

Exceptionally Large Oxygen Effect in the Belousov–Zhabotinsky Reaction

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Addition of HOBr can eliminate the induction period for oscillations in a Belousov–Zhabotinsky system, which just as Burger and Körös have previously shown is also accomplished by initial addition of bromomalonic acid. However, in a solution saturated with air, the initial addition of HOBr causes a train of only a few oscillations, and after less than 10 min, the system goes to a *reduced* steady state. If an identical system is prepared under an atmosphere of argon, oscillations will start immediately and will persist for over 16 h! This factor of over 100 in the duration of oscillations is larger than any other oxygen effect that we are aware of in such a system. An argument based on established reaction types can rationalize both this dramatic effect of air on the persistence of oscillations and also the unanticipated effect of oxygen to drive the system rapidly to a reduced steady state.

Introduction

Nearly everybody who has worked extensively with the Belousov–Zhabotinsky (B–Z) reaction has noticed that interaction with atmospheric oxygen can affect the behavior. Reports in the literature are illustrated by ref 1–6 and 21.

Those reports are not obviously consistent with each other. Thus, Roux and Rossi² report that oxygen inhibits oscillations in systems between about 0.018 and 0.4 M in malonic acid but that it causes oscillations in a composition having more than 0.4 M malonic acid. Ruoff⁶ also reports that oxygen inhibits oscillations

when malonic acid is about 0.3 M. Bar-Eli and Haddad³ report that O₂ lengthens the induction period before oscillations begin, while Treindl and Fabian⁴ report the induction period is shortened in a composition that is not conspicuously different.

These apparent discrepancies are similar to the observations of Sharma and Noyes⁷ on the oscillatory disproportionation of

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- (1) Varadi, Z.; Beck, M. T. *J. Chem. Soc., Chem. Commun.* **1973**, 30–31.
- (2) Roux, J.-C.; Rossi, A. C. R. *Seances Acad. Sci.* **1978**, C287, 151–154.
- (3) Bar-Eli, K.; Haddad, S. *J. Phys. Chem.* **1979**, 83, 2952–2958.
- (4) Treindl, L.; Fabian, P. *Collect. Czech. Chem. Commun.* **1980**, 45, 1168–1172.
- (5) Patonay, G.; Noszticzus, Z. *React. Kinet. Catal. Lett.* **1981**, 17, 187–189.
- (6) Ruoff, P. *Chem. Phys. Lett.* **1982**, 92, 239–244.

TABLE I: Initial Composition of Solution

$[\text{Ce(IV)}]_0 = 5 \times 10^{-4} \text{ M}$	$[\text{KBrO}_3]_0 = 0.1 \text{ M}$
$[\text{malonic acid}]_0 = 0.28 \text{ M}$	$[\text{H}_2\text{SO}_4]_0 = 1.0 \text{ M}$

hydrogen peroxide catalyzed by iodate (Bray-Liebafsky reaction). Those authors report that increased oxygen concentration can promote oscillations at low perchloric acid concentrations (less than about 0.05 M) but that similar increases can inhibit oscillations at higher acid concentrations of about 0.06 M. We see no reason to doubt any of the apparently contradictory facts that have been reported but note that these very sensitive systems must be characterized with great care.

We report here some observations on Belousov-Zhabotinsky systems to which hypobromous acid, HOBr, had been added. When the dissolved air was replaced with argon, the duration of the oscillations was increased by a factor of at least 100 from less than 10 min to over 16 h! This dramatic effect has mechanistic implications about which we speculate below.

Experimental Procedures

The species H_2SO_4 , KBrO_3 , $\text{Ce}(\text{HSO}_4)_4$, and malonic acid ($\text{H}_2\text{C}(\text{CO}_2\text{H})_2$) were of commercial analytical quality.

Hypobromous acid (HOBr) was prepared as described by Ruoff.⁸ About 0.5 M silver nitrate was treated with a slight excess of bromine (Br_2), and the excess bromine was removed by purging the solution with a stream of argon at 0 °C for 15–20 min. The resulting solution was filtered to remove solid AgBr, was analyzed by potentiometric titration with bromide ion, and was stored on ice during the experiments. A specific preparation was not used for more than one period in the laboratory.

