one-humped, next-maximum map is in this region. More complex maps certainly do occur in the experiments.[38,39] We never saw a truly single-valued simulated next-maximum map; nevertheless, the maps in Figures 3b and 4a would certainly appear single-valued in the presence of even a low level of experimental noise, and there are indications[39] that all experimental maps may consist of multiple sheets. We did not make a systematic attempt to search for a single-valued map by carefully tuning the flow rate or the adjustable rate constants. The simulations seem to contain larger domains of periodicity than do the experiments, although it is not clear from published experimental results how much periodicity is contained in the periodic–chaotic windows. The experimental work of Coffman et al.[12,39] certainly suggests the presence of a large variety of complex limit cycles in the regions between the major periodicities. Several bistable regions between two different periodicities or a periodicity and a strange attractor were found in the simulations at flow rates lower than shown in Figure 1. We cannot be certain from the experimental results available to us whether these hystereses occur in the real system. The same is true of the transition between sinusoidal and mixed-mode oscillations, which we found in the simulations to be a subcritical, secondary Hopf bifurcation. It was not possible to identify the nature of this transition in experiments,[39] nor could it be proved whether hysteresis exists due to difficulties associated with the large residence time where the transition occurs.

Note added in proof: Noszticzius[50] verified that the same bistability exists experimentally.

Even if these phenomena prove inconsistent with the experiments, the convincing agreement in the major characteristics of the dynamics suggests that the discrepancies may well be removed simply by choosing other values for $k_{13}-k_{15}$. The numerical difficulties mentioned above, however, indicate that in some cases the experimental phenomena may be transient or artifacts of the coupling of mixing and noise with the extremely sensitive BZ dynamics. Thus, it is unclear how close one can expect experiments to match simulations where the stable long-term behavior can almost always be elucidated.

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Competition between Silver Ions and Oxybromine Species for Bromide Ions in the Silver-Perturbed Belousov–Zhabotinskii Reaction

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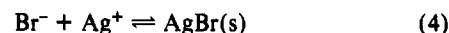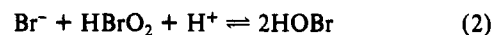
We investigated the relative rates of bromide consumption by silver ions and by the oxybromine species of the Belousov–Zhabotinskii reaction. Our results indicate that the consumption of bromide by silver is too slow to suppress bromide control of the oscillating reaction.

Introduction

The Belousov–Zhabotinskii reaction is the most thoroughly investigated oscillating chemical reaction. It has become one of the most important examples of a nonlinear dynamical system for which detailed studies are feasible.[1,2] Much attention has therefore been focused on the details of its chemistry, and in particular the control mechanisms that inhibit the autocatalytic step,[3-7] making complex behavior possible.

The major control species is bromide, as demonstrated in the landmark paper of Field, Körös, and Noyes.[8] To study the possibility of other control mechanisms, several investigators have added silver ions to precipitate the bromide. A review of these experiments is given in ref 9. There has been a controversy, also explained in ref 9, about whether the rate of silver bromide precipitation is fast enough for this method to be effective. Bromide production is a dynamic process, so the rate of precipitation is more important than the equilibrium solubility constant. It has been pointed out[10] that the maximum concentration of silver ions that can be used without precipitating silver bromate is fairly low, since the solubility product[11] for $AgBrO_3$ is 5.8×10^{-5}. Hence the rate of precipitation cannot be made arbitrarily high.

The effect of silver perturbations on the BZ reaction depends on the relative rates of the following reactions:

$$Br^- + BrO_3^- + 2H^+ \rightleftharpoons HBrO_2 + HOBr \tag{1}$$

$$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr \tag{2}$$

$$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O \tag{3}$$

$$Br^- + Ag^+ \rightleftharpoons AgBr(s) \tag{4}$$

Equation 4 is not elementary, as the precipitation requires several steps to form molecules, complexes, and nuclei.[12-14]

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TABLE I: Effective Rate Constant for Bromide Removal, $k_{4,\text{eff}}$, for Various Initial Conditions

run	$[H_2SO_4]_0$, M	$[BrO_3^-]_0$, M	$[Ag^+]_0$, mM	$[Br^-]_0$, mM	AgBr formed, mM	$10^{-3}k_{4,\text{eff}}$, $M^{-1} s^{-1}$
A	1	0	0.4	0.4	0.404	
B	1	0.025	0.4	0.4	0.224	1.8
C	1	0.050	0.4	0.4	0.188	2.3
D	1	0.100	0.4	0.4	0.184	4.2
E	1	0.025	0.8	0.8	0.555	1.9
F	1	0.050	0.8	0.8	0.468	2.0
G	2	0	0.8	0.8	0.796	
H	2	0.025	0.8	0.8	0.298	1.5
I	2	0.050	0.8	0.8	0.286	2.8
J	3	0	1.6	1.6	1.58	
K	3	0.025	1.6	1.6	0.492	1.3
L	1	0.025	1.6	1.6	1.24	1.6

