

Experimental Test for the Control Intermediate in the Belousov-Zhabotinsky (BZ) Reaction

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Abstract: The role of the control intermediate in the BZ reaction is to remove the autocatalytic intermediate HBrO_2 . As from a theoretical point of view both elementary bromine and bromide ions may act as control intermediates, an experimental test was performed. The experiments show that only the Br^- ions can react directly with the bromous acid and the elementary Br_2 reacts indirectly via its hydrolysis.

There are still some unsolved problems in the mechanism of the oscillating BZ reaction. In a recent paper Noszticzius, Farkas, and Schelly¹ criticized the Oregonator model² of the BZ reaction and proposed a new model, the so-called Explodator containing two consecutive or "serial"³ autocatalytic processes. Noyes⁴ responded to their criticism, suggesting a new revised Oregonator model containing also two consecutive autocatalytic processes. In a subsequent paper Tyson⁵ analyzed the revised Oregonator, stressing that his analysis applies equally well to a special case of the Explodator. Thus it is clear that the two models show strong similarities. One of the main differences between them is the chemical identification of the intermediates. In both cases these are the different oxidation levels of bromine: HBrO_2 , HOBr , and Br_2 in the Explodator model and HBrO_2 , HOBr , and Br^- in the revised Oregonator. That is the control intermediate is different in the two models. Both models agree that the control is due to a reaction between the autocatalytic intermediate HBrO_2 and an inhibitory agent, which is different however in the two models (Br_2 or Br^-). Even in this respect the difference is not so serious either, as there is a rapid equilibrium among HOBr , Br_2 , and Br^- . Thus both Br_2 and Br^- can be chosen as an independent variable. Nevertheless there is a difference on the level of elementary steps. That problem can be formulated in the following question: can the bromous acid react directly with elementary bromine or does that reaction take place by a previous hydrolysis of bromine followed by a direct reaction between the produced bromide ions and bromous acid? As that question cannot be answered by purely theoretical consideration,⁶ we intended to solve the problem by some decisive experiments.

Experimental Problems

Unfortunately a direct experiment, that is, to measure the reaction rate of the bromous acid-bromide reaction and the bromous acid-bromine reaction separately, is not possible. Namely if elementary bromine is present, its hydrolysis cannot be avoided, and if bromide ion is the reactant, the produced bromine may also react with bromous acid. On the other hand, the fast disproportionation rate of bromous acid^{7,8} would present further experimental problems. Thus we looked for an indirect way to answer the problem. It is known⁹⁻¹¹ that the acidic bromate-cerous ion reaction shows an induction period. That induction period can be considerably lengthened by adding bromide ions or an equivalent amount of elementary bromine (which would be produced by a bromate-bromide reaction¹¹) to the system. The inhibitory effect of bromine can be explained in two different ways: (i) The elementary bromine reacts directly with the autocatalytic intermediate HBrO_2 , or (ii) the real inhibitory agent is the bromide ion which is formed from bromine via its hydrolysis. Now that hydrolysis can be suppressed by adding hypobromous acid to the

Table I. Induction Period of the Acidic Bromate-Cerous Ion Reaction Measured at Different Initial Bromine Concentrations with and without Adding Hypobromous Acid^a

expt	$[\text{Br}_2]_0$, M	$[\text{HOBr}]_0$, M	induction period, s
a	0	0	41
b	0	1.2×10^{-4}	38
c	1.8×10^{-6}	0	404
d	7.2×10^{-6}	0	1900
e	1.8×10^{-6}	1.2×10^{-4}	38
f	1.8×10^{-5}	1.2×10^{-4}	42
g	1.2×10^{-4}	1.2×10^{-4}	37

^a Other initial conditions $[\text{H}_2\text{SO}_4] = 1.5$ M, $[\text{BrO}_3^-]_0 = 1.6 \times 10^{-3}$ M, $[\text{Ce}^{3+}]_0 = 10^{-4}$ M. In all experiments the temperature was 24 ± 0.2 °C. Experiment b shows that hypobromous acid alone does not change the induction period. Experiments e, f, and g show that the original induction period can be restored within the experimental error. (The relative standard deviation of the measured induction periods was less than 10%.)

system. This way the bromide concentration can be decreased by several orders of magnitude without any substantial change in the bromine concentration. If there is a direct reaction between bromine and bromous acid then—if elementary bromine is present—a lengthening of the induction period will be found even in the presence of hypobromous acid. On the other hand, if the extended induction period can be reduced to its original value by adding enough hypobromous acid to the system, then the direct reaction between bromine and bromous acid is negligible. A further experimental advantage of the above indirect method is that the induction period can be determined by measuring the Ce^{4+} concentration spectroscopically; consequently the problematic direct measurement of the different bromine species can be avoided.

Experimental Section

Apparatus. The Ce^{3+} - BrO_3^- reaction was followed by a dual-wavelength spectrometer at 400 nm (reference wavelength: 600 nm, optical

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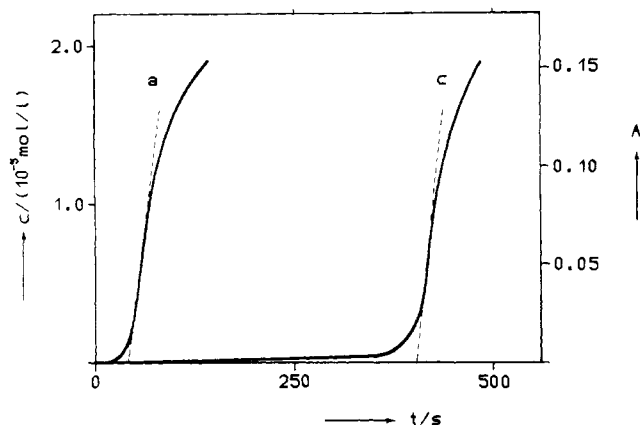


