On the other hand, it has been conclusively demonstrated that in the photolytic Wolff rearrangement-decomposition sequence of diazo ketones the ketocarbene-ketene rearrangement involves vibrationally excited singlet ketocarbenes and ground singlet state oxirenes to various degrees. The triplet state of ketocarbenes seems to play no role in these systems.[17,54-58]

In matrix isolation studies of the $O(^3P) + C_2H_2$ reaction the spectrum of ketene has been observed[59] but there were no absorptions which could be assigned to oxirene.

Further studies are in progress.

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Induction and Inhibition of Chemical Oscillations by Iodide Ion in the Belousov-Zhabotinskii Reaction

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Abstract: Initial addition of iodide ion to the oscillatory bromate-cerium-malonic acid system produces a variety of phenomena, depending on the initial iodide concentration. At moderately high and low [I⁻], the onset of oscillations is delayed, while very high [I⁻] totally suppresses oscillation. In an intermediate range of iodide concentration, oscillations which are qualitatively different from the halide-free oscillations appear with a shorter than normal induction period. These oscillations are later superceded by the ordinary, halide-free oscillations. Our observations may be accounted for by a mechanism involving (a) the direct reduction of Ce(IV) to Ce(III) by iodide, (b) the iodide-catalyzed production of glyoxylic acid, which gives rise to the induced oscillations, and (c) eventual oxidation of iodide to iodate by bromate.

The study of chemical systems which exhibit nonmonotonic[2] and, in particular, oscillatory behavior[3] has grown in the past decade from consideration of a few curious lecture demonstrations to a major area of chemical research. Oscillating reactions have yielded important insights into kinetic[4] and thermodynamic[5] problems, and provide alluring analogues of

Table I. Effects of Added Species on Oscillations in the BZ Reaction

Species added	Initial concn, M	Induction period, min[a]	No. of oscillations	Type of oscillations	Notes
None		6.6	>50	Normal	
I⁻	6.2×10^{-4}	6.9	>50	Normal	
	8.0×10^{-4}	7.7	>50	Normal	
	1.0×10^{-3}	0	7	Small	
		5.1	>50	Normal	
	1.3×10^{-3}	0	11	Small	
		4.9	>50	Normal	
	1.8×10^{-3}	6.5	15	Small	
		4.6	>50	Normal	
	2.5×10^{-3}	30.0	19	Small	
		4.0	>50	Normal	No second induction period, first few oscillations increase in amplitude
	3.8×10^{-3}	99.9	>50	Normal	
	5.0×10^{-3}	173.2	>50	Normal	
	7.5×10^{-3}	>3900[c]			
GOA	2.8×10^{-2}	3.9	>50	Small	Oscillations grow in amplitude, then damp out continuously
GOA[b]	0.45	0	7	Small	Oscillations end abruptly
Cl⁻	3.5×10^{-4}	10.7	>50	Normal	
	5.0×10^{-4}	19.5	>50	Normal	
IO₃⁻	5.0×10^{-3}	15.5	>50	Normal	

[a] When two induction periods are listed for a concentration, the first refers to the initial period before small oscillations begin, the second to the period between the small and normal oscillations. [b] No malonic acid present. [c] No oscillations after about 2.5 days.

a number of biological and biochemical processes.[6] The most thoroughly characterized and best understood of the chemical oscillators is the Belousov-Zhabotinskii[7,8] (BZ) reaction, the metal-catalyzed oxidation of certain dicarboxylic acids or related species by bromate ion in sulfuric acid solution. The detailed mechanism proposed by Field, Körös, and Noyes[9] for the cerium-malonic acid version of this system has been successfully employed to explain a wide range of experimental results.

In a recent paper,[10] we showed how small amounts of chloride ion, previously thought to totally suppress oscillations in the BZ reaction, in fact only inhibit the start of oscillations. We developed a mechanism for that inhibition, consistent with the FKN mechanism for the unperturbed BZ oscillations. We noted in that paper that iodide ion also inhibited oscillation, presumably in a manner resembling the chloride inhibition. After further study of the effects of added iodide ion on the BZ reaction, we have discovered that this system gives rise to a far richer variety of phenomena than either the halide-free or the chloride-inhibited system. In this paper, we discuss the behavior of the BZ reaction in the presence of iodide ion and present a mechanism which explains the phenomena observed and also sheds some light on other aspects of the BZ and related systems.

At concentrations comparable to those employed in our chloride studies,[10] iodide does, as reported there, inhibit oscillations in the BZ reaction. However, at somewhat higher concentrations, we find that iodide *induces* oscillation in the system, sometimes eliminating the induction period almost completely. At still higher concentrations, the inhibitory behavior returns. These observations are of interest for several reasons. First, explaining such a complex set of phenomena provides a stringent test for the FKN mechanism as well as for any other theories about the BZ reaction in general and its interaction with iodide ion in particular. Also, iodide ion constitutes the first known example of a substance which induces oscillations in the BZ reaction without itself being an intermediate or a product of the unperturbed reaction. Other inducers, particularly bromomalonic acid, have been studied,[11] but they are all thought to participate in the ordinary BZ reaction. Finally, in view of the interest in oscillating reactions as analogues of biological systems, the existence of a substance

which inhibits a form of behavior when present above or below some limiting levels, but induces that behavior within some narrow intermediate range of concentrations, constitutes a phenomenon worthy of further study.

