Thorough Study of Bromide Control in Bromate Oscillators. 4. A Quantitative and **Comparative Study on Silver Ion Perturbed Belousov-Zhabotinsky Systems**

Margit Varga and Endre Körös*

Institute of Inorganic and Analytical Chemistry, L. Eötvös University, H-1443 Budapest, Hungary (Received: October 21, 1985; In Final Form: March 5, 1986)

The distribution of bromine between bromoorganics and bromide was followed in Ag⁺-perturbed Belousov-Zhabotinsky (BZ) systems and the rate of the Br⁻ removing reaction (Ag⁺ + Br⁻ \rightarrow AgBr) was measured. A rate constant in the order of 10⁴ M⁻¹ s⁻¹ was obtained for the reaction. A comparison of bromine distribution in Ag⁺-perturbed malonic acid and malic acid containing BZ systems revealed the difference in their oscillatory behavior.

Introduction

Vavilin et al.¹ were the first to observe that the addition of silver ion had an effect on a reacting Belousov-Zhabotinsky (BZ) system: it caused phase shifting during oscillations. Later Noszticzius² reported on the behavior of catalyzed bromate oscillators when perturbed by silver ion. He found silver ion induced high-frequency redox potential oscillation and claimed, considering only equilibrium data-the solubility product of silver bromide, that in BZ systems there may exist such chemical conditions that the controlling role of the bromide ion, proposed in the Field-Körös-Noyes mechanism³ and in the Oregonator model,⁴ is replaced by another intermediate of the BZ reaction. Ganapathisubramanian and Noyes⁵ confirmed Noszticzius' observations and supported his claim that in the presence of silver ion nonbromide-controlled oscillation occurs. They postulated that control of redox potential oscillations was provided by the competition of bromide atoms and bromate ions for reaction with bromous acid; i.e., they attributed the controlling role to bromine atoms.

The most extensive studies on the effect of silver ion on a reacting BZ system have been performed by Ruoff et al.^{6,7} They could simulate semiquantitatively the behavior of a silver-perturbed BZ system by using the Oregonator model extended by the Ag⁺ $+ Y \rightarrow AgY^+$ bromide-ion-removing step. They assigned a rate constant of about 10⁴ M⁻¹ s⁻¹ to this reaction.

Whether a silver-ion-perturbed BZ system exhibits oscillatory or nonoscillatory behavior is determined by the rate of the bromide-ion-removing reaction $(Ag^+ + Br^- \rightarrow AgBr)$, i.e., among others on the actual silver ion concentration. Therefore by following the temporal change in redox potential simultaneously with that in silver ion concentration, the rate constant of the above reaction in the BZ system might be calculated.

In the present paper we report on the one hand how this goal was reached and on the other hand on the silver-ion-perturbed malic acid and malic acid containing BZ systems and thus to reveal some additional details on the prerequisite of chemical oscillation.

Experimental Part

All experiments were performed in closed system under continuous stirring, in a thermostat-regulated glass container at 25.0 \pm 0.02 °C. The redox potential of the reacting systems was measured with a smooth platinum electrode against a Hg/

 Hg_2SO_4/K_2SO_4 reference electrode and the bromide ion concentration with a bromide ion selective electrode (Orion Model 94-35), and they were recorded on a Yokogawa Technicorder F 3052 double-pen recorder.

All reagents used were of analytical reagent grade.

The reaction volume was 100 cm³ and the reaction initiated by the addition of a mixture of the catalyst (Ce^{4+}) and silver ion to a solution containing bromate, sulfuric acid, and the organic compound (malonic acid or malic acid). Aliquots of 2 mL were withdrawn from the reaction mixture at certain intervals. Some aliquots were added to a KI solution acidified with HCl, and the liberated iodine was titrated with 0.05 M standard Na₂S₂O₃ solution. Thus the total oxidizing power (TOP) of the solution, expressed in bromate molarity, could be calculated. Other aliquots (5.0 mL) were mixed to a 10% CH₃COONa solution diluted to about 50 mL, and the Ag⁺ concentration of the solution was titrated with a 0.005 M standard KBr solution using potentiometric end-point detection. (It has been confirmed in separate experiments that under our experimental conditions bromate ion did not interfere in the potentiometric determination of Ag⁺. The titration curves showed one, very sharp, end point.)

