981, 85, 2026-31.



Figure 3. Lines of equal maximum rate, $d[O_2]/dt$, for various $[H_2O_2]$ and $[IO_3^{-1}]$: $[H^+]_0$, 0.10 M; $[Mn^{2+}]$, 0.0020 M; [crotonic acid $]_0$, 0.10 M; ionic strength, 0.31; *T*, 25.0 °C. (A) $d[O_2]/dt = 1.0 \times 10^{-5}$ mol L^{-1} s⁻¹. (B) $d[O_2]/dt = 2.0 \times 10^{-5}$ mol L^{-1} s⁻¹. (C) $d[O_2]/dt = 3.0 \times 10^{-5}$ mol L^{-1} s⁻¹. (D) $d[O_2]/dt = 3.0 \times 10^{-5}$ mol L^{-1} s⁻¹. In region below dashed line $-d[IO_3^{-1}]/dt$ is faster without crotonic acid. Numbers are 100α . α is defined in text.

retards the rate. Above $\simeq 0.20$ M the rate is increased slightly, less than first order, by increasing $[H_2O_2]$. These opposing trends can be seen in Figure 3, where lines of constant rate have maxima at $[H_2O_2] \simeq 0.2$ M. Lack of major $[H_2O_2]$ effect is also shown in Figure 2B, where H_2O_2 is limiting. The rate actually increases until just before H_2O_2 runs out.

Increasing CA retards reaction C. With [CA] higher than ~0.15 M, reaction C runs very slowly. Compared to reaction A, however, under some conditions (high $[IO_3^-]$, low $[H_2O_2]$), $d[IO_3^-]/dt$ is actually faster with CA present than without. Figure 3 shows a grid with maximum d- $[O_2]/dt$ for various $[H_2O_2]$ and $[IO_3^-]$. The approximate boundary is shown where the maximum rate of reaction C exceeds the initial (maximum) rate of reaction A. (When reaction B is included, the total rate is always faster without CA.)

 $[Mn^{2+}]$ affects the rate strongly, with an order of approximately 2 under the few experiments run. Increasing $[H^+]$ also speeds up reaction C with an order of approximately 2. Most experiments were done with ionic strength ~0.31. Decreasing ionic strength to 0.15 speeded up the reaction by ~15%.

The length of time of the induction period was decreased and the quantity α increased by the same constituents which increase the rate, namely, $[IO_3^{-}]$, $[H^+]$, and $[Mn^{2+}]$.

The order of addition of reagents also affects the induction period. For most of the experiments described here, H_2O_2 was added last.

The quantity α determined by both eq 1 and 2 usually agreed within 3% or better. When α is near zero, good agreement by the two methods means that the stoichiometry is well described by eq C. For some runs, especially at low [H₂O₂] and low [IO₃⁻], α came out slightly negative. This was at first thought to be due to analytical error, but it could also indicate minor side reactions. This anomaly will be referred to in the next section.

Discussion

The addition of CA profoundly alters the kinetic behavior of the IP subsystem. It may be more accurate to say addition of an organic substrate profoundly alters the apparent kinetics, since in the complete oscillating system (with malonic acid present) rate of production of I_2 is affected in much the same direction by $[H_2O_2]$, $[IO_3^-]$, $[Mn^{2+}]$, and $[H^+]$ as is reaction C.

Elementary steps proposed for the complete oscillating system are as follows^{2c,3} (nomenclature of ref 2c):

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

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$$HIO_2 + I^- + H^+ \rightarrow 2HOI$$
 (I2)

$$\mathrm{IO}_{3}^{-} + \mathrm{I}^{-} + 2\mathrm{H}^{+} \rightarrow \mathrm{HIO}_{2} + \mathrm{HOI}$$
 (I3)

$$2\text{HIO}_2 \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+ \tag{I4}$$

$$IO_3^- + HIO_2 + H^+ \rightleftharpoons 2IO_2 + H_2O$$
 (I5)

$$2\text{HOO} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \tag{I6}$$

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O$$
 (D1)

$$IO_2 + Mn^{2+} + H_2O \rightleftharpoons HIO_2 + Mn(OH)^{2+}$$
 (M1)

