Effects of Chloride Ion on Oscillations in the Bromate–Cerium–Malonic Acid System

Steven S. Jacobs and Irving R. Epstein*[1]

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. *Received July 12, 1975*

Abstract: It has been found that the reported permanent inhibition of concentration oscillations by trace amounts of chloride ion added to the bromate-cerium-malonic acid system is of only temporary duration. The effects of adding chloride to the system under a variety of conditions are reported, and a mechanism to explain these effects is proposed. The chloride inhibition mechanism involves the oxidation of chloride to chlorous acid, which then reduces Ce(IV) to Ce(III), preventing oscillation. The oscillations resume when the chlorous acid has been completely oxidized to chlorate. The overall reaction is $2Cl^- + 3BrO_3^- + 3H^+ \rightarrow 3HOBr + 2ClO_3^-$.

Interest in chemical reactions in which the concentrations of one or more species may oscillate in time has grown markedly in recent years.[2] Such systems raise many fascinating kinetic and thermodynamic questions[3] and provide suggestive models for a number of biological processes.[4]

Perhaps the most thoroughly studied oscillating chemical reaction has been the cerium-catalyzed oxidation of certain dicarboxylic acids by bromate ion in sulfuric acid solution, which was discovered by Belousov.[5] In an early study, Zhabotinskii[6] reported that addition of "small amounts" of potassium chloride caused permanent suppression of oscillations in the Belousov reaction. Field, Körös, and Noyes,[7] in presenting a detailed mechanism for the oscillation, confirm Zhabotinskii's observation, noting that, "the oscillating reaction can be completely inhibited by traces of chloride ion. We discovered this effect, which has also been noted by Zhabotinskii, when we tried to do potentiometric measurements with a potassium chloride salt bridge. No explanation has been developed." Janjic, Stroot, and Burger[8] report that chloride completely inhibits oscillations in a Belousov-like system in which the dicarboxylic acid is replaced by acetyl acetone.

In this paper, we propose a mechanistic explanation for the effects of added chloride ion on the Belousov reaction. Our mechanism is based upon a series of experiments which shows, contrary to the generally accepted belief, that addition of chloride in concentrations comparable to those of some of the major reactants in the system *does not permanently* suppress the oscillations. Oscillations do return after a period whose duration depends upon the amount of chloride added, the stage of the reaction at which it is introduced, and the initial concentration of cerium. The mechanism derived from these experiments is consistent with that of Field, Körös, and Noyes[7] for the unperturbed reaction, and may offer an approach to determining some of the rate constants in that mechanism.

The Belousov Reaction in the Absence of Chloride

Field, Körös, and Noyes[7,9] have proposed, and have offered considerable experimental justification for, a detailed mechanism to account for the oscillatory behavior of the Belousov reaction. The principal features and some of the relevant rate constants of that mechanism are summarized in Schemes I and II for the reaction involving malonic acid as the organic species.

Scheme I is the reduction of bromate by bromide to bromine, followed by the bromination of malonic acid. Steps R1–R3 are all two-electron reductions; reaction R3 is rate determining.

Scheme I

$$Br^- + BrO_3^- + 2H^+ \rightarrow HBrO_2 + HOBr \qquad k_3 = 2.1\ M^{-3}\,s^{-1} \qquad (R3)$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr \qquad k_2 = 2 \times 10^9\ M^{-2}\,s^{-1} \qquad (R2)$$

$$3(Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O) \qquad k_1 = 1.6 \times 10^{10}\ M^{-2}\,s^{-1} \qquad (R1)$$

$$3(Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+) \qquad (R8)$$

$$2Br^- + BrO_3^- + 3H^+ + 3CH_2(COOH)_2 \rightarrow 3BrCH(COOH)_2 + 3H_2O \qquad (A)$$

Scheme II

$$2(BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O) \qquad k_5 = 1.0 \times 10^4\ M^{-2}\,s^{-1} \qquad (R5)$$

$$4(Ce(III) + BrO_2\cdot + H^+ \rightarrow Ce(IV) + HBrO_2) \qquad (R6)$$

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

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

$$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O \qquad (R1)$$

$$Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+ \qquad (R8)$$

$$BrO_3^- + 4Ce(III) + CH_2(COOH)_2 + 5H^+ \rightarrow 4Ce(IV) + BrCH(COOH)_2 + 3H_2O \qquad (B)$$

Also

$$4Ce(IV) + BrCH(COOH)_2 + 2H_2O \rightarrow 4Ce(III) + HCOOH + 2CO_2 + 5H^+ + Br^- \qquad (R10)$$

Scheme II consists of a series of one-electron transfers whereby Ce(III) is oxidized to Ce(IV). An indefinite buildup of the $HBrO_2$ produced autocatalytically in (G) is prevented by its second-order disproportionation in step R4.