In the malonic acid containing BZ system in the absence of silver ion the following overall reaction proceeds:

$$2BrO_{3}^{-} + 3CH_{2}(COOH)_{2} + 2H^{+} \xrightarrow{\text{cal.}} 2BrCH(COOH)_{2} + 3CO_{2} + 4H_{2}O$$
$$BrO_{3}^{-} \xrightarrow{\text{red.}} BrMA \qquad (1)$$

If silver ion is present, the transiently formed bromide ion (or a certain portion of it depending on the composition of the reacting BZ system) is precipitated as AgBr

$$BrO_3^- \xrightarrow{red.}_{Ag^+} BrMA + AgBr$$
 (2)

This fact should be taken into account when calculating the concentration of BrMA. Also it should be considered that BrMA is a two-electron oxidizing agent and bromate, however, is a six-electron one.

The following relations hold:

$$[BrO_{3}^{-}]_{t} = [BrO_{3}^{-}]_{0} - ([Ag^{+}]_{0} - [Ag^{+}]_{t}) - [BrMA]_{t}$$
$$[BrO_{1}^{-}]_{corr} = [BrO_{1}^{-}]_{t} - ([Ag^{+}]_{t} - [Ag^{+}]_{t}) =$$

$$[BrO_{3}]_{t} = [BrO_{3}]_{0} = ([Ag]_{0} = [Ag]_{t}) = [BrO_{3}]_{t} + [BrMA]_{t}$$
$$TOP = [BrO_{3}]_{t} + \frac{1}{3}[BrMA]_{t}$$

$$TOP = [BrO_{3}^{-}]_{t}^{corr} - \frac{2}{3}[BrMA]_{t}$$
(3)

$$[BrMA]_{t} = \frac{3}{2}([BrO_{3}^{-}]_{t}^{corr} - TOP)$$
(4)

From the above relations and the knowledge of TOP and the Ag⁺ concentration, the BrMA concentration of the reacting system couuld be obtained.8

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 ⁽²⁾ Noszticzius, Z. J. Am. Chem. Soc. 1979, 101, 3660-3663.
(3) Field, R. J.; Körös, E.; Noyes, R. M. J. Am. Chem. Soc. 1972, 94, 8649-8664

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Figure 1. Temporal change of redox potential (a) and Ag^+ concentration (a) in a system of the following initial composition: 0.075 M KBrO₃, 0.20 M malonic acid, 1.0 M H₂SO₄, 0.002 M Ce(IV), and 0.01 M Ag⁺.

TABLE I: Composition of the Reacting System 1.0 M H₂SO₄, 2.0 \times 10⁻³ M Ce(IV), and 0.01 M Ag⁹ with a Variation in [MA] and [BrO₃⁻] at 25.0 \pm 0.02 °C

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	[MA], M	[BrO ₃ ⁻], M	$10^3 k$, s ⁻¹	
	0.10	0.075	3.17	
	0.20	0.075	3.83	
	0.40	0.075	3.67	
	0.20	0.05	2.33	
	0.20	0.075	3.83	
	0.20	0.10	3.00	

In the malic acid containing BZ system the formed bromoorganic is not an oxidizing agent toward iodide; therefore its concentration can be calculated by substracting the sum of $[BrO_3^-]_t$ and $([Ag^+]_0 - [Ag^+]_t)$ from $[BrO_3^-]_0$.

Results and Discussion

Malonic Acid Containing BZ System. In BZ systems containing malonic acid and bromate ion in different concentrations, the decrease of Ag⁺ concentration over time was followed. A typical [Ag⁺] vs. time curve is shown in Figure 1 together with the corresponding redox potential trace. The initial rate of silver ion comsumption v^{0}_{AgBr} (i.e., that of the Ag⁺ + Br⁻ \rightarrow AgBr reaction) is

$$v_{\text{AgBr}}^0 = 3.2 \times 10^{-5} \text{ M s}^{-1}$$

The oscillation starts when the Ag^+ concentration drops to about one-tenth of its initial value, to 10^{-3} M. At the start of oscillation the rate of the $Ag^+ + Br^- \rightarrow AgBr$ reaction is

$$v_{\text{AsBr}}^{\text{t}} = 5.0 \times 10^{-6} \text{ M s}^{-1}$$

Plotting ln $([Ag^+]_0/[Ag^+]_i)$ vs. time until the start of oscillation gave a straight line as shown in Figure 2. From plots a first-order rate constant could be calculated. Its value practically did not depend on the malonic acid or the bromate concentration of the BZ system. Its average value was $3.31 \times 10^{-3} \text{ s}^{-1}$ (Table I). The linearlity means that the average concentration of bromide is constant during the time of observations. This fact is very important for our further considerations.