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

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

The skeleton mechanism for the oscillator contains no provisions for net oxidation of iodine species (called UP reactions). UP reactions are postulated to involve radical species, and they affect the oscillator in only a minor way presumably because the radicals are scavanged by the organic material leading to oxidized organic matter plus CO_2 . Furrow and Noyes^{2a} attempted to model the IP subsystem by including the UP reactions

$$I + H_2O_2 \rightarrow HOI + HO.$$
 (U1)

$$HO_{\bullet} + I_2 \rightarrow HOI + I_{\bullet} \tag{U2}$$

$$IO_{2} + H_{2}O_{2} \rightarrow HIO_{2} + HO_{2}$$
 (U3)

$$HOO_{\bullet} + HOI \rightarrow H_2O_2 + IO_{\bullet}$$
 (U4)

They also included the additional DOWN reactions

 $\mathrm{H}^{+} + \mathrm{HOO} \cdot + \mathrm{IO}_{3}^{-} \rightarrow \mathrm{O}_{2} + \mathrm{H}_{2}\mathrm{O} + \mathrm{IO}_{2} \cdot \quad (\mathrm{D4})$

$$HOO \cdot + I_2 \rightarrow O_2 + I^- + H^+ + I. \tag{D5}$$

and the additional OXYGEN reaction

$$HO + H_2O_2 \rightarrow HOO + H_2O$$
 (O1)

This model was able to generate I_2 and O_2 at approximately the correct rate for one set of reaction conditions for the IP subsystem. There were, however, some inconsistencies between rate constants used to model the IP subsystem^{2a} and to model the oscillator.^{2c} The constants chosen by DeKepper and Epstein³ to model the oscillator were chosen by them to fit a much wider variety of experimental conditions, and in particular their values of k_{12} , k_{14} , and k_{-15} were substantially different from those used by Furrow and Noyes.

A successful model should be able to show features associated with the full oscillator, to produce I_2 and O_2 and show an I_2 maximum in the IP subsystem (no malonic acid), and to match the much changed kinetic behavior of the IP subsystem with CA present. Furthermore, the model should be able to oxidize I_2 and generate O_2 with just IO_3^- , H_2O_2 , and H^+ present (no Mn^{2+}).⁸ Quantitative agreement has not been achieved for all of these criteria, but the model presented below does match features of a large body of experimental work. (With constants adjusted to 50 °C instead of 25 °C, the same steps should be important in modeling the Bray-Leibhafsky oscillator,⁹ though no attempt has been made here to do so.)

In order to simulate numerically the several diverse conditions given above, the following modifications have

 ⁽⁸⁾ Leibhafsky, H. A. J. Am. Chem. Soc. 1931, 53, 2074-90.
 (b) Leibhafsky, H. A.; McGavock, W. C.; Reyes, R. J.; Roe, G. M.; Wu, L. S. Ibid. 1978, 100, 87-91.

Ibid. **1978**, 100, 87-91. (9) (a) Bray, W. C. J. Am. Chem. Soc. **1921**, 43, 1262-67. (b) Leibhafsky, H. A. *Ibid.* **1931**, 53, 896-911.