A crucial feature of the mechanism is the competition between bromate and bromide for $HBrO_2$ in steps R2 and R5, respectively. Since $[BrO_3^-] \gg [Br^-]$, $[HBrO_2]$, the bromate concentration is effectively constant, and the fate of the bromous acid is determined by the instantaneous level of $[Br^-]$. There is a critical bromide concentration which determines whether (R2) or (R5) is dominant:

$$[Br^-]_{crit} = (k_5/k_2)[BrO_3^-] \qquad (1)$$

If $[Br^-] > [Br^-]_{crit}$, then (R2) and Scheme I determine the behavior of the system. If $[Br^-] < [Br^-]_{crit}$, then (R5) and Scheme II are dominant.

To see how oscillations occur, we enter the cycle when

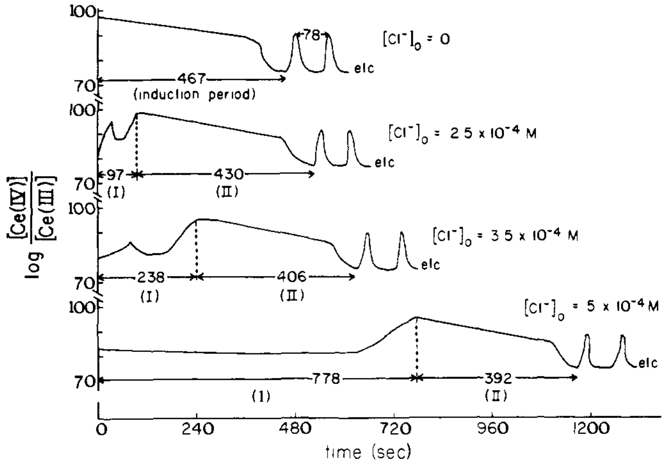

Figure 1. Potentiometric traces (without absolute calibration, arbitrary scale) for reactions with various amounts of KCl added to initial reaction mixture. Initial concentrations of other species are given in Table 1.

there is sufficient bromide to favor Scheme I. Bromide is being consumed in (R2), and eventually its concentration drops below the critical level. At this point Scheme II is turned on with the accompanying autocatalytic production of bromous acid, which consumes the remaining bromide. The Ce(IV) produced in Scheme II now drives step R10, in which Ce(IV) is reduced and bromide is regenerated. The bromide level soon rises above $[Br^-]_{crit}$, and Scheme I is switched on again. The cycle is thus completed.

An initial induction period, during which the concentrations of bromide and bromomalonic acid are built up, generally precedes the oscillatory behavior described above. The induction period can be shortened or even suppressed entirely by the addition of bromomalonic acid to the initial reaction mixture.

Experimental Results. The Return of Oscillations

A series of experiments was carried out in which chloride was present as a constituent of the original reaction mixture. The initial concentrations of the other species are given in Table I and the results are shown in Figure 1. In the absence of chloride the system exhibited an induction period of 467 ± 10 s, with an oscillation period of 78 ± 1.5 s.

The effect of initial added chloride was to lengthen the preoscillation period, and to divide that period into two parts. The length of part I varied significantly with the chloride concentration, while part II was relatively invariant. The general characteristics of part II resemble those of the unperturbed induction period, though part II is always somewhat shorter in length.

It was found that for $[Cl^-]_0 \leq 10^{-4}$ M, no observable inhibition was produced. For $[Cl^-]_0 \gtrsim 2 \times 10^{-3}$ M, oscillatory behavior was totally suppressed. In all cases in which oscillation did occur, the oscillation period after the inhibitory stage was identical with that of the unperturbed system. Also of interest are the variations in the shape of part I as $[Cl^-]_0$ increases.

Addition of chloride at later stages in the reaction produces similar results. The Ce(IV) concentration drops and oscillations cease, then return after an inhibition period, the length of which depends upon both the amount of chloride and the stage of the reaction at which it is added. The system appears somewhat more sensitive to chloride addition after the reaction has started. Relative to the experiments in which chloride is added initially, smaller amounts of chloride are now required either to produce inhibition or to suppress oscillation completely.