Simultaneously with the decrease of silver ion concentration, the total oxidizing power of the system was followed by iodometric titration.

The overall rate of the reaction, $-d[BrO_3^-]/dt$, could be fitted to the following rate equation:

$$-\frac{d[BrO_3^{-}]}{dt} = k_b[MA]_0^{0.5}[BrO_3^{-}]_0^{0.5}$$
(5)
$$k_b = 5.3 \times 10^{-4} \text{ s}^{-1}$$



Figure 2. Plot of ln $([Ag^+]_0/[Ag^+]_i)$ vs. time at 25.0 \pm 0.02 °C of a system of the following initial composition: 0.075 M KBrO₃, 0.20 M malonic acid, 1.0 M H₂SO₄, 0.002 M Ce(IV), and 0.01 M Ag⁺.

TABLE II: Composition of the Reacting System 1.0 M H₂SO₄, 2.0 × 10^{-3} M Ce⁴⁺, and 0.01 Mg Ag⁺ with a Variation in [MA] and [BrO₃⁻] at 25.0 ± 0.02 °C

[MA], M	[BrO3], M	d[BrMA]/dt, 10 ⁵ M s ⁻¹	$10^4 k_1, s^{-1}$
0.40	0.075	6.67	3.85
0.20	0.075	3.08	2.52
0.10	0.075	2.45	2.82
0.20	0.05	2.87	2.87
0.20	0.075	3.08	2.52
0.20	0.10	3.33	2.35

which agreed with that reported previously, when the overall rate of the BZ reaction during the preoscillatory period was measured by the accumulation of BrMA⁹

$$\frac{d[BrMA]}{dt} = -\frac{d[BrO_3^{-}]}{dt} = k_2[MA]^{0.5}[BrO_3^{-}]^{0.5}[Ce^{3+}]$$
(6)

In eq 5 the catalyst concentration does not appear since it was kept constant $(2.0 \times 10^{-3} \text{ M})$ throughout the experiments. Dividing k_b by 2.0×10^{-3} gives a second-order rate constant. Its value, 0.265 M⁻¹ s⁻¹, agrees very well with k_2 reported previously (0.259 M⁻¹ s⁻¹).⁹

Thus it can be concluded that the addition of silver ion to a reacting BZ system does not alter the overall rate of the reaction; the only difference is that here two reduction products of bromate are formed: BrMA and AgBr.

From the time dependence of TOP and the silver ion concentration was calculated the rate of BrMA production. The results obtained are given in Table II.

For the calculation of k_1 the following rate equation was used: d[BrMA]

$$\frac{dt}{dt} = k_1 [MA]_0^{0.5} [BrO_3^-]_0^{0.5}$$
(7)

The average value of k_1 is 2.83 \times 10⁻⁴ s⁻¹.

From eq 1 it is obvious that in absence of silver ion the rate of bromate consumption (v_{BrO_3}) is equal to the rate of formation of bromomalonic acid (v_{BrO_3}) : $v_{-\text{BrO}_3} = v_{\text{BrMA}}$. If silver ion is present $v_{-\text{BrO}_3} > v_{\text{BrMA}}$ since bromide ion formed as an intermediate is precipitated as AgBr.

The experimental results (the initial rates) are compiled in Table III. It can be seen that the rate of bromate consumption agrees well with the sum of rates of AgBr and BrMA accumulation: $v_{ABFQ^{-}}^{0} = v_{ABF}^{0} + v_{BFMA}^{0}$.

 $v_{-BrO_3}^0 = v_{AgBr}^0 + v_{BrMA}^0$. It has been found that optimal conditions for the silver-ioninduced (i.e., high-frequency) oscillations are met if $v_{BrMA}^0 > v_{AgBr}^0$. As the difference between the two rates becomes greater, the time that the optimal conditions for oscillation are sustained is prolonged. If $v_{BrMA}^0 \approx v_{AgBr}^0$ only a few silver-ion-induced oscillations occur.