TABLE I: Values of Constants Used for Simulation

reaction	forward constant	reverse constant
I1	$3.1 \times 10^{12} \text{ M}^{-2} \text{ s}^{-1}$	2.2 s^{-1}
I2	$2.0 imes 10^{10} \ { m M}^{-2} \ { m s}^{-1}$	90 $M^{-1} s^{-1}$
13	1430 M ⁻³ s ⁻¹	2.8 M ⁻¹ s ⁻¹
I4	$6.0 imes 10^{5} \mathrm{M}^{-1} \mathrm{s}^{-1}$	$0.86 \text{ M}^{-2} \text{ s}^{-1}$
15	$7.3 imes 10^3~{ m M}^{-2}~{ m s}^{-1}$	$1.7 imes 10^{7}~{ m M}^{-1}~{ m s}^{-1}$
17	$1.0 imes 10^9 \ { m M}^{-2} \ { m s}^{-1}$	
18	$1.05 imes 10^{6} \ \mathrm{M^{-1} \ s^{-1}}$	
D1	$37 \text{ M}^{-1} \text{ s}^{-1}$	
M1	$1.0 imes 10^4 \ \mathrm{M^{-1} \ s^{-1}}$	$2.5 imes 10^{8}~{ m M}^{-1}~{ m s}^{-1}$
M2	$3.2 imes 10^4~{ m M^{-1}~s^{-1}}$	$2.0 imes 10^3~{ m M^{-1}~s^{-1}}$
01	$4.5 imes 10^7~{ m M^{-1}~s^{-1}}$	
O2	$7.5 imes 10^5 \ \mathrm{M^{-1} \ s^{-1}}$	
U1	$5.0 imes 10^7 \ \mathrm{M^{-1} \ s^{-1}}$	
U2	$1.0 imes 10^{8}\ { m M}^{_{-1}}\ { m s}^{_{-1}}$	
U 3	$1.0 imes 10^7~{ m M^{-1}~s^{-1}}$	
U4	$1.45 imes 10^{6}~{ m M}^{-1}~{ m s}^{-1}$	
C_5	$3.7 imes 10^3 \ \mathrm{M^{-2} \ s^{-1}}$	

been made in the Furrow-Noyes model of the IP subsystem: ^{2a} Reaction D4 has been dropped, since it was not necessary to the full oscillating system. Reaction D5 was dropped, since inclusion leads to too much oxygen with only H_2O_2 , IO_3^- , and H^+ present. Reaction C5 has been

 $H^+ + CA + HOI \rightarrow CH_3CH(OH)CHICOOH + H^+$ (C5)

added, as the only known pathway for reaction with CA. Evidence was found for acid catalysis in this step,⁵ so H⁺ is included.

Reaction I7 was added as a means of converting IO₂.

$$IO_2 + I^- + H^+ \rightarrow I + HIO_2$$
 (I7)

radicals to species which could be involved in an UP reaction (in the absence of Mn^{2+}). However, even with $k_{17} = 1.0 \times 10^{10} M^{-2} s^{-1}$, the rate for step I7 was too slow too be significant. This step could be dropped with very little effect on the model (at the assumed value for k_{17}).

Step I8 was therefore added since (I7) was too slow. The

$$IO_2 + HOI \rightarrow IO + HIO_2$$
 (I8)

IO· produced by reaction I8 allows net oxidation of HOI to occur by the reaction sequence U3 + O1 + U4. In order to model oxidation of I_2 (H_2O_2 , IO_3^- , H^+ , I_2 system), some direct oxidation of HOI must occur at a rather fast rate. Otherwise step D1 produces far too much O_2 .

Values of k_{12} , k_{14} , and k_{-15} are the same as the values chosen by DeKepper and Epstein³ since their model successfully exhibited many features of the full oscillating system. The general features of the subsystems modeled here are not nearly so sensitive to values chosen as is the oscillating system. The only changes in constants from values used previously are increased values for k_{-M1} and k_{-M2} , to try to improve the fit for the IP subsystem; decreased values for k_{U2} , to reduce O₂ produced with H₂O₂ and I₂ when Mn²⁺ is absent; and new values for k_{18} and k_{U4} , to achieve the best fit for iodine production with Mn²⁺ present and iodine consumption with Mn²⁺ absent. Table I shows the values of all constants used.