Experimental Results

In this section we present our experimental observations: first, the behavior of the BZ system as the amount of iodide initially added to the system is increased, and then several other results which bear on our analysis.

A. Very Low Iodide. $[I^-]_0 < 10^{-4}$ M. Unless explicit mention is made to the contrary, all the experiments to be described were carried out at 25 °C using the same initial concentrations of BZ reactants as in the chloride study,[10] i.e., $[Ce(NH_4)_2(NO_3)_6] = 1.0 \times 10^{-3}$ M, $[KBrO_3] = 4.0 \times 10^{-2}$ M, $[CH_2(COOH)_2] = 1.0 \times 10^{-1}$ M, and $[H_2SO_4] = 1.5$ M. Addition of sufficient iodide ion to produce an initial concentration less than 10^{-4} M produced no observable effects on either the length of the induction period or the frequency and shape of the oscillations.

B. Low Iodide. 10^{-4} M $< [I^-]_0 < 10^{-3}$ M. In this range of concentrations, the effects of added iodide in the initial reaction mixture were qualitatively similar to those of added chloride.[10] That is, the induction period was lengthened, and was composed of two parts, one (part I) in which the $[Ce(IV)]/[Ce(III)]$ ratio rose to a maximum, and another (part II) in which this ratio gradually declined until full-blown oscillations suddenly began. The oscillations had the same frequency and amplitude as those observed in the absence of iodide. The lengths of the total induction period and of part I increased as $[I^-]_0$ was raised, while the duration of part II decreased slightly with increasing $[I^-]_0$ in the low-iodide concentration range. In general, a given amount of added iodide resulted in less inhibition than the same amount of added chloride. Typical behavior is illustrated in Figures 1 and 2, while numerical results are given in Table I.

C. Intermediate Iodide. 10^{-3} M $< [I^-]_0 < 3 \times 10^{-3}$ M. This regime is characterized by a most surprising phenomenon, the appearance of what we shall call "small oscillations". At the lower end of the concentration range, these oscillations begin almost immediately. As can be seen in Figure 3, the small oscillations are qualitatively different in nature from the "nor-
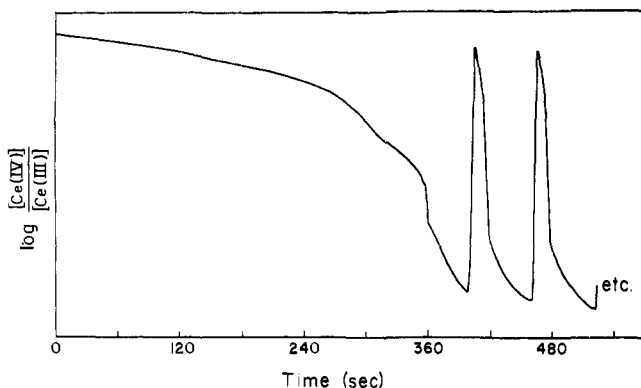
Figure 1. Potentiometric traces (without absolute calibration, arbitrary scale) showing oscillations in the "ordinary" BZ reaction. Initial concentrations: total $[Ce] = 1.0 \times 10^{-3}$ M, $[BrO_3^-] = 4.0 \times 10^{-2}$ M, $[CH_2(COOH)_2] = 1.0 \times 10^{-1}$ M, $[H_2SO_4] = 1.5$ M.
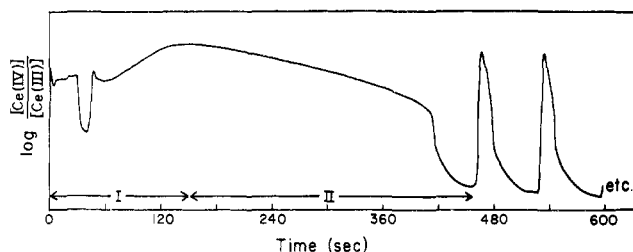
mal" BZ oscillations. The small oscillations grow continuously in amplitude, starting from essentially zero. In this sense, the onset of oscillations resembles the smooth change, analogous to a second-order phase transition, observed by Turner et al.[12] in their modified BZ system, rather than the abrupt or first-order transition to the ordinary BZ oscillations. The period of the small oscillations, like their amplitude, is considerably smaller than that of the normal oscillations, but grows at a relatively rapid rate as the oscillations continue. The small oscillations end abruptly as seen in Figure 3, and a second induction period which resembles part II of the chloride-modified induction period in both shape and duration ensues. This period concludes with the sudden initiation of the "normal" BZ oscillations. Both the small and the normal oscillations may be monitored with a platinum redox electrode or with bromide or iodide (vide infra) specific ion electrodes.

As $[I^-]_0$ is increased, the number of small oscillations that occur before their abrupt halt increases and the length of the second induction period decreases. We also observe (Table I) the appearance of an induction period preceding the small oscillations. As $[I^-]_0$ is increased still further, this period grows until it eventually exceeds the halide free induction period.