Experiments were run in a Metrohm polarographic cell thermostated at 25.0 ± 0.1 °C. Reactions were followed potentiometrically simultaneously with a platinum electrode (Metrohm) and with a bromide-ion-selective electrode (Orion). The reference electrode was Ag/AgCl double junction with saturated KCl solution in the inner compartment with 1 M sulfuric acid as the outer electrolyte.

Mixtures for a run were prepared from 10 cm³ of 2.27 M H_2SO_4 , 4 cm³ of 1.75 M malonic acid, 10 cm³ of 0.25 M KBrO_3 , and 1 cm³ of 0.0125 M $\text{Ce}(\text{HSO}_4)_4$ (dissolved in 2.27 M H_2SO_4). The composition of this standard mixture is shown in Table I. Various amounts of HOBr solution were also added to some runs, but those additions did not affect the concentrations of the other species by more than about 10%.

Aerobic experiments were carried out with either the solution being in contact with air or else air being bubbled through the reaction solution. No distinct differences were observed between the two procedures.

For runs under anaerobic conditions, the sulfuric acid and bromate were added first to the reactor, and argon (which had been saturated with water by being passed through a washing bottle) was bubbled vigorously for 5–10 min. The other reagents were then added quickly, and argon bubbling was continued throughout the entire time of the reaction. The reactor was covered except for one opening in which a loose paper stopper permitted escape of argon.

Experimental Observations

Figure 1 shows that initial addition of HOBr can shorten the induction period ordinarily observed at the start of an aerobic run, and 0.06 M can eliminate that induction period for a system with 0.1 M bromate. However, addition of HOBr also shortens the duration of the oscillations when they do start, and Figure 1D shows that duration is only about 5 min when 0.06 M HOBr is present initially.

Figure 2 shows behavior at the start and at selected subsequent times of a system identical with that in Figure 1D except that air had been removed with argon. Oscillations began without an induction period and remained regular with decreasing amplitude

