

step Dx took place directly, there would be no manganous catalysis.

We believe the paradox can be resolved by distinguishing between electron transfer and hydrogen atom transfer mechanisms. A 1-equiv reductant like H_2O_2 or an organic compound can be oxidized either by abstraction of a hydrogen atom in a single step or by abstraction of an electron and a proton in successive steps. Other 1-equiv reductants like Fe^{2+} or I^- can be oxidized only by electron abstraction. If a 1-equiv oxidant like $\text{HO}\cdot$ or $\text{Cl}\cdot$ has an odd electron localized on a single atom, it can abstract either a hydrogen atom or an electron depending on the chemistry of the reductant with which it reacts. However, if the odd electron is delocalized as in $\cdot\text{IO}_2$, the oxidant is sluggish at abstracting a hydrogen atom regardless of the thermodynamic driving force.

When these principles are applied to the present system, $\cdot\text{IO}_2$ reacts only slowly or not at all by step Dx and preferentially abstracts an electron from Mn^{2+} while simultaneously or subse-

quently accepting a proton from the solvent as summarized by step M1. The resulting Mn(III) complexes with H_2O_2 and removes an electron by an intramolecular rearrangement while a proton is lost to solvent either at the same time or at some other stage of the process as summarized by step M2.

The above argument is developed as a rationalization to explain some interesting and unusual chemistry. It remains to be seen whether it has utility beyond the system for which it was developed.

Acknowledgment. This research was supported in part by a Grant from the National Science Foundation to the University of Oregon. Susan Tuckey^{2b} and Robert Gay^{2b} made some of the spectrophotometric studies on the iodate-peroxide-manganous subsystem. Dr. D. O. Cooke of the Hastings College of Further Education kindly made a manuscript available to us in advance of publication.

The Oscillatory Briggs-Rauscher Reaction. 2. Effects of Substitutions and Additions¹

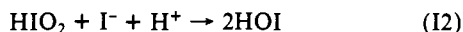
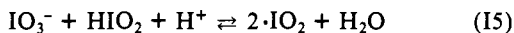
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Abstract: Addition of malonic acid can cause oscillatory behavior in the subsystem of the previous paper. Effects of various other organic and inorganic adducts have been examined to seek evidence on the mechanism of those oscillations. Methylmalonic acid, which has only one enolizable hydrogen, iodates by procedures similar to, but slower than, those observed for malonic acid. Crotonic acid is an efficient scavenger of HOI; its presence slows and alters the stoichiometry of reaction in the iodate-peroxide-manganous subsystem. Phenol is an even more efficient radical scavenger and acts as an inhibitor of reaction in the subsystem. Acrylamide does not seem to be a particularly effective radical scavenger in this subsystem. Silver ion, which is a scavenger of I^- , has rather little effect on the behavior of the subsystem. Oxalic acid, pyrophosphate, and dichromate exhibit complex effects that have not been studied in detail. The importance of malonic acid to the oscillating reaction is ascribed to the fact that its enol scavenges iodine species with oxidation numbers +1 and 0. That scavenging reduces the total quantity $[\text{HOI}] + 2[\text{I}_2] + [\text{I}^-]$, but it may increase the $[\text{I}^-]/[\text{HOI}]$ ratio enough that $[\text{I}^-]$ actually increases.

The previous paper¹ shows that manganese salts catalyze an initial reaction in which hydrogen peroxide reduces iodate and the concentration of iodine rises to a maximum; that concentration subsequently declines as hydrogen peroxide oxidizes much of the iodine back to iodate. We believe that steps involving 1-equiv change are important at all times in this subsystem. The initial reduction of IO_3^- by H_2O_2 is initiated by step I5 and results in



an autocatalytic increase of $[\text{HIO}_2]$. We believe that in the subsystem of the previous paper this autocatalysis is always faster than the rate of HIO_2 destruction by step I2.

The iodate-peroxide-manganous subsystem is not an oscillator in spite of the single maximum in iodine concentration. However, Briggs and Rauscher³ have shown that addition of malonic acid to such a subsystem can create an extremely effective oscillator. Our experience with bromate-driven oscillators⁴ suggests that

during a portion of each cycle $[\text{I}^-]$ becomes large enough that step I2 is faster than the HIO_2 -promoted reduction of IO_3^- .