Simulations were run on The Pennsylvania State University IBM 370/3033 computer, using the numerical integration program of Gear, modified by Hindmarsh.¹⁴

same as in ref 2a,c and 3; from ref 10
same as in ref 3
same as in ref 2a,c and 3; from ref 11
same as in ref 3
same as in ref 3
assumed fast
adjusted
same as in ref 2a,c and 3; from ref 12
same as in ref 2a,c and 3; reverse increased
same as in ref 2a,c and 3; from ref 13; reverse increased
same as in ref 2a
same as in ref 2c
assumed fast
assumed fast
assumed fast
adjusted
calculated from
$5(3.2 \times 10^{-3})^2 [IO_3^{-}]^{0.3}/(4K_{I_1}k_{I_3}) \text{ (ref 5)}$

ref

TABLE II: Comparison of Model with Experiment forthe Iodine-Production Subsystem without CA^a

time.	10 ⁵ [I ₂], M		$10^{3}[O_{2}], mol L^{-1}$		α ^b		
s	exptl	calcd	exptl	calcd	exptl	calcd	
0	0.0	0.0	0.0	0.0			
60	4.37	4.1	1.41	0.53	11	3	
120	6.59	6.3	2.64	1.1	14	5	
180	7.74	7.7	3.59	1.7	17	7	
240	8.41	8.4	4.37	2.3	19	9	
300	8.75	8.7	5.09	2.9	21	11	
360	8.82	8.7	5.79	3.5	24	14	
480	8.95	8.4	7.08	4.6	30	20	
600	8.61	7.7	8.32	5.7	37	28	
840	7.67	6.3	10.75	7.8	54	48	
1200	5.99	4.5	14.26	10	93	92	
1680	3.40	2.9	18.63	14	$1.9 imes10^2$	$1.9 imes10^{2}$	
2040	2.36	2.1	21.35	15	$3.6 imes10^2$	$3.0 imes10^{2}$	
2340	1.55	1.6	22.90	17	$5.9 imes10^2$	$4.4 imes10^2$	
2640	0.67	1.2	23.74	18	$1.7 imes 10^3$	$6.3 imes10^{\mathrm{2}}$	

^a $[H_2O_1]_0 = 0.049 \text{ M}, [IO_3^-]_0 = 0.015 \text{ M}, [H^+]_0 = 0.10 \text{ M}, [Mn^{2+}] = 0.0020 \text{ M}, T = 25.0 °C.$ ^b This α (defined in text) is the overall quantity from the beginning of a run, calculated from $\alpha = 2(\Delta [O_2]/\Delta [I_2] - 5)/5$.

Effect on the Briggs-Rauscher Oscillator. Inclusion of all of these steps perturbs the model for the H_2O_2 , IO_3^- , Mn^{2+} , H⁺, malonic acid system so that it does not oscillate. At conditions similar to those modeled by DeKepper and Epstein³ (flow system, $[H_2O_2]$, 0.33 M; $[IO_3^-]$, 0.035 M; [H⁺], 0.056 M; [Mn²⁺], 0.004 M; [malonic acid], 0.0015 M) the model attains a radical steady state. $[HIO_2]$ stays high and prevents $[I^{-}]$ from increasing to the critical switching concentration. Organic radical reactions, however, have been entirely omitted from the skeleton scheme. Inclusion of a step which can compete with reaction O1 (such as OH-+ RH or RI \rightarrow oxidized products) or a step which can compete with reaction U4 (such as HOO- + RH or RI \rightarrow oxidized products) restores oscillations to the system since UP sequences are prevented from starting. CO_2 is known to be produced while I_2 is increasing, so inclusion of steps like these would help model all features of the oscillator. A small contribution from UP sequences would improve the model in another way. According to DeKepper and Epstein,³ an extra source of HIO_2 would lengthen the time which the model spends in the radical mode, compared to what they found.

IP Subsystem without Crotonic Acid. The model was adjusted to fit the I_2 and O_2 data at $[H_2O_2] = 0.05$ M, $[IO_3^-] = 0.015$ M, $[H^+] = 0.10$ M, and $[Mn^{2+}] = 0.002$ M. The overall fit is approximately the same as previously re-

 ⁽¹⁰⁾ Eigen, M.; Kustin, K. J. Am. Chem. Soc. 1962, 84, 1355-61.
 (11) Furnichi, R.; Leibhafsky, H. A. Bull. Chem. Soc. Jpn. 1975, 48,

^{745-50.} (12) Leibhafsky, H. A. J. Am. Chem. Soc. 1932, 54 3504-8.