D. High Iodide. 3×10^{-3} M $< [I^-]_0 < 6 \times 10^{-3}$ M. When $[I^-]_0$ reaches 3×10^{-3} M, the second induction period disappears, and the small oscillations grow directly into the normal oscillations as shown in Figure 4. In this concentration range, the distinction between small and normal oscillations is somewhat vague. The induction period is significantly greater than in the low iodide range (see Table I), and the $[Ce(IV)]/[Ce(III)]$ ratio during this period is quite low. At the high end of this concentration range, the oscillations begin abruptly, grow somewhat in amplitude, and resemble the normal oscillations in shape.

E. Very High Iodide. $[I^-]_0 > 6 \times 10^{-3}$ M. When the initial iodide concentration exceeds 6×10^{-3} M, the $[Ce(IV)]/[Ce(III)]$ ratio remains at a low level, and no oscillations are found, even after many hours.

F. Fate of the Added Iodide. Consideration of the possible reactions of iodide in this system suggested that iodate was the likely final product for most if not all of the added iodide. Most of the standard tests for iodate are unsatisfactory in this system because of the presence of a variety of interfering ions, particularly bromate. However, a modification of the method of Hashmi et al.,[13] described in the Experimental Section, was found to be applicable. The test unequivocally shows the presence of iodate at the conclusion of an iodide-supplemented BZ reaction. Within a rather large range of uncertainty, the test also shows that the oxidation of iodide to iodate is virtually quantitative, with the $[IO_3^-]$ found being equal to $95 \pm 30\%$ of the initial $[I^-]$.

Figure 2. Inhibition of oscillations at low $[I^-]_0$. All initial concentrations as in Figure 1, except $[I^-] = 8.0 \times 10^{-4}$ M. Note division of the induction period into parts I and II, as in chloride inhibition.[10]
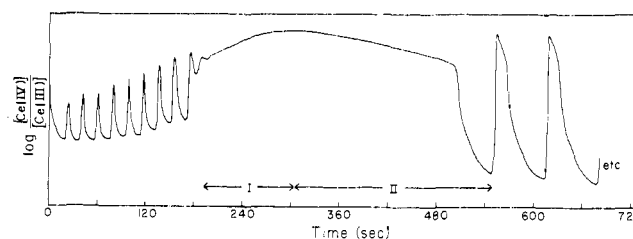

Figure 3. Appearance of small oscillations at intermediate $[I^-]_0$. All initial concentrations as in Figure 1, except $[I^-] = 1.3 \times 10^{-3}$ M.

G. Effects of Added Iodate. Chlorate, the proposed end product of added chloride in the BZ reaction, is inert in the system.[10] We find, in contrast, that iodate ion acts as a mild inhibitor of oscillations. In general, whenever $[I^-]_0$ is in one of the inhibitory ranges, addition of equal amounts of iodate and iodide results in a greater lengthening of the induction period in the latter case. The oscillations which take place after iodate inhibition are always normal in appearance, begin full blown, and are constant in amplitude and frequency. The induction period resembles period II of the chloride-inhibited reaction.

H. Effects of Added Glyoxylic Acid. In our discussion of the mechanism of the small oscillations, we postulate a key role for glyoxylic acid (GOA), OCH–COOH. Our interest in this species was prompted by the "stunning effect" of GOA on the BZ reaction noted by Field.[2] Since the implications of this effect are indeed dramatic for our interpretation of the iodide-induced behavior, we present our observations in some detail. Figure 5 shows the behavior observed when GOA is added initially to the BZ reaction. Small oscillations begin after a shortened induction period, increase in period and amplitude, and finally die out as the amplitude decreases in a continuous fashion. No normal oscillations are seen. If a similar amount of GOA is added to a BZ system already in oscillation, oscillations resembling those in Figure 5 "take over" and persist until the system gradually subsides into monotonic behavior. If very large amounts of GOA ($[GOA]_0 > 0.1$ M) are added to the system, then oscillation is inhibited or even suppressed completely.