⁽⁸⁾ In the Ag⁺-perturbed BZ system BrMA cannot be determined by the polarographic method suggested earlier (Burger, M.; Körös, E. J. Phys. Chem. **1980**, *84*, 496-500) since the fine AgBr particles plug the dropping-Hg electrode.

TABLE III: Composition of the Reacting Systems 1.0 M H₂SO₄, 2.0×10^{-3} M Ce(IV), and 0.01 M Ag⁺ with a Variation in [MA] and [BrO₃⁻] at 25.0 ± 0.02 °C

[MA], M	[BrO₃⁻], M	υ ⁰ _{AgBr} , 10 ⁵ M s ⁻¹	10^{5} M s^{-1}	$v_{AgBr}^{0} + v_{BrMA}^{0},$ 10 ⁵ M s ⁻¹	$v_{-BrO_3}^0$, 10 ⁵ M s ⁻¹	note
 0.10	0.075	3.17	2.45	5.62	5.42	max no. of oscillations
0.20	0.075	3.83	3.08	6.91	6.25	
0.40	0.075	3.67	6.67	10.34	11.16	
0.20	0.05	2.33	2.87	5.20	4.90	max no. of oscillations
0.20	0.075	3.83	3.08	6.91	6.25	
0.20	0.10	3.00	3.33	6.33	6.10	

These results are in qualitative agreement with our studies on the Tl(III)-containing BZ system.¹⁰ At high Tl(III) concentrations (~10⁻² M) when $v_{BrMA}^0 \approx v_{TlBr^{2+}}^0$ only a few oscillations appeared. When TlBr₂⁺ was added to the system instead of Tl(III), and therefore $v_{BrMA}^0 > v_{TlBr_2}^0$ prolonged oscillation (100-200 oscillations) was observable.

Figure 3 shows the [BrMA] and $([Ag^+]_0 - [Ag^+]_t)$ vs. time plots at different malonic acid concentrations. The pair of curves shows that at higher concentrations of malonic acid the deviation between v_{BrMA} and v_{AgBr} is greater even early during reaction. This can be explained by considering that at higher malonic acid concentrations $v_{-BrO_3^-}$ and therefore also v_{Br} becomes greater and bromate ion competes more effectively with Ag⁺ for bromide.

A change of composition of the reacting system can be defined in terms of the three rates v_{-BrO_3} , v_{BrMA} , and v_{AgBr} . Only two of these rates are independent, and they can all be calculated from the rates of change of [Ag⁺] and TOP.

On the basis of major bromine species $(BrO_3, Br, and BrMA)$ we can describe a change of composition in terms of four overall processes designated a-d. We also consider that the source of bromide is bromate and not BrMA (for details see ref 11).

$$2BrO_3^- \rightarrow BrMA + Br^- \qquad (a)$$

$$BrO_3^- + Br^- \rightarrow 2BrMA$$
 (b)

$$BrO_3^- + 2Br^- \rightarrow 3BrMA$$
 (c)

$$Ag^+ + Br^- \rightarrow AgBr$$
 (d)

Process a is accompanied by oxidation of 10 equiv of reducing agent and b is accompanied by oxidation of 2 equiv.

The three rates that define the change of composition can be related to the rates of these four overall processes

$$v_{-BrO_3^-} = 2v_a + v_b + v_c$$
$$v_{BrMA} = v_a + 2v_b + 3v_c$$
$$v_{AgBr} = v_d$$

We have shown (see eq 5 and 6) that v_{-BrO_3} is the same whether or not silver ion is present; i.e., silver ion does not have any effect on processes destroying bromate except to the extent that process d affects bromide concentration.

We can write

$$v_{\rm d} = k_{\rm p} [\mathrm{Ag^+}] [\mathrm{Br^-}]$$

and assume that this process is so far from equilibrium that the reverse is unimportant.

We then obtain

$$[Br^{-}] = \frac{v_{a} - v_{b} - 2v_{c}}{k_{p}[Ag^{+}]} = \frac{v_{-BrO_{3}} - v_{BrMA}}{k_{p}[Ag^{+})}$$

The linearity in Figure 2 require that the concentration of bromide ion be almost constant until oscillations begin, at which time we know the concentration is $[Br^-]_{crit}$. $[Br^-]_{crit} = 5 \times 10^{-6} [BrO_3^-]$; for details see ref 3. Furthermore, we know that when