⁽¹³⁾ Davies, G.; Kirschenbaum, L. J.; Kustin, K. Inorg. Chem. 1968, 7, 146–54.

⁽¹⁴⁾ Hindmarsh, A. C. Livermore, CA, 1972, Lawrence Livermore Laboratory Technical Report No. UCM-30001, Rev. 2.

TABLE III: Comparison of Model with Experiment and Trends with Concentration for the Iodine-ProductionSubsystem without CA

•	$d[I_2]/dt dep$	pendence	time of	$I_2(max)$		α
component	exptl	calcd	exptl	calcd	exptl	calcd
H,O,	1st order	1st order	increase	increase	decrease	decrease
IÓ,-Í	small	small	decrease	decrease	increase	increase
H⁺	inverse	small increase	а	decrease	а	increase
Mn ²⁺	1st to 2nd order	1st order	а	decrease	decrease	small increase

^a Not determined.

TABLE IV:Comparison of Model with Experiment forthe Iodine-Production Subsystem with CA^a

time, s	exptl $10^{5} \times (d[O_{2}]/dt),$ mol L ⁻¹ s ⁻¹	time, ^b s	calcd $10^{s} \times$ $(d[O_2]/dt),$ mol L ⁻¹ s ⁻¹
0	0		
300	015		
600	0.63		
720	0.75	0	
900	0.69	180	0.59
1200	0.66	480	0.57
1500	0.58	780	0.54
1800	0.52	1080	0.49
2400	0.41	1680	0.45
3600	0.26	2880	0.33
6000	0.16	5280	0.20
9000	0.05	8280	0.11

^a $[H_2O_2]_0 = 0.048 \text{ M}, [IO_3]_0 = 0.015 \text{ M}, [H^+]_0 = 0.10 \text{ M}, [Mn^{2+}] = 0.0020 \text{ M}, [CA]_0 = 0.10 \text{ M}, T = 25.0 °C.$ ^b Time scale is displaced for the model because induction period is not simulated.

ported.^{2a} In particular, the maximum in I_2 is not broad enough in the simulation, and the initial rapid O_2 evolution observed experimentally is too slow in the simulation. A significant improvement, however, is that most trends with concentrations are reproduced qualitatively (see Tables II and III). The inverse effect of acid concentration is not shown by the model.

IP Subsystem with Crotonic Acid. With CA present the overall reaction is considerably simplified. The reaction sequence 2(I5) + 4(M1) + 4(M2) + 2(O2) + I4 + C5 adds up to reaction C. All of the UP steps are minor side reactions. The speed of all other steps in the reaction model is at least a factor of 5 or 6 lower than any in the main sequence.

An approximate rate law can be derived assuming steady-state conditions for the intermediates HIO_2 , IO_2 , HOI, $Mn(OH)^{2+}$, and HOO. Neglect of one smaller term leads to the approximation

$$-d[CA]/dt = k_{15}[H^+][IO_3^-](k_{M1}[Mn^{2+}])^{4/3}/(16k_{-15}k_{14}^{1/3})$$

which shows a dependence on $[Mn^{2+}]$, $[H^+]$, and $[IO_3^-]$, and lack of H_2O_2 dependence, similar to experiment.

Comparison of model with experiment is shown in Tables IV and V. No constants were adjusted to fit those data. The trends with concentration are mostly in the right direction, though the initial retarding effect of H_2O_2 is not seen in the model. In table IV, the rate of oxygen evolution is compared as well as total oxygen evolution. The quantity α is somewhat high in the model (experimental α , 0.03, calculated α , 0.14). In general, the speed of reaction with time resembles the plot in Figure 2A. The increase in rate shown in Figure 2B (at high iodate) is not shown by the model.