Table I. Initial Concentrations of Species Used in the Belousov Reaction

$[Ce(NH_4)_2(NO_3)_6]$	1.0×10^{-3} M
$[KBrO_3]$	4.0×10^{-2} M
$[CH_2(COOH)_2]$	1.0×10^{-1} M
$[H_2SO_4]$	1.5 M

When the initial chloride addition experiments are carried out at higher total cerium concentrations, the length of part I decreases roughly in proportion to the increase in $[Ce]_0$, while the length of part II is slightly less than that of a choride-free oscillating system with the same (increased) value of $[Ce]_0$.

Mechanism of Chloride Inhibition

In light of the above observations and further experiments noted below, we propose the following mechanism for the action of added chloride ion in the cerium-bromate-malonic acid system. Cerium and chlorine species potentials are taken from Latimer[10] while oxybromine species potentials are from the work of Field, Körös, and Noyes.[7]

$$Cl^- + HBrO_2 + H^+ \xrightarrow{k_{I1}} HOBr + HOCl$$

$$E_1^0 = 0.25 \text{ V} \qquad (I1)$$

In this first step, chloride successfully competes with both bromide and bromate for the bromous acid. The chloride concentrations used in this work imply that $k_{I1} \sim 10^7\text{-}10^8$ M^{-2} s^{-1}, a not unreasonable value in view of the fact that the rate constant for the analogous reaction involving bromide, (R2), is on the order of 10^9 M^{-2} s^{-1}. The bromous acid will be principally consumed by chloride as long as

$$[Cl^-] > [Cl^-]_{crit} = (k_2/k_{I1})[Br^-] + (k_5/k_{I1})[BrO_3^-] \qquad (2)$$

Also note that (I1) is thermodynamically favored.

The chlorine species is now further oxidized by another two-electron process.

$$HOCl + BrO_3^- + H^+ \xrightarrow{k_{I2}} HBrO_2 + HClO_2$$

$$E_2^0 = -0.40 \text{ V} \qquad (I2)$$

While there appears to be no reference to this reaction in the literature, transfer of an oxygen atom from the larger to the smaller halogen should have no prohibitive steric or energy barriers. The large concentrations of BrO_3^- and H^+ and the consumption of $HBrO_2$ by steps I1, R2, and R5 and of $HClO_2$ by step I3 should help to drive the reaction to the right in spite of the negative E^0 value. At first glance it might seem that bromous acid would be a more plausible oxidant for the hypochlorous acid than bromate. However, the full reaction scheme would then involve the overall consumption of bromous acid. Since bromous acid is being produced only by the slow step R3, the amount required to fully consume the hypochlorous acid could not possibly be generated in the time scale of the inhibition period. Finally, note that in (I2) the bromous acid intermediate is regenerated, so that the $HBrO_2$ required in (I1) need not be produced by step R3.

$$HClO_2 + Ce(IV) \xrightarrow{k_{I3}} ClO_2\cdot + Ce(III) + H^+$$

$$E_3^0 = 0.17 \text{ V} \qquad (I3)$$

Thompson[11] uses Ce(IV) as a chlorous acid trap in his experiments with bromate and chlorous acid. He describes (I3) as "rapid and quantitative". However, since there is not always enough Ce(IV) to react with all of the chlorous acid produced from the initially added chloride, this step is apparently the reason for the duration of the inhibition. A lag occurs while Ce(IV) is regenerated in step R6.

Now,

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O$$

$$E_5{}^0 = -0.18 \text{ V} \qquad (R5)$$

$$BrO_2\cdot + ClO_2\cdot + H_2O \xrightarrow{k_{14}} H^+ + HBrO_2 + ClO_3^-$$

$$E_4{}^0 = 0.18 \text{ V} \qquad (I4)$$

The chloride has been depleted to the point where the bromate can react with the bromous acid. In step I4 bromine dioxide completes the oxidation of the chlorine species to chlorate, which is presumably inert in our system. Step I4 plays an important role in Thompson's mechanism[11] for the oxidation of chlorous acid by acid bromate.

Summing these reactions, we get (I′) = (I1) + (I2) + (I3) + (R5) + (I4):

$$Cl^- + 2BrO_3^- + H^+ + Ce(IV) \rightarrow HOBr + BrO_2\cdot + ClO_3^- + Ce(III) \qquad (I')$$

The reaction is the oxidation of chloride to chlorate by bromate and ceric ions. The mechanism is consistent with, but different in emphasis from, Zhabotinskii's more general hypothesis[6] that chloride inhibits oscillations by preventing the oxidation of Ce(III) to Ce(IV) by bromate.