Figure 3. Temporal change in BrMA (a) and Ag^+ (b) concentrations at 25.0 \oplus 0.02 °C in systems of the following initial composition: 0.075 M KBrO₃, 1.0 M H₂SO₄, 0.002 M Ce(IV), 0.01 M Ag⁺, and (I) 0.10 M malonic acid, (II) 0.20 M malonic acid, (III) or 0.40 M malonic acid. Arrow indicates the start of oscillation.

there is enough silver ion to suppress oscillations [Br] is less or equal to $[Br]_{crit}$. Under our experimental conditions

$$[Br^{-}]_{crit} = 5.0 \times 10^{-6} \times 0.075 = 3.75 \times 10^{-7} M$$

The initial rate of silver bromide formation is 3.31×10^{-5} M s⁻¹ (the average of the k values in Table I multiplied by the initial silver ion concentration, 10^{-2} M).

$$v_{\text{AgBr}} = k_{\text{p}}[\text{Ag}^+][\text{Br}^-]$$

At the start of the reaction $[Ag^+] = 1.0 \times 10^{-2} \text{ M}$. Thus

$$k_{\rm p} = \frac{3.31 \times 10^{-5}}{3.75 \times 10^{-7} \times 1.0 \times 10^{-2}} = 0.88 \times 10^4 \,{\rm M}^{-1} \,{\rm s}^{-1}$$

It has been shown above (see Table III) that

$$v_{-\mathrm{BrO}_{3}^{-}} = v_{\mathrm{AgBr}} + v_{\mathrm{BrMA}}$$

$$v_{AgBr} = v_{-BrO_3} - v_{BrMA}$$

Thus k_p can also be calculated by using the $v_{-BrO_3^-}$ and v_{BrMA} values in Table III. The average value of v_{AgBr} is 3.10×10^{-5} M s⁻¹ and then

$$k_{\rm p} = \frac{3.10 \times 10^{-5}}{3.75 \times 10^{-7} \times 1.0 \times 10^{-2}} = 0.83 \times 10^4 \,{\rm M}^{-1} \,{\rm s}^{-1}$$

⁽¹⁰⁾ Körös, E.; Varga, M.; Györgyi, L. J. Phys. Chem., 1984, 88, 4116-4121.

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

TABLE IV: Percent Distribution of Bromine^a among the Different Oxidation States of Bromine during the Reaction of the System 0.10 M KBrO₃, 0.20 M Malic Acid, 1.0 M H₂SO₄, 2×10^{-3} M Ce(IV), and 0.01 M Ag⁺

% distribution				
Br(V) (BrO ₃)	$Br(-I)^{b} (AgBr)$	Br(I) (Br-org)		
100	0	0		
97.5	2.5	0		
96.5	3.9	0		
96.0	4.6	0		
95.2	5.2	0		
95.0	5.8	0		
94.0	6.4	0		
93.3	7.0	0		
92.5	7.9	0		
91.5	9.1	0		
90.1	10.0	0		
	Br(V) (BrO ₃) 100 97.5 96.5 96.0 95.2 95.0 94.0 93.3 92.5 91.5 90.1	$\begin{tabular}{ c c c c c } \hline & $distribution$ & $dist$		

 $^{a}100\% = 0.10$ M Br(V). b From the concentration ratio it is obvious that at 10.0% Br(-I) the total amount of Ag⁺ precipitated as AgBr.

Thus we obtained the minimum value of $k_p (0.85 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})$.

If we use $v_{AgBr}^{r} = 5.0 \times 10^{-6}$ M s⁻¹, which is the rate of AgBr formation at the start of oscillation (see above) we obtain the highest possible value for k_{p} . For when oscillation starts [Ag⁺] = 10^{-3} M and the lowest possible value for [Br⁻] is [Br⁻]_{crit}. Thus

$$k_{\rm p} = \frac{5.0 \times 10^{-6}}{3.75 \times 10^{-7} \times 10^{-3}} = 1.33 \times 10^4 \,{\rm M}^{-1} \,{\rm s}^{-1}$$

Both values $(0.85 \times 10^4 \text{ and } 1.33 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})$ are very close to $10^4 \text{ M}^{-1} \text{ s}^{-1}$, which value was used by Ruoff⁶ and Ruoff and Schwitters⁷ in the simulation by the extended Oregonator model, silver-ion-induced frequencies, excitation thresholds, and amplitudes of excitable BZ systems.

Malic Acid Containing BZ System. The Ag⁺-perturbed BZ system containing malic acid exhibits a considerably different behavior than the malonic acid system.