An even more surprising result, not previously reported, is shown in Figure 6. Within a relatively narrow range of GOA concentrations (~ 0.02 to ~ 0.8 M), glyoxylic acid may be substituted for malonic acid and small oscillations are obtained, *with no malonic acid whatsoever*. This observation is unexpected because GOA does not have the acidic methylenic hydrogen attached to two electron-withdrawing groups thought to be necessary for its function as the organic component of a BZ-like system. We suggest below elements of a mechanism for the GOA-driven oscillations which involve key features fundamentally different from the BZ oscillations. Of considerable importance to our later arguments is the fact that in the absence of malonic acid, the GOA-driven small oscillations persist only briefly and stop abruptly, at a point at which the
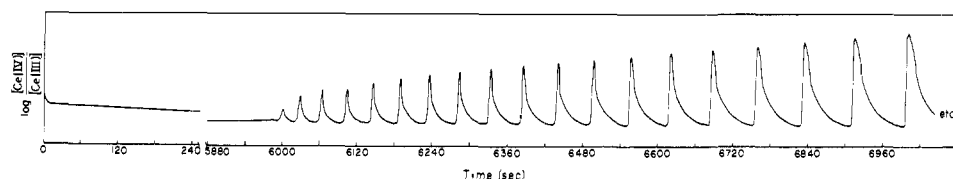
Figure 4. Oscillations at high $[I^-]_0$. The induction period between the small and normal oscillations has disappeared. All initial concentrations as in Figure 1, except $[I^-] = 3.8 \times 10^{-3}$ M.
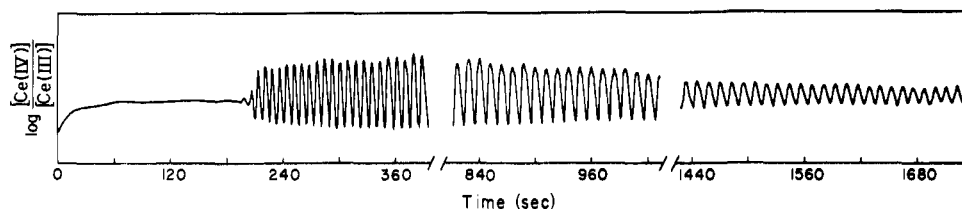
Figure 5. Glyoxylic acid driven oscillations in the BZ reaction. All initial concentrations as in Figure 1, except [GOA] = 0.068 M.

Time (sec)
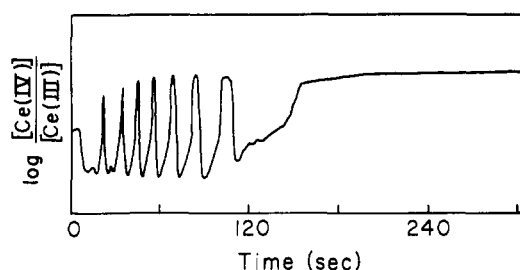
Figure 6. Oscillations when glyoxylic acid is substituted for malonic acid in the BZ system. Note resemblance to the small oscillations in Figure 3. All initial concentrations as in Figure 1, except $[CH_2(COOH)_2] = 0$, [GOA] = 0.45 M.

[Ce(IV)]/[Ce(III)] ratio is high (cf. Figures 3 and 6). GOA concentrations above or below the limits noted above give rise to only a single maximum in the cerium ratio followed by monotonic approach to equilibrium.

I. Effects of Added Iodine. Experiments were performed in which a few crystals of solid I_2 were added to the initial BZ mixture. A few small oscillations were obtained, resembling those in Figure 3. A second induction period was then followed by normal oscillations which ceased after only a few cycles, in contrast to the large number of normal oscillations seen in halide-free or iodide-containing BZ systems. Excluding light from these experiments had no effect on the observed behavior.

Experimental Section

Materials. Ceric ammonium nitrate, malonic acid, potassium bromate, sodium iodate, sodium iodide, iodine, sulfuric acid, and glyoxylic acid were of the highest purity available from commercial sources, as were the reagents used in the iodate test described below.

Apparatus and Procedures. The [Ce(IV)]/[Ce(III)] ratio was monitored by recording the potential between a platinum electrode and a double junction reference electrode constructed by immersing an Ag|AgCl reference electrode in a Fisher reference electrode sleeve filled with a saturated solution of KNO_3 in 1.5 M H_2SO_4, which was in contact with the reaction mixture. In some experiments the bromide or iodide concentration was monitored with specific ion bromide- (Orion 94-35A) or iodide- (Orion 94-53A) sensitive electrodes.

Cerium, malonic acid, and bromate solutions were prepared in 1.5 M sulfuric acid. Except where noted, the reagents were added in the order cerium, iodide (iodate, iodine, GOA), malonic acid, bromate. The iodide was prepared in distilled water, ultrasonicated to remove dissolved oxygen, and stored under argon to prevent oxidation, though this procedure appeared to have little if any effect on our observations. The iodide (iodate, GOA) was delivered from a 1-mL graduated hy-

podermic syringe. Mixing time was estimated to be 1 s. All measurements were carried out in a thermostated constant temperature bath at 25 °C.

Iodate Test. A spectrophotometric test for iodate in the presence of bromate based on the formation of a pink formazan has been developed.[13] To 1 mL of solution was added enough concentrated ammonium hydroxide to adjust the pH to about 9. One milliliter each of 0.2% solutions of 2,3,5-triphenyl-2H-tetrazolium chloride and isonicotinic acid hydrazide were then added. The pH was adjusted to 1.6–1.7 with 0.1 N hydrochloric acid, and distilled water was added to bring the volume to 10 mL. Ten minutes later the volume was adjusted to 50 mL by adding methanol and shaking. After another 10 min, the solution was filtered through sintered glass to eliminate cloudiness, and the absorbance at 480 nm was read on a Bausch and Lomb Spectronic 20 spectrophotometer. An oscillating solution with no added iodide or iodate exhibited negligible absorbance after undergoing the above procedure. Tests of oscillating solutions containing initially added iodate of varying concentrations followed Beer's law and were used as a standard. The tests were carried out at 25 °C.