However, it is of value for BZ studies to consider eq 4 to be an overall reaction with a rate constant for the effective removal of bromide from the solution.[13,14]

One previous work[14] investigated the competition between $HBrO_2$ and Ag^+ for reaction with Br^-. From spectroscopic measurement of the amount of Br_2 produced, Försterling and Schreiber concluded that the rate constant for reaction 4 must be less than 3×10^4 M^{-1} s^{-1}, assuming standard rate constants for the oxybromine chemistry.[15]

In this paper we present an alternate method for determining the effective rate constant for bromide removal by silver in the presence of the oxybromine species of the BZ reaction. We mixed bromide, bromate, silver, and sulfuric acid and measured the amount of silver bromide produced. Numerical integration of eqs 1–4 with varying rate constants for eq 4 indicated the best value for the experimental data.

Experimental Section

Materials. All chemicals were reagent grade, and all solutions were prepared from distilled, deionized water. H_2SO_4 (Baker), NaBr (MCB), and $AgNO_3$ (Baker) were used without further purification. $KBrO_3$ (Baker) was recrystallized twice from distilled, deionized water.

Formation and Isolation of Silver Bromide. All experiments were performed at room temperature, 23 ± 1 °C. A 1-L solution containing the desired concentrations of $AgNO_3$, $KBrO_3$, and H_2SO_4 was prepared for each run. To this solution, a small amount (1.6 mL or less) of stock NaBr solution was injected, to obtain the desired initial concentration of Br^-. The yellow color of Br_2 appeared immediately upon injection. The solution was stirred for 20 s and then immediately filtered through a previously weighed cellulose nitrate membrane, with pore size of 0.45 μm. The filtering process took about 5 min. The membrane with AgBr was then dried to constant weight.

To determine how much AgBr could have been lost by passing through the filter or other experimental error, the runs were then repeated without the $KBrO_3$. All the AgBr was recovered in the precipitate, to an accuracy of 1% or better.

Numerical Predictions

Equations 1–4 were integrated numerically by using the rate constants of Field and Försterling[15] for the oxybromine chemistry. The concentration of H^+ was taken from ref 16. The forward rate constant for eq 4 was varied for each set of initial conditions, to find the best fit to the data. The reverse rate constant was calculated from the solubility constant: $k_{-4} = K_{sp}k_4$. K_{sp} was taken as[11] 7.7×10^{-13}. The activity of AgBr was taken to be 1.
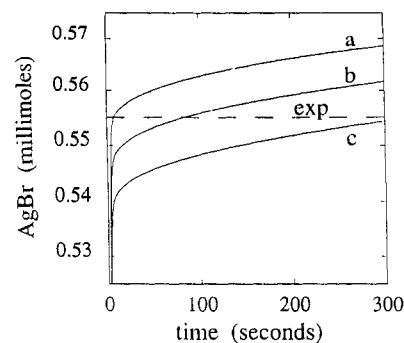

Figure 1. Computer simulation showing how the effective rate constant for bromide removal, $k_{4,\text{eff}}$, was determined for run E of Table I. The three solid curves show AgBr as a function of time, as calculated from eq 1–4 for three values of $k_{4,\text{eff}}$, all in M^{-1} s^{-1}: (a) $k_{4,\text{eff}} = 2.0 \times 10^3$, (b) $k_{4,\text{eff}} = 1.9 \times 10^3$, (c) $k_{4,\text{eff}} = 1.8 \times 10^3$. The dotted line (labeled exp) is the experimental value. The initial conditions for both experiment and calculations were $[H_2SO_4]_0 = 1$ M, $[BrO_3^-]_0 = 0.025$ M, $[Ag^+]_0 = [Br^-]_0 = 8 \times 10^{-4}$ M. For the experiment, the filtering process was begun at 20 s and finished at approximately 300 s.

The effects of bromine loss to the air were tested by adding a fifth equation:

$$Br_2 \rightarrow Br_2(\text{gas}) \qquad (5)$$

The rate constant for reaction 5 was taken as 2×10^{-2} s^{-1}, which is the highest value given in ref 17 for a solution with nitrogen bubbling through to deliberately remove the Br_2. The inclusion of reaction 5 made no difference in the resulting value of $k_{4,\text{eff}}$ within the two significant figure accuracy we report in Table I. Actually, the rate of bromine removal in our system should be much less than 2×10^{-2}, since our solution was exposed to air only at the free surface, while the data of ref 17 were taken with a flow rate of 140 cm^3 min^{-1} through a solution of volume 6 cm^3. So we assume no loss of Br_2 as a good approximation for our system.