We can imagine the following number of ways in which an organic compound, RH, might interact with the reacting subsystem. (a) The organic compound might be attacked by the oxyhydrogen radicals $\text{HOO}\cdot$ and particularly $\text{HO}\cdot$. (b) The organic compound might be oxidized by iodine species with oxidation number greater than +1. (c) RH might be converted to RI, thereby acting as a sink for I_2 and for the species HOI and I^- in equilibrium with it. (d) Iodination of RH might shift the ratio $[\text{I}^-]/[\text{HOI}]$. (e) Subsequent reaction of RI might liberate the I^- necessary to affect the rate of step I2.

In order to assess the relative importance of these effects, we have compared the behaviors in this system of several selected organic compounds. Malonic acid is the substrate of choice for studies of oscillations and provides the reference for comparison with other adducts. Methylmalonic acid has only one enolizable hydrogen and does not form any of the especially reactive diiodo compounds. Crotonic acid, phenol, and 2-naphthol were selected as scavengers of iodine and hypoiodous acid. Studies with all of these compounds were particularly relevant to understanding the mechanism of the oscillations and are reported in the second part of this paper.

We also examined the effects of acrylamide, oxalic acid, and various inorganic species. These adducts were selected in an-

(1) Part 41 in the series Chemical Oscillations and Instabilities. Part 40: Furrow, S. D.; Noyes, R. M. *J. Am. Chem. Soc.*, part 1 in this issue.

(2) (a) University of Oregon. (b) Pennsylvania State University.

(3) Briggs, T. S.; Rauscher, W. C. *J. Chem. Educ.* 1973, 50, 496.

(4) Noyes, R. M. *J. Am. Chem. Soc.* 1980, 102, 4644-4649.

tipication of effects that would be mechanistically significant. Often these systems were more complex than anticipated or the interpretations were ambiguous; no further studies were attempted. We report these qualitative observations in the third section even though we do not use them much for drawing mechanistic conclusions. We hope those reports may stimulate the thinking of others.

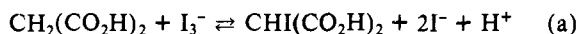
The discussion in the fourth section uses the observations from the second section to reach more specific conclusions about the ways in which organic substrates can act to promote oscillations.

Details of experimental procedures are described at the end of the paper.

Organic Substrates of Particular Mechanistic Significance

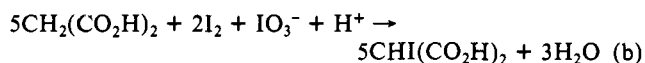
Reactions of Malonic Acid (MA). Malonic acid, $\text{CH}_2(\text{CO}_2\text{H})_2$, is the organic substrate that has been used most often in oscillating systems. It can be oxidized at higher temperatures either by IO_3^- or by H_2O_2 , but both reactions are negligibly slow at room temperature. Spectrophotometric observations indicate malonic acid forms a complex with Mn^{2+} , but at pH 1 most of these species are uncomplexed.

Leopold and Haim⁵ studied the kinetics of reaction a. The



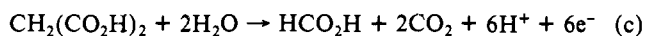
mechanism involved prior enolization of the malonic acid, and the process went to a measurable equilibrium at the iodide concentrations they used. At the iodide concentrations in an oscillator,⁶ reaction a must be almost irreversible.

If I_2 and IO_3^- are both present, the iodide produced in (a) reacts further with iodate and the stoichiometry becomes that of (b).



Because enolization of malonic acid is rate determining, stoichiometries a and b require that rate of consumption of I_2 is 40% as much when iodate is present as when it is absent.

Jwo and Noyes⁷ showed that 6 equiv of cerium(IV) oxidized malonic acid according to stoichiometry c. Manganese(III) can

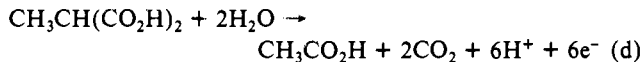


also oxidize organic compounds, but it is not easy to do quantitative experiments with this oxidant. However cerium(III) behaves very much like manganese(II) in catalyzing the reduction of IO_3^- by H_2O_2 . We hope as a trial assumption that Mn(III) will behave similarly to Ce(IV) in its reactions with organic species like malonic acid.