Combining the potentials of the constituent steps, we find that ΔG^0 for reaction I′ is 3.0 kcal/mol, which corresponds to an equilibrium constant of 0.006 M^{-1} at 25 °C. If we make the following estimates, $[H^+] \approx [H_2SO_4]_0 \approx 1.5$ M, $[BrO_3^-] \approx [BrO_3^-]_0 \approx 4 \times 10^{-2}$ M, $[Ce(IV)]/[Ce(III)] = 0.1$, and $[BrO_2] \approx [HOBr] \approx 10^{-5}$ M, we find that $[ClO_3^-]/[Cl^-] \approx 10^4$. Thus the high concentrations of the species on the left and the low concentrations of the species on the right drive process I′ essentially to completion.

Finally, adding to (I′) the oxidation of Ce(III) by $BrO_2\cdot$ and the disproportionation of $HBrO_2$, we get the overall reaction (I) = 2(I′) + 2 (R6) + (R4).

$$2Cl^- + 3BrO_3^- + 3H^+ \rightarrow 3HOBr + 2ClO_3^- \qquad (I)$$

Discussion and Further Observations

The proposed mechanism appears to explain essentially all of the experimental results. Part I of the inhibition stage may be viewed as the time required for the system to regenerate enough Ce(IV) to consume the chlorous acid via step I2. If the $HClO_2$ is allowed to build up, step I2 may be reversed, thereby maintaining $[Cl^-]$ above the critical level of eq 2 and shutting down steps R2 and R5 which are essential for oscillations. Clearly, increasing the amount of chloride added should lengthen part I, as shown in Figure 1. Increasing the initial cerium concentration should shorten part I, and this behavior is also observed. If sufficiently large amounts of chloride are added, the bromate concentration may be sufficiently depleted by step I2 and by the other reactions which also occur during part I, that the system will be incapable of resuming oscillation at the conclusion of part I and equilibrium will be reached monotonically. An obvious upper limit to this fatal amount of Cl^- is $[BrO_3^-]_0$, but our experimental results indicate that far less chloride, perhaps on the order of $0.05\text{-}0.1[BrO_3^-]_0$, suffices to kill the oscillations.

A maximum in $[Ce(IV)]/[Ce(III)]$ is observed in part I for low initial $[Cl^-]$, but disappears as the amount of added chloride increases. When $[Cl^-]_0$ is low, chlorous acid is produced slowly, and at first Ce(IV) may be formed by the autocatalytic process G faster than it is consumed in (I3). As we add more chloride initially, the rate of (I3) becomes increasingly competitive with that of (R6) until finally no initial rise in [Ce(IV)] is observed.

If the amount of chloride added is less than the amount of Ce(IV) present initially, we would expect essentially no observable inhibition, i.e., part I would be of zero duration. From Figure 1 of Field, Körös, and Noyes,[7] we estimate the maximum value of log ([Ce(IV)]/[Ce(III)]) during the induction period to be about −0.7. For our system this gives $(Ce(IV))_{max} \approx 1.5 \times 10^{-4}$ M. As noted above, no inhibition was observed for initial Cl^- concentrations less than about 1.2×10^{-4} M.

When all the $HClO_2$ is consumed, part I ends. The system is now in a state very much resembling that at the start of the chloride-free reaction. We therefore expect part II to be quite similar to a normal induction period, and both the concentration profile and the length of part II in Figure 1 suggest that this is so. Part II is somewhat shorter than a chloride-free induction period because Scheme I will occur at a small, but nonzero, rate during part I of the inhibition. The bromomalonic acid thus produced serves to shorten the induction period.[7] This hypothesis is further supported by our observation that if the chloride is added *after* the induction period has commenced, part II is shortened, roughly in proportion to the length of time elapsed before adding the chloride.

An interesting point to be noted is that although the chloride ion acts as a reducing agent, it inhibits the system by holding it in the oxidized state. This offers further support for (I3), i.e., that a product of the initially added chloride is removing Ce(IV), thus blocking the oxidation of organic bromine compounds and the consequent production of bromide ion which would have yielded the reduced state of the system.

Several other experimental results have some bearing on the validity of our proposed mechanism. We have hypothesized that the ultimate fate of any chloride in the system is oxidation to chlorate, which has no effect on the oscillations. The considerable analytical difficulty of detecting chlorous acid in this system precluded direct proof of its existence, and the possibility exists that some or all of the chloride is ultimately incorporated into an organic form. However, addition of chlorate ion in concentrations equal to the chloride concentrations needed to cause inhibition produced no observable effect on the oscillating reaction.