The induction periods observed experimentally are consistent with slow formation and increase in some of the intermediates. The simulation does not attempt to deal with the initial intermediate formation. In the model some

TABLE V:Comparison of Model with Experiment andTrends with Concentration for the Iodine-ProductionSubsystem with CA

com-	$d[O_2]/dt$	lependence		α
ent	exptl	calcd	exptl	calcd
H ₂ O ₂	variable, but small	small increase	variable	small increase
[O ₃ -	0.5-1.5 order	near 1st order	increases	increases
H⁺	near 2nd order	near 1st order	increases	decreases
Mn ²⁺	1st to 2nd order	near 1st order	increases	increases
CA	inverse	very small inverse	decreases	decreases

TABLE VI: Comparison of Model with Experiment for the H_2O_2 , IO_3^- , H^+ , I_2 System^a

	$10^{4}[I_{2}], M$		$10^{4}[O_{2}], mol L^{-}$	
time, s	exptl	calcd	exptl	calcd
0	12.7	12.7	0	0
60	8.8	9.3	1.33	11
120	6.1	6.9	2.81	20
180	4.3	5.1	4.37	27
240	3.0	3.9	5.30	32
360	1.6	2.4	6.08	40
600	0.7	1.1	8.50	49

$$[H_2O_2]_0 = 0.05 \text{ M}, [IO_3]_0 = 0.025 \text{ M}, [H^*]_0 = 0.10 \text{ M}, T = 25.0 \text{ °C}.$$

intermediates are initially set to values near their steady-state concentrations; no induction period is produced. Only the data after $(d[O_2]/dt)_{max}$ are used for comparison.

Another defect of the model is lack of dependence on CA. Experimentally higher [CA] slows down the reaction, and, at higher concentration, the reaction nearly stops. One possibility of explanation is that CA may undergo side reactions with higher oxidation states of iodine such as HIO_2 . Further evidence of this type of reaction is that in some runs the amount of oxygen produced experimentally was slightly less than 2 times the IO_3^- consumed.

 H_2O_2 , IO_3^- , H^+ , I_2 System. This system, which leads to fairly rapid oxidation of I_2 , has been treated by Liebhafsky.⁹ He allows a I⁺ cation to be oxidized by H_2O_2 . The model proposed here allows radical oxidation of HOI and neglects such species as I⁺, considering it as being in rapid equilibrium with HOI.

Removal of Mn^{2+} and organic matter from the model (with I_2 present) shows oxidation of I_2 to be approximately first order as given by experiment. The oxygen evolution in the model, however, is about 6-8 times too fast. [HOI] is high enough in the simulation that step D1 completes with step U4 and too much O_2 is formed. Table VI compares model with experiment.

Comments on the Different Systems. It is satisfying that the same model can account for oscillations in the H_2O_2 , IO_3^- , IO_3^- , H^+ , Mn^{2+} , malonic acid system, for production and disappearance of I_2 in the H_2O_2 , IO_3^- , H^+ , Mn^{2+} system, for very different concentration dependences in the H₂O₂, IO₃⁻, H⁺, Mn²⁺, CA system, and for oxidation of I₂ in the H₂O₂, IO₃⁻, H⁺ system. The rates are modeled within a factor of 2 for a wide variety of conditions except for the high rate of oxygen evolution accompanying I₂ oxidation in the model. With the thermodynamics and individual rate constants for many of the individual steps still unknown, further refinement and agreement between simulation and experiments has not been attempted. The individual steps used here, particularly the steps needed for I₂ oxidation, U4 and I8, were introduced mainly because better alternatives have not been found. For instance, direct oxidation of HOI by OH· still seems unfeasible because most OH· reacts by eq O1.¹⁵ Step I8 could probably be replaced by step I7 if k_{17} were of order of magnitude ~10¹² M⁻² s⁻¹.