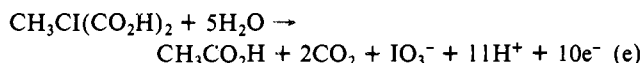
We also wished to study the stoichiometry of oxidation of monoiodomalonic acid, $\text{ICH}(\text{CO}_2\text{H})_2$. We were unable to isolate this material in pure form. We did try to oxidize a solution prepared by iodination of malonic acid; that solution consumed more than 10 equiv of cerium(IV) for each mole of malonic acid before iodination. This stoichiometry suggests that some of the material had been diiodinated and that the iodine was oxidized to iodate in addition to the stoichiometry of (c). However, conclusions were not firm.

Reactions of Methylmalonic Acid (MMA). As mentioned above, malonic acid is subjected to diiodination, and $\text{Cl}_2(\text{CO}_2\text{H})_2$ might exhibit complex behavior. Such complexities can be reduced by using methylmalonic acid, $\text{CH}_3\text{CH}(\text{CO}_2\text{H})_2$. This compound is also iodinated by an enolization mechanism, and the kinetics have been studied by Furrow.⁸ The iodination of MMA is several times slower than that of malonic acid, but no major mechanistic differences were indicated. Thus, the effect of added iodate is the same as with MA.

Just like malonic acid, MMA is oxidized by 6 equiv of cerium(IV). The indicated stoichiometry is (d).



Iodomethylmalonic acid consumes 10 equiv of Ce(IV) consistent with stoichiometry e.

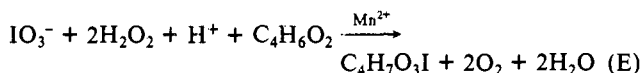
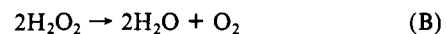
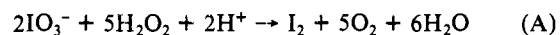


Reactions of Crotonic Acid. Crotonic acid, *trans*- $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$, was anticipated to scavenge iodine in 0 and +1 oxidation states. A detailed study of its reactions will be presented elsewhere⁹ and only summarized here.

Crotonic acid irreversibly adds HOI to form an iodohydrin with empirical formula $\text{C}_4\text{H}_7\text{O}_3\text{I}$. The kinetics at 25 °C correspond to eq 1.

$$-d[\text{HOI}]/dt = 4500[\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}][\text{HOI}][\text{H}^+] \text{ M s}^{-1} \quad (1)$$

Crotonic acid reacts negligibly slowly or not at all with any of the individual species IO_3^- , H_2O_2 , Mn^{2+} , and I_2 . However, when crotonic acid is added to the iodate-peroxide-manganous subsystem of the first paper, the stoichiometry is changed from (A) to (E). At the same time, induced disproportionation of hydrogen peroxide by reaction B is very much reduced.



The rate of reaction E can be followed conveniently by oxygen evolution. It exhibits a rather poorly defined induction period that depends upon various things including the order of addition of reagents. Other complexities of the kinetics will be described elsewhere.⁹

The change in stoichiometry from (A) to (E) demonstrates that crotonic acid is scavenging HOI and preventing the further reduction to I_2 that would otherwise occur. The scavenging should greatly reduce the concentrations of I_2 , $\cdot\text{I}$, and I^- . The simultaneous great reduction in rate of induced reaction B supports our previous¹ proposal that this reaction occurs by a radical chain involving iodine atom intermediates.

Reactions of Phenol. Phenol, $\text{C}_6\text{H}_5\text{OH}$, is a still more effective scavenger of iodine in low oxidation states. The rate of reaction with HOI is approximated by eq 2.

$$-d[\text{HOI}]/dt = (8 \times 10^4)[\text{C}_6\text{H}_5\text{OH}][\text{HOI}] \text{ M s}^{-1} \quad (2)$$

A little phenol was added to a subsystem like that of the previous paper to create a solution having composition $[\text{IO}_3^-] = 0.025 \text{ M}$, $[\text{H}^+] = 0.1 \text{ M}$, $[\text{H}_2\text{O}_2] = 0.1 \text{ M}$, $[\text{Mn}^{2+}] = 0.002 \text{ M}$, and $[\text{C}_6\text{H}_5\text{OH}] = 1 \times 10^{-4} \text{ M}$. This system exhibited an extreme induction period such that during 4 h only about 1 mL of oxygen was evolved. Then during a few minutes the rate of O_2 evolution increased by 2 orders of magnitude!