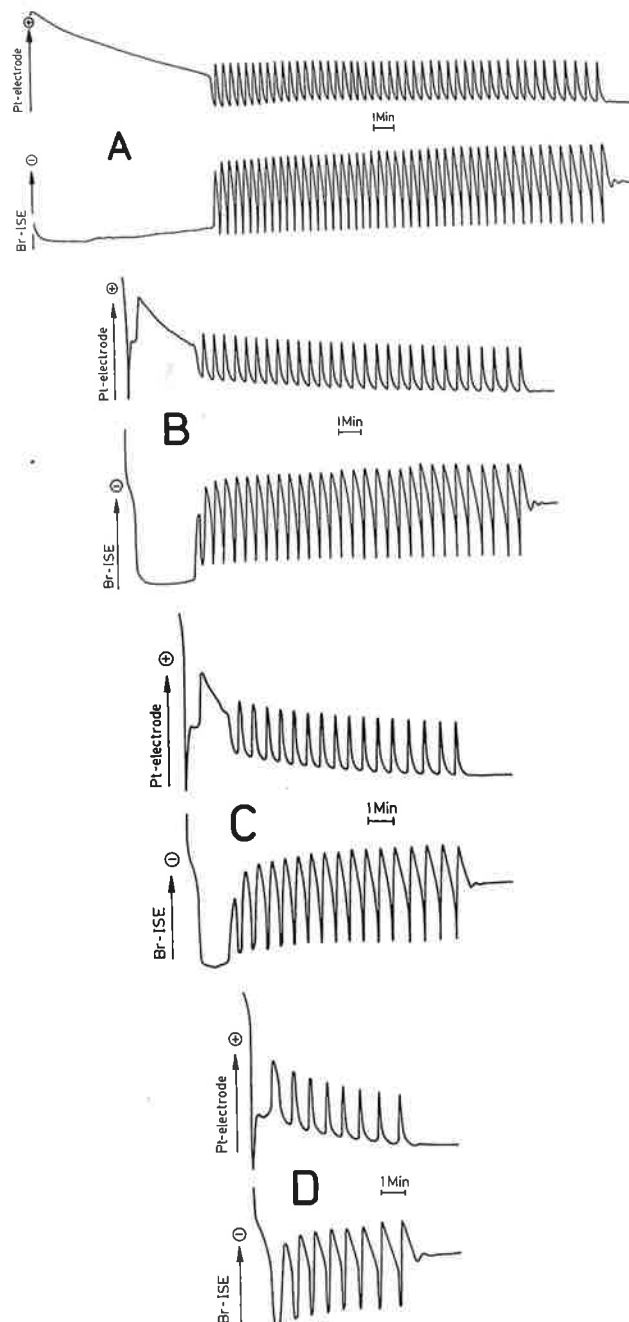


Figure 1. Uncalibrated potentials of the platinum electrode and bromide-selective electrode (Br-ISE). Arrows with signs indicate the direction by which potentials become more positive or negative, respectively. Key: (A) no HOBr addition; (B) 0.02 M HOBr; (C) 0.04 M HOBr; (D) 0.06 M HOBr.

until they died away after about 1000 min or 16 h. The contrast between Figure 1D and 2 is more dramatic than any other reported oxygen effect for a Belousov-Zhabotinsky system that oscillates both in the presence and absence of air.

Discussion

Facts To Be Considered. The information available to us does not permit a full elucidation of the mechanism of this large oxygen effect. However, the following facts exert very strong constraints on any mechanisms that can be suggested:

(i) Contrary to what might have been anticipated, the effect of the oxidizing species O_2 is to drive the system to a *reduced* steady state. Everything we know about mechanisms in B-Z systems then requires that O_2 promotes the formation of Br^- .

(ii) The induction period occurs because the system persists in an *oxidized* steady state until oscillations commence.

(7) Sharma, K. R.; Noyes, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 202–204.
(8) Ruoff, P. J. *Phys. Chem.* **1984**, *88*, 2851–2857.

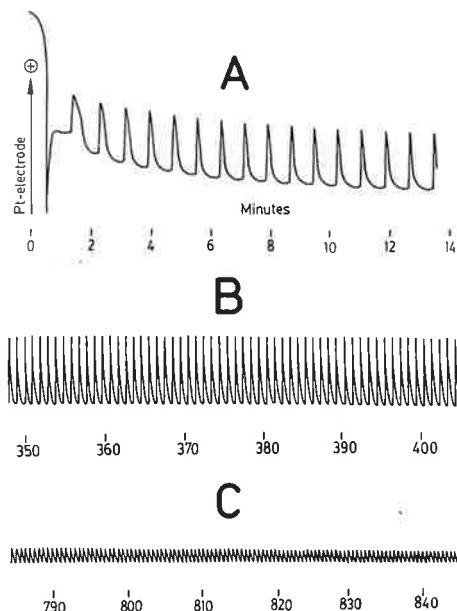


Figure 2. Same system as in Figure 1D but with continuous bubbling of argon. Numbers indicate minutes from start of the reaction. Key: (A) start of oscillator; (B) virtually undamped oscillations observed for many hours. (C) damped oscillations at the end of the oscillating regime. Oscillations ended at about 1000 min.

(iii) Burger and Körös^{9,10} observed that initial addition of sufficient bromomalononic acid (BrMA, $\text{BrCH}(\text{CO}_2\text{H})_2$) could eliminate the induction period. Even in the presence of air, the oscillations then persisted for a considerable time. However, Varga, Györgyi, and Körös¹¹ showed that at least in the presence of silver ion, most of the bromide ion produced came from the original bromate rather than from the original BrMA.

(iv) We now find that initial addition of sufficient HOBr can also eliminate the induction period. However, in air, we observe oscillations for only a few minutes before the system goes to a reduced steady state. A reviewer has pointed out that the amount of HOBr necessary to eliminate the induction period is several times the amount of BrMA necessary to accomplish the same effect in ref 10. Furthermore, $[\text{HOBr}]$ may even be decreasing during the few oscillations we observe in air while $[\text{BrMA}]$ always increases monotonically in these systems. If no HOBr is present initially in an anaerobic system, there is an induction period but the subsequent oscillations persist about 24 h or even longer than if no HOBr had been added at the start. As the reviewer pointed out, the low concentration of catalyst is more important than the initial presence of HOBr in generating the long duration of oscillations in Figure 2.