No attempt has been made here to model the Bray-Liebhafsky system (H_2O_2 , IO_3^- , H^+ , I_2) which produces oscillations in a limited concentration region at 50–70 °C. Many of the same steps used here have already been invoked by Edelson and Noyes in modeling that system.¹⁶ Their iodine oxidation phase used oxygen as a means to

(15) Sharma, K.; Noyes, R. M. J. Am. Chem. Soc. 1976, 98, 4345–61.
(16) Edelson, D.; R. M. Noyes, R. M. J. Phys. Chem. 1979, 83, 212–20.

bypass HOI. At lower acidities oxygen is important and involved in I_2 oxidation, but at higher acidities a sequence is needed where oxygen is not involved.¹⁷ The model used here has not included O_2 as a reactant.

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Supplementary Material Available: Two tables listing maximum $d[I_2]/dt$, maximum $[I_2]$, maximum $d[O_2]/dt$, time of maximum $[I_2]$, for different starting concentrations in H_2O_2 , IO_3^- , H^+ , Mn^{2+} system, and also maximum $d_{[O_2]}/dt$, time to maximum, and extent of reaction for H_2O_2 , IO_3^- , H^+ , Mn^{2+} , CA system at different starting concentrations (4 pages). ordering information is available on any current masthead page.

Primary Processes in the Photolysis of Acetaldehyde at 3000 Å and 25 °C

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The quantum yields of the gaseous products CH_4 , CO, and H_2 have been determined in 3000-Å photolyses of acetaldehyde and its mixtures with CO_2 , *i*- C_4H_8 , and O_2 . The results help define the nature and the quantum yields of the primary processes: $CH_3CHO^* \rightarrow CH_3 + HCO$ (I); $CH_3CHO^* \rightarrow CH_4 + CO$ (II); $CH_3CHO^* \rightarrow H + CH_3CO$ (III). The absence of ketene among the products argues against the origin of H_2 in the alternative process: $CH_3CHO^* \rightarrow H_2 + CH_2=CO$ (IV). Process I is dominant with $\phi_I \simeq 0.93$ at low pressures; process II is unimportant at this wavelength ($\phi_{II} \simeq 0.01$); process III (or possibly process IV) occurs with $\phi_{III} \simeq 0.059$. Collisional quenching of the vibrationally rich excited-state precursors to these processes and a variety of other evidence suggests that process I occurs from the decay of a vibrationally rich, triplet state, while processes II and III occur from high vibrational levels of the excited singlet. If process IV is unimportant here, as we have tentatively concluded, then the H atoms formed in process III must be translationally rich and react readily to abstract H atoms from CH_3CHO as well as added isobutene. Alternatives are considered to the recent hypothesis of Gill et al. concerning the slow appearance of HCO radicals following the flash excitation of acetaldehyde.

Introduction

Leighton and Blacet³ published their first quantitative study of acetaldehyde photochemistry almost 50 years ago. Since then literally hundreds of further studies have been made to help define the details of the primary processes and the secondary reactions involved in the photochemistry of this simple molecule. In view of this extensive effort, it is surprising that uncertainty remains today concerning the nature and extent of the primary photodissociative reactions. Three channels have been suggested in previous work for the primary photodecomposition:

$$CH_3CHO^* \rightarrow CH_3 + HCO$$
 (I)

$$CH_3CHO^* \rightarrow CH_4 + CO$$
 (II)

$$CH_3CHO^* \rightarrow CH_3CO + H$$
 (III)

Here CH_3CHO^* represents an electronically excited singlet, a triplet formed by intersystem crossing (isc), or a vibrationally rich ground-state molecule formed by internal conversion; all processes do not necessarily originate from the same state. Most previous workers interpreted their results in terms of processes I and II; process I was favored at long wavelengths and presumably involved the triplet molecule. Process II appeared to increase in importance as acetaldehyde was excited at the shorter wavelengths of light and was commonly thought to originate from the excited singlet state. Process III was considered to be

⁽¹⁷⁾ Odutola, J. A.; Bohlander, C. A.; Noyes, R. M. J. Phys. Chem. 1982, 86, 818-24.

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⁽³⁾ P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc., 55, 1766 (1933).

⁽⁴⁾ For some examples and current discussion of the extensive literature, see E. K. C. Lee and R. S. Lewis, Adv. Photochem., 12, 1 (1980).