A comparison of eq 1 and 2 indicates that 10^{-4} M phenol should scavenge HOI less efficiently than 0.1 M crotonic acid. However, the phenol system inhibits the manganous-catalyzed oxidation of peroxide by iodate while the crotonic acid system does not. We conclude that the phenol is also scavenging some essential oxyiodine species intermediate between IO_3^- and HOI. A plausible interpretation is that phenol competes with Mn^{2+} for the $\cdot\text{IO}_2$ radical. We have no direct evidence for this suggestion. However, phenol and other aromatic substrates react in precisely this way with $\cdot\text{BrO}_2$ radicals during uncatalyzed bromate-driven oscillations.^{10,11}

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2-Naphthol, like phenol, is a powerful inhibitor, and a concentration of only 1×10^{-6} M causes a 10-min induction period.

Adducts Providing More Equivocal Evidence

Reactions of Acrylamide. Acrylamide, $\text{CH}_2=\text{CHCONH}_2$, is often an effective radical trap and has been used in this way with the oscillatory Bray-Liebafsky mixture.¹² However, it has a rather minor effect on the iodate-peroxide-manganous subsystem. Thus 10^{-3} M acrylamide reduced the rate of I_2 formation by only 15% and 10^{-2} M reduced by only about 70%. We find that acrylamide reacts with a mixture of I_2 and IO_3^- much the way crotonic acid does. Apparently acrylamide exerts at least much of its influence by reacting with HOI rather than by trapping radicals.

Reactions of Oxalic Acid. Oxalic acid, $(\text{CO}_2\text{H})_2$, forms weak complexes with Mn(II) ¹³ and is both a complexing agent and 1-equiv reductant of Mn(III) .¹⁴ When 0.026 M oxalic acid was added to a system having composition $[\text{IO}_3^-] = 0.025$ M, $[\text{H}^+] = 0.1$ M, $[\text{H}_2\text{O}_2] = 0.1$ M, and $[\text{Mn}^{2+}] = 0.002$ M, an induction period of 5 min was followed by a slower rate of I_2 production than in the absence of oxalic acid. If the concentration was increased to 0.10 M (where approximately 25% of the Mn^{2+} is complexed), the induction period was lengthened and the maximum rate of I_2 production was reduced by 2 orders of magnitude. However, this system was more complex than anticipated; after about 3 h when $[\text{I}_2]$ had gone through its maximum and decreased, it rapidly increased again. Oxalic acid is not only a complexing agent and reductant for manganese but can also react with HOI.¹⁵ These studies provide less information than had been hoped.

Effects of Pyrophosphate. Pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$, complexes Mn(II) and particularly Mn(III) and lowers the reduction potential from about 1.5 to 1.15 V.¹⁶ If a subsystem of iodate, peroxide, and manganous ions was made 0.05 M in $\text{Na}_4\text{P}_2\text{O}_7$ and adjusted to pH 1.0 with perchloric acid, reaction A was about 30% faster than at the same pH in the absence of pyrophosphate. If such a system also contained crotonic acid and was made 0.02 M in pyrophosphate, the rate of oxygen evolution increased by a factor of 3 and the fraction α (see first paper¹) of induced peroxide disproportionation increased from 0 to 0.25.

If 3×10^{-4} M Mn(III) in excess pyrophosphate was added to an acidic mixture of H_2O_2 and IO_3^- , some I_2 was rapidly produced. However, the ratio of $[\text{I}_2]$ formed to $[\text{Mn}^{3+}]$ consumed was no more than 0.17 and production of I_2 soon stopped. Apparently Mn(III) oxidation of H_2O_2 induces the simultaneous reduction of IO_3^- by H_2O_2 as would be expected from the mechanism of the previous paper.¹ However, that induction was not a true catalysis. If crotonic acid was also present, the ratio of O_2 formed to Mn^{3+} consumed was about unity, indicating that Mn(III) and iodate contributed about equally to the initial oxidation of peroxide.

Effects of Silver Ion. Silver ion is an obvious reagent to inhibit reactions of iodide ion. A precipitate of silver iodate, AgIO_3 , also forms in the subsystem, but with iodate in excess the equilibrium $[\text{Ag}^+]$ of about 10^{-6} M is sufficient to keep $[\text{I}^-]$ about 10^{-10} M or less. Addition of silver ion has little effect on $-d[\text{IO}_3^-]/dt$ in the subsystem of the first paper, but oxygen evolution is faster. When most of the silver ion has been converted to AgI , $[\text{I}_2]$ and $[\text{I}^-]$ both increase and the rate of oxygen evolution decreases.