(v) Both HOBr and BrMA contain bromine that can be assigned a formal 1+ oxidation state and that can be reduced to bromide ion. The different behaviors in persistence of oscillations in (iv) suggest that the mechanisms of reduction need not be identical.

(vi) Oxygen has somewhat different effects on B-Z systems when the organic substrate is malonic acid (MA) and when it is methylmalonic acid (MeMA, $\text{CH}_3\text{CH}(\text{CO}_2\text{H})_2$). With MA, bubbling with oxygen generates a nonoscillatory reduced and excitable steady state that does not change further. With an otherwise identical MeMA system, oxygen inhibits oscillations only temporarily and does so by generating an oxidized steady state (see Figure 6 in ref 12). The differences in oxygen effects with malonic and methylmalonic acids suggest that both of the

methylene hydrogens in malonic acid are important to the mechanism.

Additional Mechanistic Principles. Our efforts below to explain the large oxygen effect are complicated. Those readers who do not wish to follow these arguments in detail may prefer to go directly to the Summary of Arguments near the end of the paper. Those who do wish to follow the details may be helped by the following statement of the principles that have guided our mechanistic efforts:

(a) Organic radicals, R^\bullet , with an odd electron in an orbital on carbon will rapidly and almost irreversibly add oxygen to form ROO^\bullet peroxy radicals.

(b) Because O-H bonds are stronger than C-H bonds in malonic acid, radicals with an odd electron on oxygen (whether C-O^\bullet or C-O-O^\bullet) will abstract hydrogen atoms.

(c) Bromine atoms can also abstract hydrogen atoms from MA.

(d) The C-H bonds to the central carbons in BrMA and in $\text{HOCH}(\text{CO}_2)_2$ are probably somewhat weaker than the corresponding bonds in MA.

(e) Bonds like O-O and O-Br between electronegative atoms are broken homolytically by organic radicals in which the odd electron is on the less electronegative carbon atom.

(f) Cerium(IV) oxidizes organic molecules by complex formation and electron transfer. Oxidations of organic radicals to ROH compounds by $\text{Ce}(\text{IV})$ are slower but are not forbidden.

(g) An organic radical containing the odd electron on a carbon attached to bromine will hydrolyze to bromide ion much more rapidly than will comparable singlet organic bromide molecules.

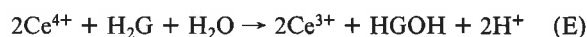
Net Chemical Change. If an anaerobic system under argon has the initial composition shown in Table I with no initial HOBr addition, then the total net chemical change can be described to a very good approximation by means of eq T.



In this equation, H_2G represents the substrate malonic acid, HGBr is bromomalononic acid (BrMA), and HGOH is an abbreviated designation for substrate oxidized by 2 equivalents. The exact organic chemistry of the total reaction may be very complicated, including oxidation of some of the malonic acid all the way to carbon dioxide, but the explanation of the oscillations need consider only the total number of equivalents by which organic matter has been oxidized regardless of whether a few molecules have been extensively oxidized or whether many molecules have been oxidized by only 2 equivalents each.

Of course, many other chemical species are formed and destroyed by the reactions taking place, but those species are always in very small concentrations so that process T remains an excellent description of the total net chemical change in the system. If we are to discuss the mechanism, we must do so in terms of additional species not appearing in process T.

Component Stoichiometric Processes. It is convenient to define a number of component stoichiometric processes. These processes may take place by complex mechanisms and may involve other transient species in addition to those appearing in eq T. However, eq T can always be generated from a linear combination with positive coefficients of the component stoichiometric processes. The rationale for such an approach has been presented elsewhere.¹³ Equations A-F are the component stoichiometric processes we have selected.



(9) Körös, E.; Burger, M.; Friedrich, V.; Ladanyi, L.; Nagy, Zs.; Orban, M. *Faraday Symp. Chem. Soc.* **1974**, 9, 28-37.

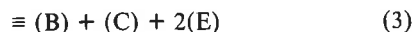
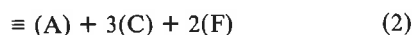
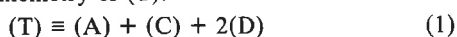
(10) Burger, M.; Körös, E. *J. Phys. Chem.* **1980**, 84, 496-500.