Discussion

A. General Mechanistic Considerations. As so beautifully shown by FKN,[9] the BZ system without added iodide is an extremely complex one, involving an almost bewildering array of inorganic and organic intermediates. Nevertheless, the FKN mechanism, which has now been supported by numerical integration studies,[14] accounts for nearly all observations made on the system. We therefore adopt the essential features of the FKN mechanism as a starting point for our mechanistic discussions of the effects of iodide on the BZ system. Some reference will also be made to the mechanism of chloride inhibition, though as we proceeded in this work, we were constantly surprised to discover how dissimilar the actions of iodide and chloride are in this system.

The main observations which we shall seek to explain are the inhibition of oscillations at low $[I^-]_0$, the induction of small oscillations and their qualitative behavior (duration, increasing amplitude and period) in the intermediate iodide range, and the return to inhibitory behavior and ultimate suppression of oscillations when large amounts of iodide are added.

B. Inhibition of Oscillations at Low $[I^-]_0$. When the amount of iodide added is less than the total cerium content of the solution, the principal reaction is oxidation of I^- to I_2 by Ce(IV):

$$Ce(IV) + I^- \rightarrow Ce(III) + \tfrac{1}{2}I_2 \qquad (1)$$
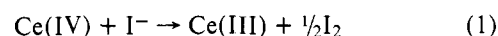
Reaction 1 is extremely rapid and goes essentially to completion, having a potential $E_1^0 = 0.905$ V.[9,15] This reaction has

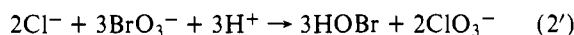been used as the basis of a procedure for the standardization of Ce(IV) solutions.[16]

When chloride is added to the BZ system, cerium is also reduced, thereby inhibiting oscillations. Chloride, however, does not reduce the cerium directly as in reaction 1, but initiates a sequence of reactions[10] involving bromate and several oxybromine intermediates, with the overall stoichiometry of the reaction
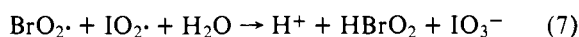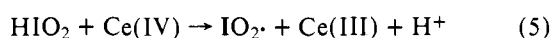
$$Cl^- + 2BrO_3^- + H^+ + Ce(IV) \rightarrow HOBr$$
$$+ BrO_2 + ClO_3^- + Ce(III) \quad (2)$$
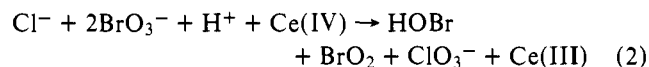
which, when combined with reactions R4 and R6 of the halide-free system[9]

$$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ \quad (R4)$$

$$Ce(III) + BrO_2 + H^+ \rightarrow Ce(IV) + HBrO_2 \quad (R6)$$
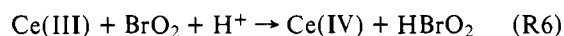
yields the net reaction $(2') = 2 \times (2) + (R4) + 2 \times (R6)$:

$$2Cl^- + 3BrO_3^- + 3H^+ \rightarrow 3HOBr + 2ClO_3^- \quad (2')$$

The iodide analogue of eq 2 is thermodynamically feasible. Indeed, each of the constituent reactions has a potential[9,10,15,17] which is at least as positive as that of the counterpart reaction in the chloride scheme[10] which leads to eq 2. However, the pathway represented by eq 3–7 is not kinetically competitive with the direct reduction eq 1.

$$I^- + HBrO_2 + H^+ \rightarrow HOBr + HOI \quad (3)$$

$$HOI + BrO_3^- + H^+ \rightarrow HBrO_2 + HIO_2 \quad (4)$$

$$HIO_2 + Ce(IV) \rightarrow IO_2\cdot + Ce(III) + H^+ \quad (5)$$

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O \quad (6)$$

$$BrO_2\cdot + IO_2\cdot + H_2O \rightarrow H^+ + HBrO_2 + IO_3^- \quad (7)$$

Although the mechanism of reduction of cerium differs in the two cases, the inhibitory effects produced by low concentrations of iodide and chloride are strikingly similar. In both cases, the induction period may be separated into two components: part I, in which the cerium is being reoxidized by oxybromine species, and part II, during which sufficient bromomalonic acid is produced to bring about the start of oscillation. With both iodide and chloride, increasing the halide concentration lengthens part I, since more cerium is reduced initially, so more time is required to reoxidize it. Part II, on the other hand, decreases in length as more halide is added, because during the longer part I more bromomalonic acid has time to build up, so less need be produced in part II.

The observation that a given iodide concentration gives less inhibition than the same amount of added chloride (see Table I) has two major causes. First, iodide has other possible fates in addition to reaction 1. In particular, as we discuss below, some of the iodide will be oxidized to iodate by reaction with bromate:

$$I^- + BrO_3^- \rightarrow IO_3^- + Br^- \quad E_8^0 = 0.36 \text{ V} \quad (8)$$
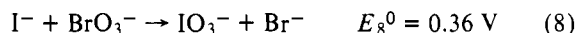
The corresponding reaction of chloride with bromate is far less favorable, having a potential of −0.01 V. Thus the "effective" iodide concentration is somewhat less than the total added, while all the chloride acts to reduce cerium. A second, and probably more important, factor is that iodide catalyzes the production of glyoxylic acid in the BZ system. This reaction is crucial to our understanding of the small oscillations. It is also of interest here, since we find that while bromate alone cannot oxidize Ce(III) in any reasonable period of time, this oxidation is quite rapid in the presence of GOA. Hence the small amounts of GOA produced speed the reoxidation of the cerium, thereby counteracting in part the inhibition due to the reduction of Ce(IV) by iodide.