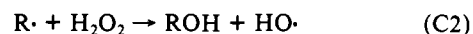
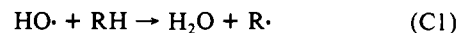
Effects of Other Additives. A few other additives were studied with the iodate-peroxide-manganous subsystem. Dichromate, $\text{Cr}_2\text{O}_7^{2-}$, at 5×10^{-6} M prevents iodine from forming; therefore cleaning solution was not used on our glassware and the reagents were never allowed to contact stainless steel. Chloride ion at 2×10^{-4} M noticeably slows the reaction; but fluoride ion at the same concentration has little effect. Ferric ion at the same concentration also has little effect even though this species is a

catalyst for hydrogen peroxide disproportionation.

Discussion

These observations demonstrate that crotonic acid and phenol, which are scavengers for HOI, have major effects on behavior of the iodate-peroxide-manganous subsystem. On the other hand, silver ion, which scavenges I^- and I_2 , has relatively little effect. We must conclude that *HOI is a very important intermediate in the manganous catalysis of reaction A* while I^- appears rather unimportant. According to superficial consideration, the mechanism of the previous paper¹ is not entirely consistent with that conclusion. We should now consider the possible reactions of organic matter as outlined in the Introduction.

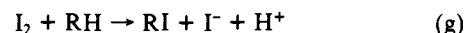
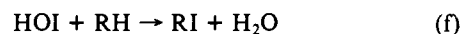
(a) Organic matter may be attacked by oxyhydrogen radicals. Such attack is eminently plausible and must occur. The gas evolved from a Briggs-Rauscher³ oscillator is mostly oxygen, but it also contains significant amounts of carbon dioxide. Some induced hydrogen peroxide oxidation of malonic acid evidently occurs. A schematic mechanism is illustrated by steps C1 and C2.



These steps provide a chain by which hydrogen peroxide can oxidize organic matter without net depletion of the $\text{HO}\cdot$ radicals. We choose to regard such steps as side reactions that consume some hydrogen peroxide and organic matter but that are not essential to the mechanism of the oscillating reaction itself.

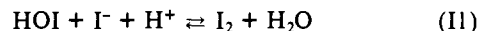
(b) The organic matter may be oxidized by iodine species with oxidation number greater than +1. The discussion above found it necessary to invoke just such processes in order to explain the extremely efficient inhibition by phenol. However, by invoking them for phenol, we concluded they were much less important for crotonic acid. They should be less important still for malonic acid. Unless and until further evidence requires a change, we shall assume that the only iodine species reacting directly with malonic acid and its derivatives are included in the set HOI, I_2 , $\cdot\text{I}$, and I^- .

(c) Iodination of RH may serve as a sink for I_2 and for the species HOI and I^- in rapid equilibrium with it. Malonic acid certainly serves as just such a sink. The reaction passes through an enol intermediate and generates the net stoichiometries f and g.



The discussion of the next paper will show that this sink function is essential to the mechanism of the oscillating reaction. However, a sink depletes the concentrations of all three species, I_2 , HOI, and I^- . The Introduction pointed out that oscillatory behavior required $[\text{I}^-]$ to increase enough to enhance the importance of step I2. It is not sufficient that malonic acid serve as a sink for iodine species with low oxidation number.

(d) Iodination of RH may shift the ratio $[\text{I}^-]/[\text{HOI}]$. Eigen and Kustin¹⁷ have shown that equilibrium I1 is established within



a time of the order of 1 s. Reactions f and g both have the effect of increasing the ratio $[\text{I}^-]/[\text{HOI}]$. By serving as a sink, those reactions indubitably decrease the sum $[\text{HOI}] + 2[\text{I}_2] + [\text{I}^-]$. However, they may actually serve to increase the value of $[\text{I}^-]$. We believe such an increase is necessary if malonic acid is to convert the iodate-peroxide-manganous subsystem to an oscillator.