(11) Varga, M.; Györgyi, L.; Körös, E. *J. Am. Chem. Soc.* **1985**, 107, 4780-4781.

(12) Ruoff, P.; Schwitters, B. *Z. Phys. Chem. (Munich)* **1983**, 135, 171-184.

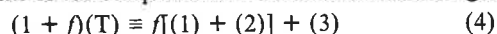
(13) Noyes, R. M. In *Non-Equilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer-Verlag: Berlin, 1984; p 60-64.

Because (D) = (C) + (F), eq C, D, and F are not stoichiometrically independent. Equations 1-3 show three different ways in which these six component processes can be combined to generate the stoichiometry of (T).



In general, at any time in any system, either process A or B will be dominant and the other will be going at a negligible rate. When A is dominant, the system is in a reduced state; when B is dominant, the state is oxidized. If the solution is exhibiting relaxation oscillations, transitions between dominance by A or by B take place almost discontinuously. The mechanism for such transitions has been discussed in several other places, including ref 14 and 15, and will not be presented here.

In any steady state or for an integral number of periods of any limit cycle, let f be the ratio of the amount of bromate reduced by process A to that reduced by process B. Then, eq 4 describes the contributions of various paths to the total chemical change.



Experience with the Oregonator¹⁶ approximation indicates that when f is less than 0.5, the system is in an oxidized steady state while for f more than 2.4 it is in a reduced steady state. Depending upon the values of individual rate constants, intermediate values of f may be associated with oscillatory behavior.

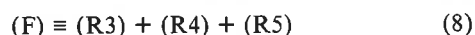
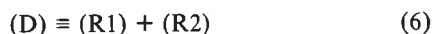
If an anaerobic system initially contains negligible amounts of HOBr and of BrMA, processes D and F that produce Br⁻ will be slow and most chemical change will be initiated by process B. Therefore, the behavior will first correspond to an oxidized steady state as required by fact ii above.

If sufficient HOBr or BrMA is added initially, process D or F, respectively, can be producing bromide ion from the start of the reaction and f may be large enough to cause oscillations without an induction period. Therefore, facts iii and iv are accommodated.

Because processes C, D, and F are stoichiometrically dependent, we do not know whether processes D and F are coupled kinetically. We must go beyond these stoichiometric arguments and consider mechanisms to determine whether or not we were justified to suggest in fact v that independent processes might be producing bromide ion from HOBr and from BrMA.

Pseudoelementary Processes. All chemical change no matter how complicated is ultimately the consequence of elementary processes, each of which takes place in a single step passing over a single potential energy maximum with identical kinetics and stoichiometry and proceeding in the direction dictated by thermodynamics. In a system as complicated as this one, it is convenient to combine some steps into single pseudoelementary processes such that reactants and products need not be single species but may also be groups of species in rapid equilibrium with each other. It may even be that these groups may go from one to the other by parallel paths so that multiple energy maxima may separate the same groups of reactants and products.

Table II contains a set of pseudoelementary processes sufficient to generate the stoichiometric processes C-F. The ways in which those processes can be generated are shown in eq 5-8.



Selection of the radical processes in Table II is based on the mechanistic principles stated above. These processes are not a complete set of all those that are possible, but they are sufficient to generate all of the component stoichiometric processes presented

TABLE II: Pseudoelementary Processes Generating Stoichiometric Processes C-F

reaction	eq no.
Processes Involving No Radicals	
HOBr + Br ⁻ + H ⁺ ⇌ Br ₂ + H ₂ O	(P1)
H ₂ G + Br ₂ → HGBr + Br ⁻ + H ⁺	(P2)
Processes Forming Radicals	
Ce ⁴⁺ + H ₂ G → Ce ³⁺ + H ⁺ + HG [•]	(Q1)
Processes Conserving Radicals	
HG [•] + HOBr → HGOH + Br [•]	(R1)
Br [•] + H ₂ G → Br ⁻ + H ⁺ + HG [•]	(R2)
HG [•] + HGBr → H ₂ G + [•] GBr	(R3)
[•] GBr + H ₂ O → Br ⁻ + H ⁺ + [•] GOH	(R4)
[•] GOH + H ₂ G → HGOH + HG [•]	(R5)
Processes Consuming Radicals	
Ce ⁴⁺ + GH [•] + H ₂ O → Ce ³⁺ + HGOH + H ⁺	(S1)