Efforts were made to monitor the various oxychloride intermediates spectrophotometrically, but their low concentrations and small extinction coefficients as well as interference from Ce(IV) precluded this possibility.

Experiments were also performed in which other anions were added to the Belousov system. Iodide and the pseudohalide azide caused inhibition qualitatively similar to the chloride inhibition, while nitrate, sulfate, and perchlorate had no effect.

We now turn to the question of how the present results and mechanism may be reconciled with the reports of previous investigators[6-8] that small or trace amounts of chloride permanently eliminate oscillations in the Belousov reaction. The observation[7] that the presence of a salt bridge suppresses oscillations is consistent with the fact that maintenance of even a relatively low *steady state* concentration of chloride will make it possible for (I) to compete successfully with Schemes I and II. In fact, by deliberately adding Cl^- to the system at a constant, measured rate, it may be possible to obtain relations among the rate constants in our scheme and in Schemes I and II by observing the chloride-addition rate just sufficient to suppress oscillations.

The results of Zhabotinskii[6] and of Janjic et al.[8] that "small amounts of chloride" permanently prevent oscillation are less easy to explain. However, neither of these authors reports how much chloride was added, and in some of his experiments Zhabotinskii[6] employs BrO_3^- concentrations lower than in ours, while the acetyl acetone system[8] exhibits a much more rapid cessation of oscillations, even in the absence of chloride, than the malonic acid system. Thus, in both sets of experiments the threshold value of $[Cl^-]$ for elimination of oscillations noted above may well have been exceeded. It should also be noted that at some Cl^- concentrations, oscillations resume only after an inhibition period of 10–15 h.

Finally, we wish to point out that the mechanism proposed here is by no means the only one which may account for the effects of added chloride in the Belousov reaction. While our experimental results are in good agreement with this mechanism, the number of possible intermediates and steps in such a complex system is truly overwhelming. Current interest in the Belousov reaction and the possible relation between inhibition/modification of this oscillating reaction and of other, biologically important analogues should ensure that the phenomena discussed here will receive the further attention that they deserve.

Experimental Section

Materials. Ceric ammonium nitrate, malonic acid, potassium bromate, sulfuric acid, and potassium chloride were of the highest purity available from commercial sources, as were the salts used in the anion addition experiments discussed in the final section.

Methods. Cerium, malonic acid, and bromate solutions were prepared in sulfuric acid. The reagents were added in the order: cerium, chloride, malonic acid, bromate. The chloride was added from a 50- or 100-μl graduated hypodermic syringe, and mixing time was estimated to be about 1 s. All measurements were carried out at 25 °C.

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 reference electrode sleeve (Fisher) filled with a saturated solution of KNO_3, which was in contact with the reaction mixture.

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Structural Entropy Changes in Infinitely Dilute Solutions and Pure Liquids

Howard DeVoe

Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742. *Received February 3, 1975*

Abstract: A molar structural entropy change is defined which measures the change in the structural order of an infinitely dilute solution caused by the introduction of the solute, or the degree of structural order in a pure liquid, based upon the mixing of hard spheres as a reference process. Some values, calculated using scaled-particle theory and experimental entropy data, are reported which demonstrate that nonpolar solute molecules cause large increases in the degree of structural ordering in water compared to nonpolar solvents.

The anomalously large and negative entropy of solution in water which is exhibited by nonpolar liquids and gases, as compared to entropies of solution in other solvents, has generally been interpreted as evidence that the dissolved solute molecules cause an increase in the spatial ordering or structuring of the surrounding water molecules.[1] Kauzmann[2] has pointed out the significance of this solvent structuring to the hydrophobic interaction in proteins (the tendency of nonpolar groups to cluster together in water). While the molecular details of this structuring effect cannot be determined by purely thermodynamic measurements, entropies of solution can provide information about the relative magnitudes of the structuring induced by a solute in different solvents.

This paper defines a new thermodynamic solvation entropy, called the molar structural entropy change, which is characteristic of the change in structural order of an infinitely dilute liquid solution when a solute is introduced from the gas phase. The definition is based upon the mixing of hard spheres, of appropriate size and at the same density as the solution, as a reference process. An analogous treatment of the condensation of a vapor allows one to define a molar structural entropy change which measures the degree of structural order in a pure liquid. The next two sections give physical interpretations of these structural entropies, and derive the equations needed to evaluate them from experimental quantities. The last section applies the equations to several aqueous and nonaqueous solutions and liquids, and