(e) Subsequent reactions of RI may liberate I^- . Just such an organic bromide reaction is essential to the original FKN¹⁸ mechanism of the Belousov¹⁹-Zhabotinsky²⁰ oscillator. Subsequent

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considerations⁴ indicate it is not necessary in all bromate-driven oscillators. Iodomalonic acid is indubitably subject to attack by species like Mn^{3+} and $HO\cdot$; I^- should be one of the products. Cooke²¹ specifically invokes this very process in his mechanistic proposals for the Briggs-Rauscher³ oscillator. Briggs and Rauscher themselves noted that $[I^-]$ oscillated somewhat in a system containing no manganous compounds; that observation might suggest that radical species were attacking RI to form I^- . However, the next paper shows we can model oscillations by a skeleton mechanism that regards iodination of malonic acid as irreversible. We choose for now to ignore the potential complexities of other assumptions.

Conclusions

Malonic acid or a similar organic compound is an essential component of the oscillating reaction, and we have identified five reaction types that might occur. Three of these are considered unnecessary for oscillations. The essential characteristic of malonic acid is that its enol scavenges low oxidation states of iodine by

net processes f and g. That scavenging reduces the total concentration $[HOI] + 2[I_2] + [I^-]$, but it simultaneously increases the ratio $[I^-]/[HOI]$ and may actually increase $[I^-]$ itself enough to shut off the 1-equiv processes that dominate the iodate-peroxide-manganous system.

Experimental Section

Reagent grade chemicals were used whenever obtainable. H_2O_2 was Fisher stabilizer free. KIO_3 and crotonic acid were recrystallized from water. Triple-distilled water was used to prepare all solutions. Ionic strength was adjusted to 0.3 with $NaClO_4$.

Spectrophotometric measurements were done on either a Beckman DU or Beckman DBGT spectrophotometer, both with thermostated cell compartments. All solutions were brought to constant temperature before mixing; all measurements were made at 25.0 °C.

Gas evolution was conducted with a thermostated gas buret with the solution rapidly stirred by a submersible magnetic stirrer. Iodide ion was monitored by an Orion iodide sensitive electrode vs. a $Ag/AgCl$ double junction reference electrode with $NaClO_4$ in the outer compartment.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation to the University of Oregon. Mrs. Constance Ivey^{2b} conducted cerium oxidations of iodomalonic acid and iodomethylmalonic acid solutions.

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The Oscillatory Briggs-Rauscher Reaction. 3. A Skeleton Mechanism for Oscillations¹

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Abstract: The essential mechanistic features of the full iodate-peroxide-manganous-malonic acid system can be modeled with a skeleton mechanism involving only 11 pseudoelementary processes. The rate constants of seven of those processes are known from experiment. Judicious assignment of the other four values creates a system that mimics the essential feature of oscillations. This mechanism differs from those of other known oscillators in that both radical and nonradical paths generate the same net chemical change.

The first paper of this series³ reported and attempted to explain the remarkably effective catalysis by manganous ion of the oxidation of hydrogen peroxide by iodate. The second paper¹ discussed the reactions by which malonic acid and other organic species act as sinks to remove iodine present as I_2 and HOI . In this paper, we attempt to show how these mechanisms can be combined to generate the oscillations observed in the full Briggs-Rauscher⁴ system.

We have not attempted a detailed experimental study of the malonic acid, MA, oscillator. Such studies have been carried out by others including Cooke,⁵ De Kepper,⁶ Roux and Vidal,⁷ and Dutt and Bannerjee.²⁷ Because MA can add two iodines, it was considered desirable to make some observations of oscillations with the substrate methylmalonic acid, MMA, which can only undergo monoiodination. Those observations are reported elsewhere.⁸ Oscillations with MMA exhibit longer periods than with MA, apparently because enolization of MMA⁹ is several fold slower than that of MA.¹⁰ However, we did not find any reason to believe

the two substrates reacted by significantly different mechanisms.

This oscillatory system is so complex it is not considered profitable to attempt to model the full experimental system quantitatively. We choose rather to assign plausible rate constants to a skeleton mechanism which then reproduces the essential experimental fact of oscillation.

A Set of Elementary Processes

The objective of mechanistic understanding is to identify the elementary processes occurring in a complex system. Such a process takes place in a single step and involves no more than two or at most three reactant species. We have simplified the description by assuming that proton transfers to and from oxygen and iodine are so rapid they can be considered equilibrated at all times. The effects of such equilibration are superimposed on the truly elementary steps.

The listing in Scheme I organizes reaction types according to a useful system originally developed by Liebhaufsky¹¹ for consideration of the simpler Bray¹² oscillatory system. An IODINE step involves two species containing this element; one is oxidized and one is reduced, but the average oxidation number must remain constant. An OXYGEN step involves mutual oxidation and

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