After the reactants are mixed, the catalyst remains in its oxidized form for a prolonged period of time and then a sudden change in the potential occurs (the catalyst is reduced); oscillation, however, is not observable. The same behavior has been found in the Tl(III)-containing system as reported in and shown in Figure 7 of ref 10.

From the temporal decrease in silver ion concentration a first-order rate constant was calculated as described above. The average value is 3.3×10^{-3} s⁻¹ and practically independent of the bromate ion and malic acid concentration and identical with that obtained in the malonic acid system.

In the Ag⁺-perturbed malic acid containing BZ system organic bromo compounds do not form during the reaction. The sum of the bromate ion and bromide ion (in the form of AgBr) concentrations was equal to the initial bromate concentration (Table IV).

On the basis of our experience gained on the malonic acid BZ system, we attempted to force the malic acid BZ system to a transition from an excitable state into an oscillatory one by increasing the rate of bromide ion production. Indeed, when the malic acid concentration was increased to 0.40 M the reacting system exhibited high-frequency oscillation that changed abruptly into normal BZ oscillation as shown in Figure 4. In this reacting system approximately at the start of high-frequency oscillation bromoorganics started to accumulate. The results of the analysis are complied in Table V.

From our present studies, it can be concluded that in the presence of silver ion in a closed BZ system oscillation occurs only if the Ag⁺ concentration has dropped—as a consequence of the Ag⁺ + Br⁻ \rightarrow AgBr reaction (bromide is continuously generated in the BZ system by the reduction of oxybromine compounds¹¹)—to such a low value that bromide ion cannot react preferentially with silver ion. Our present and earlier experiments,^{10,12} and Schwitters and Ruoff's recent calculations¹³ reveal



Figure 4. Temporal change of redox potential (a) and Ag^+ concentration (b) in a system of the following composition: 0.10 M KBrO₃, 0.40 M malic acid, 1.0 M H₂SO₄, 0.002 M Ce(IV), and 0.01 M Ag⁺.

TABLE V: Percentage Distribution of Bromine^a among the Different Oxidation States of Bromine during the Reaction of the System 0.10 M KBrO₃, 0.40 M Malic Acid, 1.0 M H₂SO₄, 0.002 M Ce(IV), and 0.01 M Ag⁺

	% distribution					
reactn time, min	$Br(V)$ (BrO_3^{-})	Br(-I) (AgBr)	Br(I) (Br-org)			
0	100	0	0			
1.0	97.8	2.5	0			
1.9	96.5	4.1	0			
3.2	94.6	5.9	0			
4.3	93.8	6.8	0			
5.3	93.0	7.4	0			
6.6	92.0	8.0	0			
8.2	89.6	9.5	0.9			
10.9	87.5	10.0	2.5			

 $^{a}100\% = 0.10 \text{ M Br}(\text{V}).$

that in bromate-driven oscillatory systems bromide ions play an essential role. The rate constant ($\sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$) experimentally obtained by us for the bromide-removing reaction is a further support for the usefulness of the Oregonator model extended by Ruoff.⁶

Important consequences can be drawn by comparing the behavior of the malonic acid and malic acid containing BZ systems. Our observations that in the Ag⁺-perturbed malic acid containing BZ system bromoorganics are not formed, i.e., bromate ion is converted to bromide ion which reacts with silver ion, refer to the fact that the bromination of malic acid by the respective oxybromine compounds (e.g., HOBr) is much slower than that of malonic acid. This is also a support for our recent finding that the source of bromide ion is not the bromoorganics.¹¹

In the malic acid containing BZ system oscillation starts immediately after mixing the reagents; i.e., a preoscillatory period is not observable. This can be explained by considering that early during reaction bromide ion concentration rapidly reaches that value which is required for the initiation of oscillation. In the malonic acid containing BZ system the bromide ion concentration is very low at the start of the reaction and increases rather slowly till the onset of oscillation.

The difference in behavior of the two BZ systems discussed above prompts us to examine other catalyzed bromate oscillators especially those containing a ketone (either aliphatic or alicyclic) as an organic substrate. The results will be published in a forthcoming paper.

Registry No. Ag, 7440-22-4; CH₂(COOH)₂, 141-82-2; BrO₃⁻, 15541-45-4; Ce, 7440-45-1; malic acid, 6915-15-7.

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