C. Induction of Small Oscillations at Intermediate $[I^-]_0$. The I_2 formed in reaction 2 can be further oxidized by bromate, ultimately forming iodate. Alternatively, and more significantly, it can bring about the iodination of malonic acid. Leopold and Haim[18] have studied the formation of iodomalonic acid from malonic acid under slightly less acidic conditions than employed here ($[H^+] = (2.09–95.0) \times 10^{-3}$ M). They obtain a complex rate law, with terms proportional both to $[I_2]$ and to $[I_3^-]$. Under the conditions of our experiments the most significant terms in the rate of iodination are probably

$$k_2[I_2][CH_2(COOH)_2]$$
$$+ k_5[H^+][I_3^-][CH_2(COOH)_2] \quad (9)$$
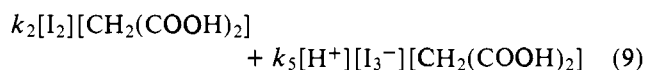
with $k_2 = (2.41 \pm 0.15) \times 10^1$ and $k_5 = (3.20 \pm 0.56) \times 10^1$ M^{-2} s^{-1}. If the amount of I_2 produced by reaction 1 is of the same order of magnitude as the total cerium in the solution, i.e., $[I_2] + [I_3^-] \sim 10^{-3}–10^{-4}$ M, then, according to eq 9, significant concentrations on the order of $10^{-5}–10^{-6}$ M of iodomalonic acid should accumulate in our system in a matter of seconds.
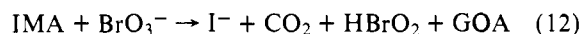
It will suffice to represent the iodination of malonic acid by Leopold and Haim's[18] expression, eq 10, though this may not be the complete stoichiometry.
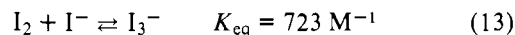
$$CH_2(COOH)_2 + I_3^- \rightarrow CHI(COOH)_2 + 2I^- + H^+ \quad (10)$$
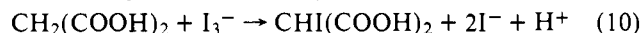
We postulate that the iodomalonic acid (IMA) thus formed is now oxidized by bromate to GOA via eq 11 or a similar scheme.

More compactly,

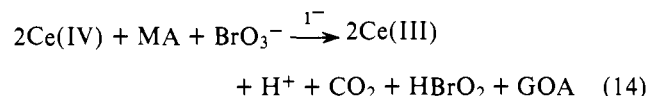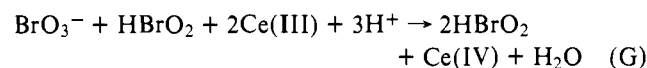$$IMA + BrO_3^- \rightarrow I^- + CO_2 + HBrO_2 + GOA \quad (12)$$
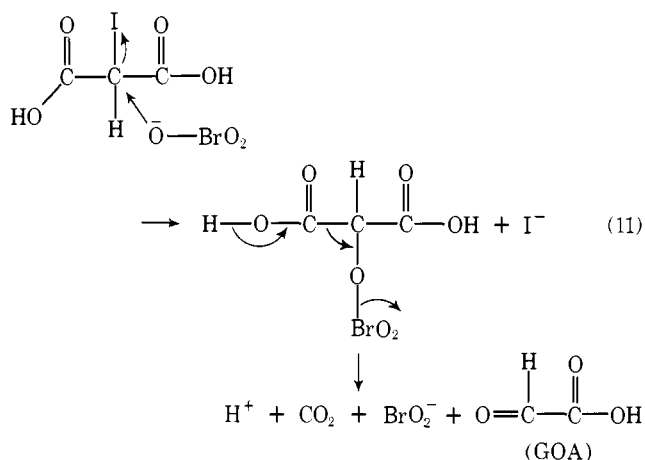
Reaction 12 is the key step in the induction of the small oscillations. If we add the rapid equilibrium

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K_{eq} = 723 \text{ M}^{-1} \quad (13)$$

we obtain reaction $14 = 2 \times (1) + (10) + (11) + (13)$:

$$2Ce(IV) + MA + BrO_3^- \xrightarrow{I^-} 2Ce(III)$$
$$+ H^+ + CO_2 + HBrO_2 + GOA \quad (14)$$

where MA = malonic acid, $CH_2(COOH)_2$. On combining eq 14 with the autocatalytic production of $HBrO_2$[9]

$$BrO_3^- + HBrO_2 + 2Ce(III) + 3H^+ \rightarrow 2HBrO_2$$
$$+ Ce(IV) + H_2O \quad (G)$$

and the disproportionation of $HBrO_2$ in eq R4, we have the overall stoichiometry

$$BrO_3^- + MA + H^+$$
$$\rightarrow HOBr + CO_2 + GOA + H_2O \quad (14')$$
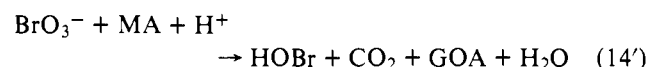
Thus the iodide is regenerated, and eq 14 represents the iodide-catalyzed oxidation of MA to GOA. Note that the molar ratio of GOA produced to Ce(IV) utilized[19] is 0.5. Note also that, as is mentioned in section B, the $HBrO_2$ and GOA produced are capable of participating in reactions to reoxidize the cerous ion. Further support for the above scheme is provided by the fact that solid I_2 also induces small oscillations.