above. In the subsequent discussion, we shall consider some other pseudoelementary processes that are also conceivable and shall present other processes that are necessary in order to explain effects of oxygen on this system. Note that eq 6 and 8 do generate alternative paths to produce bromide ion as required by fact v in spite of the stoichiometric identity (D) = (C) + (F).

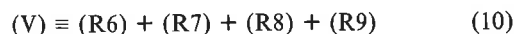
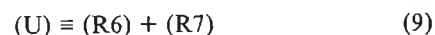
Rationalization of Oxygen Effect. If O₂ is also present in an aerobic system, net stoichiometric processes U and V may take place in addition to process T. In eq U, HGOOH is hydroperoxymalonic acid, HOOCH(CO₂H)₂.



These stoichiometric processes can be generated by pseudoelementary processes R6-R9, all of which conserve radicals and also conform to our mechanistic principles.



Stoichiometric processes U and V can be generated by the sequences of eq 9 and 10.



Fact i asserts the observations require that oxygen promotes the formation of bromide ion in a B-Z system, but processes R6-R9 have nothing to do with bromide formation. Furthermore, to the extent that HG[•] radicals (which can attack HOBr) are converted to HGOO[•] radicals (which probably cannot), formation of bromide by process D will actually be inhibited. Our rationalization of the oxygen effect must consider the various processes in more detail. The radicals HG[•], Br[•], and [•]GOH are present in B-Z systems whether aerobic or anaerobic. The radicals HGO[•] and HGOO[•] occur only if oxygen is present.

All radicals can extract H from organic matter, and the direction of any process depends upon the relative strengths of bonds that are broken and formed. The five radicals listed above react by H abstraction in steps R3, R2, R5, R9, and R7, respectively. If anything, the oxygenated radicals HGO[•] and HGOO[•] probably abstract H more readily than do the radicals with the odd electron on carbon or on bromine, and the presence of oxygen will favor formation of bromide from BrMA by process F (R3-R5) more than from HOBr by process D (R1-R2).

Hydrolysis reaction R4 was first invoked by Edelson et al.¹⁷ to account for formation of bromide from BrMA (HGBr); the argument presented here directly supports the existence of reaction

(14) Field, R. J.; Noyes, R. M. *Acc. Chem. Res.* 1977, 10, 214-221.

(15) Noyes, R. M. *J. Am. Chem. Soc.* 1980, 102, 8644-8649.

(16) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* 1974, 60, 1877-1884.

(17) Edelson, D.; Field, R. J.; Noyes, R. M. *Int. J. Chem. Kinet.* 1975, 7, 417-432.

R4, which is an example of principle g.

Some radicals can react to break O—O or O—Br bonds between electronegative elements according to principle e. HG^\bullet radicals react this way in steps R8 and R1, respectively. Oxygenated radicals will not behave this way, and oxygen inhibition of step R1 would be expected to move the system toward an oxidized state if nothing else happened also.

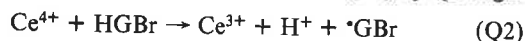
The significant difference we see is that cerium(IV) can oxidize HG^\bullet radicals by step S1 (Table II) while HGOO^\bullet radicals will not react in this way. Step S1 has been studied under anaerobic conditions by Brusa, Perissinotti, and Colussi.^{18,19} We are not aware of any effort to study an analogous reaction of Ce(IV) with HGOO^\bullet radicals and doubt that such a process would occur. Oxygen thus serves to inhibit termination of radical chains and therefore increases the amount of bromide ion produced by process F whenever step Q1 initiates radical formation. We do not presently see any other way to explain the observed effects.