Figure 1. Kinetics of the acidic bromate-cerous ion reaction by measuring the absorbance A at 400 nm (right-hand scale). The concentration c of Ce^{4+} (left-hand scale) was calculated by using the extinction coefficient $800 \text{ L mol}^{-1} \text{ cm}^{-1}$ (optical path length 10 cm). Cases a and c correspond to the initial conditions in Table I. The induction periods were determined from the above curves by the intersection of the dashed lines with the abscissa.

path length 10 cm). The experimental device was the same as it is described by Försterling and his co-workers.¹²

Chemicals. Acidic bromate solutions were prepared from $NaBrO_3$ recrystallized 2 times from hot water to remove bromide, bromine, and hypobromite impurities.^{8,13}

Silver ion free hypobromous acid was produced by a method of Noszticzus et al.¹⁴

Results

Our results are displayed in Figure 1 and Table I.

Discussion

Our experiments show convincingly that there is no measurable direct reaction between bromine and bromous acid. Thus, the inhibitory effect of bromine is due to its hydrolysis. Consequently the kinetics of the second step of the Explodator has to be modified as Noyes⁴ and Tyson⁵ have proposed. Another conclusion is that the hydrolysis of bromine can play a crucial role in some BZ systems and in these cases the "bromine hydrolysis controlled" models of Field¹⁵ will be of prime importance.

Plans for Some Further Experiments and Estimation of the Critical Bromide Concentration. In our experiments we could establish extremely low bromide levels simply by applying different bromine and hypobromous acid concentrations. Actually these mixtures are excellent bromide buffers. We hope that with these buffer solutions we shall be able to get some information about the critical bromide concentration (which prevents the start of the autocatalytic Ce^{3+} -bromate reaction) without applying a bromide-selective electrode.

From our present experiments, a rough estimation of the critical bromide concentration can already be given. Our estimation is based on the equilibrium (R1)



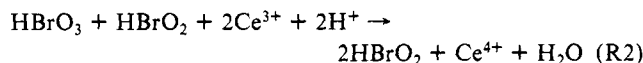
which was investigated by Eigen and Kustin.¹⁶ The equilibrium constant

$$K = [Br_2] / ([HOBr][Br^-][H^+]) \quad (1)$$

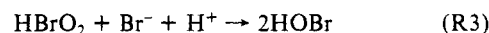
was estimated by Field, Körös, and Noyes¹⁷ for 1 M sulfuric acid medium: $K = 7 \times 10^7 \text{ M}^{-2}$ at 20 °C. Lamberz¹⁸ was able to confirm this value by direct experiments, if $[H^+] = 1.24 \text{ M}$ was inserted for the H^+ concentration in 1 M H_2SO_4 .¹⁹

Now let us regard the experiment depicted in Figure 1c. In the beginning of the reaction, the concentration of added Br_2 is $1.8 \times 10^{-6} \text{ M}$. As no added $HOBr$ is present, the relation $[Br^-] = [HOBr]$ is valid. In our experiments the concentration of H_2SO_4 is 1.5 M, leading to $[H^+] = 1.9 \text{ M}$ according to ref 19, and $[Br^-] = 1.2 \times 10^{-7} \text{ M}$ follows from eq 1. Apparently this value is high enough to prevent any autocatalytic formation of $HBrO_2$. Thus, we may assume that throughout the induction period—that is, up to the beginning of the exponential growth of Ce^{4+} —the concentration of $HBrO_2$ is very low.

Actually in a mixture of acidic bromate and bromine, a very low equilibrium concentration of $HBrO_2$ is established. This equilibrium situation is disturbed by the introduction of Ce^{3+} , initiating reaction R2. During the induction period, the con-



centration of Ce^{4+} grows very slowly (nearly linearly); thus, approximately any $HBrO_2$ production in (R2) must be cancelled out by its destruction in (R3). (Another possibility of the $HBrO_2$



destruction would be its disproportionation. We neglect this reaction, however, due to the very low $HBrO_2$ concentration.) Now, regarding (R1), (R2), and (R3), there is a stoichiometric relationship between the $HOBr$ and Ce^{4+} produced during the induction period:

$$[HOBr] = 1.5 \times [Ce^{4+}] \quad (2)$$

In Figure 1c, the concentration of Ce^{4+} increases nearly linearly during the induction period and reaches the value $5 \times 10^{-7} \text{ M}$ at $t = 360 \text{ s}$. Now according to (2), $[HOBr]$ is expected to be $7.5 \times 10^{-7} \text{ M}$ at this point, and $[Br_2]$ is decreased by $2.5 \times 10^{-7} \text{ M}$. Inserting these values into (1), we calculate $[Br^-]_{crit} = 1.6 \times 10^{-8} \text{ M}$; at this "critical" value, the autocatalytic growth starts immediately. A similar calculation for experiment "d" gives $[Br^-]_{crit} = 2.1 \times 10^{-8} \text{ M}$.

Finally it is interesting to point out that these rough estimates agree rather well with $[Br^-]_{crit} = 2.9 \times 10^{-8} \text{ M}$, whose value can be calculated from the ratio

$$[Br^-]_{crit} / [BrO_3^-] = 18 \times 10^{-6}$$

obtained in the experiments of Field, Körös, and Noyes¹⁷ regarding that $[BrO_3^-]$ was $1.6 \times 10^{-3} \text{ M}$ in our experiments.

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Registry No. $HBrO_2$, 37691-27-3; Br_2 , 7726-95-6; Br^- , 24959-67-9; Ce , 7440-45-1; BrO_3^- , 15541-45-4.

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