Since eq 12 plays a key role in the proposed mechanism, we attempted to study this reaction more directly. Unfortunately, however, while diiodomalonic acid was synthesized some 75 years ago,[20] no synthetic route to the monoiodinated species appears to exist in the literature. Numerous attempts on our part to synthesize IMA by a variety of methods were unsuccessful owing to the susceptibility of this species to both diiodination and decarboxylation.

The small oscillations, in our view, are GOA-driven oscillations essentially identical in nature with those found in the system shown in Figure 6. Comparing Figures 3 and 6, we see that both are characterized by continuous, almost immediate growth of oscillations with increasing period and amplitude. Both sets of oscillations end abruptly with the cerium in a relatively oxidized state. While we have no direct experimental evidence for the presence of GOA, the above results as well as Field's experiments[21] which show that of the important organic intermediates in the BZ system[22] only GOA produces dramatic effects when added initially to the BZ reaction tend to support our identification of GOA as the key species.

We attribute the abrupt cessation of the small oscillations to the exhaustion of the GOA before sufficient bromomalonic acid (BrMA) has built up to sustain normal oscillations. Thus the second induction period resembles period II of the chloride inhibition, i.e., the period characterized by the generation of BrMA. This period decreases in length as we raise $[I^-]_0$ because a longer time elapses before the small oscillations, so more BrMA has accumulated. When enough iodide has been added initially, so much BrMA builds up before the end of small oscillations that when the GOA falls below its critical level, no break in the oscillations occurs, and normal oscillations begin immediately. Recall, however (Figure 5), that in the presence of adequate amounts of both GOA and BrMA, the GOA-driven oscillations are dominant.

In the system containing both MA and GOA, the small oscillations are maintained for a considerable time in spite of the finite amount of GOA added because of the existence of a second pathway, present in the iodide-free BZ system, which produces GOA, though considerably more slowly than reaction 14. This pathway, which appears to involve such radical intermediates as hydroxymalonyl and tartronyl radicals, is discussed by Jwo and Noyes.[22] The relatively short duration of the small oscillations in the presence of iodide suggests that this pathway may be disrupted, perhaps by iodine atoms or by $IO_2\cdot$ radicals generated in reaction 5.

As the amount of added iodide is increased, several effects are observed. The appearance of an induction period before the small oscillations may be attributed to the reduction of a greater amount of cerium via eq 1. Any free I^- remaining after reaction 1 has depleted the Ce(IV) should be effectively scavenged by bromate. Barton[23] has found a rate expression

$$-d[BrO_3^-]/dt = k_{15}[H^+]^2[BrO_3^-][I^-] \qquad (15)$$

with $k_{15} = 50.3$ M^{-3} s^{-1}. Iodide which reacts in this manner apparently reaches the level of iodate relatively rapidly (though perhaps a stoichiometry such as

$$2I^- + 3BrO_3^- + 3H^+ \rightarrow 2IO_3^- + 3HOBr$$
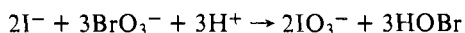
seems more likely than the simple eq 8). Interchanging the normal order of adding the reagents by mixing the bromate and iodide before adding the cerium eliminated the small oscilla-

tions. The induction period found in these experiments was lengthened by an amount roughly equal to that caused by adding an amount of IO_3^- equal to the added iodide. Thus reaction 8 or its equivalent is extremely rapid in our system, going essentially to completion in the few seconds required to add another reagent.

Although free iodide will not persist in the system for long, reactions 10–12 do provide a way of maintaining a low pseudo-steady-state level of I^-. This mechanism may also help to keep the cerium in a reduced state during the initial induction period. The increased number of small oscillations at higher $[I^-]_0$ arises from the greater amount of GOA produced and the resulting longer time required to consume it.

It might seem that once the induction period preceding the small oscillations exceeds the normal BZ induction period, no second induction period should be required, since an amount of BrMA adequate to sustain oscillation should have been produced by the end of the small oscillations. The persistence of the second induction period, even after initial induction periods of considerable length, suggests that BrMA is produced more slowly in the presence than in the absence of iodide. The most likely explanation for this effect is that iodide competes for some key species in the production of BrMA, probably bromous acid via reaction 3.