This argument concludes that oxygen will hinder bromide formation by process D initiated by step R1 but will perhaps accelerate formation by process F provided HGOO^\bullet radicals react with HGBr more rapidly than HG^\bullet radicals do by step R3. Perhaps the most important effect of oxygen will be to inhibit termination step S1 and thus to lengthen the chain lengths of the radical processes that produce bromide. A final decision would depend upon relative values of rate constants that are not presently known, but there is no intrinsic reason why oxygen might not react to generate a reduced state, implausible as such a situation first sounds.

This argument also helps to explain fact vi because the analogue of step R3 is not accessible to the methylmalonic acid substrate, which cannot have a hydrogen on a carbon that contains a bromine.

Possible Additional Processes. Although the above argument is more complicated than is desirable, it appears to use a virtual minimum number of steps in order to explain all of the experimental facts i–vi. Our argument has tried to select those steps we expect to be the most probable by analogy with other reactions, but some other steps should be considered in a thorough analysis.

Thus, Q1 is the only process proposed for initiating chains, although many organic species in addition to malonic acid can be oxidized by Ce(IV) . Attack on most of them would not change the conclusions, but reaction of BrMA with Ce(IV) by Q2 might



be followed by R4 and thus promote process F. However, the rate constant for Q2 is only a few percent of that for Q1,²⁰ and relative amounts of MA and of BrMA would combine with the relative rate constants to make Q2 unimportant.

We have also neglected termination of chains by radical–radical processes. Such a decision may be acceptable in an anaerobic system. However, if step S1 is inhibited by Q2 as argued above, it might be desirable to add the well-known type of process illustrated by step S2.



Summary of Arguments. The above arguments are based on several individual processes and cannot be appreciated without very careful reading. Perhaps a few summarizing statements can explain how we rationalize the dramatic oxygen effect:

If the substrate is malonic acid (MA) and no oxygen is present, the organic radicals can initiate bromide production by reacting either with HOBr or with brominated organic matter. These chain-propagating reactions are in competition with chain termination by reactions with cerium(IV).

If the substrate is methylmalonic acid (MeMA), bromo-methylmalonic acid cannot produce bromide as a consequence of radical attack and the transition to a reduced state is less favorable.

If oxygen is also present in a system with MA substrate, the peroxy radicals will not attack HOBr but will still produce bromide ion attack on brominated organic matter followed by hydrolysis of the resulting bromo-organic radical. The chain-terminating reactions of radicals with cerium(IV) will also be inhibited. The overall effect of the increased chain length will be that oxygen actually promotes the production of bromide ion and the transition to a reduced state.

If oxygen is present with MeMA substrate, the peroxy radicals will not react to generate bromide ions either from HOBr or from brominated organic matter, and any steady state is likely to be oxidized.

Concluding Remarks. R.M.N. was embarrassed when one of his own previous papers²¹ was cited by a reviewer! That paper reported that with ferriin instead of cerium as catalyst a thin layer of solution could be maintained in a reduced steady state as long as it was saturated with air. However, if the dish was tilted so that oxygen became partially depleted in the thickened layer, an oxidative excursion could be initiated. Those previous observations are consistent with the arguments developed in the present paper.

The oxybromine chemistry of the Belousov–Zhabotinsky system appears to be unequivocally established by now. The detailed radical reactions of the organic substrate are not as well elucidated, and efforts at modeling have almost always been satisfied with the use of stoichiometric factors rather than with pseudoelementary processes. The remarkable oxygen effect reported here has offered a handle to provide more insight into the complicated chemistry glossed over with step O5 of the Oregonator model. The mechanism developed here is still complicated, but it proposes several steps whose kinetics could be studied independently in order to develop still more understanding of this remarkable chemical system. It is an open question whether such study would contribute greatly to additional understanding and control of these reactions.

Acknowledgment. This work was supported by a grant from the National Science Foundation to the University of Oregon. P.R. also received a travel grant from the Rogaland University Center. This is No. 85 in the series “Chemical Oscillations and Instabilities”; No. 84 is Noyes, R. M. *J. Chem. Educ.* **1989**, *66*, 207.

Registry No. $\text{H}_2\text{C}(\text{CO}_2\text{H})_2$, 141-82-2; BrO_3^- , 15541-45-4; Ce , 7440-45-1; O_2 , 7782-44-7; HOBr , 13517-11-8.

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