Finally, the question arises whether the iodide concentration oscillates or changes in a monotonic fashion during the small oscillations. The small oscillations observed on the iodide and bromide electrodes are identical in shape. The free iodide level is likely to be exceedingly low by virtue of its reactions with Ce(IV) and BrO_3^-. Also, the envelope of the small oscillations observed on both halide-sensitive electrodes has a slight upward trend. We therefore conclude that interference from bromide makes it impossible to detect the iodide level in the system with the iodide electrode after the initial instant. This observation implies that[24]

$$[I^-] \leq 2 \times 10^{-4}[Br^-] \qquad (16)$$

Thus the iodide concentration may or may not be oscillating at the very low levels implied by eq 16.

D. Inhibition of Oscillations at High $[I^-]_0$. Initial iodide concentrations above 3×10^{-3} M result in long induction periods and oscillations which grow in amplitude until they become "normal". These iodide levels are considerably above the chloride concentrations that suffice to permanently prevent oscillation. The inhibition at high $[I^-]_0$ cannot be attributed to the formation of large amounts of iodate, though this undoubtedly occurs. Iodate inhibition is characterized by a high Ce(IV) level resembling period II, while in the induction period observed at high $[I^-]_0$ the ceric/cerous ratio is quite low.

We suggest that at high $[I^-]_0$, relatively large amounts of IMA are formed and provide a pseudobuffering mechanism which maintains a relatively stable (though quite low, probably 10^{-8} M or less) level of $[I^-]$ for a fairly long time via eq 10–12. This level is apparently sufficient to maintain most of the cerium in the reduced state. While this claim may seem surprising in view of the low value likely for the pseudo-steady-state iodide concentration, we recall that the chloride level produced in a BZ solution by contact with a salt bridge is sufficient to suppress oscillations indefinitely.[9]

When very high amounts of iodide are added initially, the time required to consume the iodide and its products is sufficiently long that other processes have time to carry the system relatively close to equilibrium. Thus even though the system may finally be "ready" to oscillate, nonmonotonic behavior may no longer be thermodynamically feasible[5] because the departure from equilibrium is insufficient.

E. Iodate Inhibition. We have observed above that iodate ion is a mild inhibitor of oscillations over a wide range of concentrations. We have little light to shed on the mechanism of this

inhibition, though we can say definitely that it must be different from that of either chloride or iodide inhibition, since the cerium is maintained in an oxidized rather than a reduced state. This observation follows almost trivially, of course, from consideration of the relevant oxidation potentials.

F. Glyoxylic Acid Oscillations. We have no definitive mechanism to propose for the oscillations found in systems with GOA and no MA. We should like to suggest, however, one attractive aspect for incorporation into future mechanistic efforts. The apparent impossibility of generating BrMA in this system and the lack of an acidic methylenic hydrogen easily replaceable by bromine make the GOA-driven oscillations puzzling.

It seems likely to us that the organic bromine-containing species in the GOA system is dibromoacetic acid[25] (DBA) produced by bromination of the *aldehyde* group. We propose that DBA is produced by a mechanism which starts with attack of Br_3^- on GOA. A possible stoichiometry for such a reaction is

$$H^+ + Br_3^- + CHO(COOH) \rightarrow CHBr_2COOH + HOBr$$
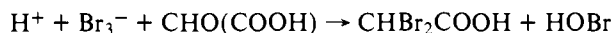
The availability of tribromide ion in this solution seems assured by the fact that the GOA reaction produces a noticeable orange color and a strong, characteristic odor of bromine. DBA seems an attractive candidate for the BrMA analogue since (a) it should be a relatively labile source of bromide ion; (b) it is found, though in rather small quantities, as a product in the normal BZ reaction[26] in which glyoxylic acid is thought to be present in low concentration;[22] and (c) when added initially to a BZ solution it is considerably more effective than BrMA in reducing the length of the induction period.[11]

The details of the GOA-driven oscillation, including its continuous initiation and abrupt cessation, and its growing period and amplitude are beyond the scope of this work.

G. Other Observations. Adding a small amount of GOA to an iodide-containing system during the small oscillation increases the number of small oscillations seen and decreases their period. This observation supports our suggestion that the termination of small oscillations is associated with the exhaustion of the GOA produced by reaction 14.

An initial iodide concentration of 1.75×10^{-3} M gives an induction period preceding the small oscillations equal in duration ($\sim$390 s) to the induction period which precedes normal oscillations in the unperturbed BZ system. On carrying out these reactions at 40 °C, we observed that the induction period of the iodide-containing system decreased to 45 s while the iodide-free system had an induction period of 135 s at the elevated temperature. These results suggest that the activation energy for the process which characterizes the iodide induction period is significantly greater than that for the halide-free induction period.

Conclusion

We believe that the mechanism proposed here, while certainly not complete, does contain the essence of the fascinating

and surprising variety of phenomena which occur in iodide-containing BZ systems. Our methods have been very much in the spirit of the Noyes–Holmes[27] approach to mechanistic studies, and we feel that, having eliminated the impossible, we are now left with a true picture, however improbable it may have seemed at the beginning of these investigations.

Clearly, further studies of this and related systems would be well worthwhile. In particular, a more thorough exploration of the glyoxylic acid "small" oscillations should prove quite revealing. This investigation has also shown that the use of inorganic perturbations may provide the simplest way to probe the nature of the organic reactions possible in a complex system.

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