The simulations show that most of the AgBr is formed in the first few seconds. Some additional AgBr is formed as bromine hydrolysis, the reverse reaction of eq 3, releases Br^-. Ideally, we would like to filter the solution instantaneously at some time after the start of the reaction, but the real filtering process takes about 5 min. A reasonable estimate for the effect of the finite filtering time is to take the value for AgBr formed in the middle of this time.

Figure 1 illustrates how the effective rate constant for bromide removal, $k_{4,\text{eff}}$, was determined. This figure shows simulations of the AgBr formed as a function of time for initial conditions $[H_2SO_4]_0 = 1$ M, $[BrO_3^-]_0 = 0.025$ M, and $[Ag^+]_0 = [Br^-]_0 = 8 \times 10^{-4}$ M. The three curves represent three possible values of $k_{4,\text{eff}}$, all in M^{-1} s^{-1}: (a) 1.8×10^3, (b) 1.9×10^3, and (c) 2.0×10^3. The experimental value for the AgBr formed for these conditions is 5.55×10^{-4} M. We choose 1.9×10^3 M^{-1} s^{-1} as the best value for the rate constant, with an error of $\pm 0.1 \times 10^3$.

Results and Discussion

Table I summarizes the results. The effective rate constant for Br^- removal depends on the initial concentrations of Ag^+, BrO_3^-, and H^+. This result supports the idea that AgBr precipitation is a complicated process.[13,14] Thus, using a single effective rate constant for bromide removal is not entirely justified. However, we see that for a range of initial conditions the effective rate constant is of the order of 10^3, consistent with the results of Försterling et al.[14]

Ruoff et al.[18-20] have shown that oscillations in the Belousov–Zhabotinskii reaction can still be controlled by bromide in the

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presence of excess silver ions, in the concentrations typically used,[21] if the rate constant for removal of Br⁻ by Ag⁺ is 10^4 M⁻¹ s⁻¹ or less. Thus our results support the conclusions of Ruoff[18-20] and of Noyes et al.[9] that observation of oscillations in the presence of silver is not sufficient evidence for alternate control mechanisms.

From Table I, we see that the expected amount of AgBr is formed and recovered in the absence of BrO_3^-. With added BrO_3^-, roughly half of the Br⁻ is prevented from precipitating. We believe that the Br⁻ not found in the precipitate is converted mainly to Br_2, according to eqs 1–3. Försterling and Schreiber[14] have already measured the formation of Br_2 in a similar experiment. Our results for the effective rate of Br⁻ removal as AgBr, obtained by weighing the AgBr precipitate, are in agreement with their results, obtained

by spectroscopically following the formation of Br_2.

The surprisingly low value of the effective bromide removal rate constant found in our experiments indicates that addition of silver ions to the BZ reaction is generally not effective in suppressing bromide control. Direct investigation of mechanisms involving other control intermediates, such as malonyl radicals,[4] is to be preferred. Also there exist concentration regimes where the bromide concentration is too low to inhibit the autocatalytic reaction.[6]

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Solvent Effects on the a_g C=C Stretching Mode in the $2^1A_g^-$ Excited State of β-Carotene and Two Derivatives: Picosecond Time-Resolved Resonance Raman Spectroscopy

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Picosecond time-resolved resonance Raman spectra in the C=C stretching region are presented for β-carotene and two of its derivatives, β-apo-8'-carotenal and ethyl β-apo-8'-carotenoate. The solvent effects on the Franck–Condon-active a_g C=C stretching mode in the $^1A_g^-$ ground state (S_0) and the $2^1A_g^-$ excited state (S_1) of each carotenoid are described. The C=C stretching frequencies in S_1 are affected by the solvent and show a correlation with the absorption maxima of the S_2 ($^1B_u^+$) ← S_0 transition, while those in S_0 are not significantly affected. These results are interpreted in terms of the vibronic coupling among the S_0, S_1, and S_2 electronic states, the solvent effect on the energy of the S_1 and S_2 states, and the structures of carotenoid molecules.

Introduction

Carotenoids have two important roles in photosynthetic systems: (i) photoprotection fulfilled by quenching the triplet state of either chlorophyll (Chl) or bacteriochlorophyll (Bchl), which thereby eliminates sources of harmful singlet oxygen, and by the direct quenching of singlet oxygen and (ii) light-harvesting involving singlet–singlet energy transfer from carotenoids to Chls or Bchls.[1,2] Carotenoids absorb light in the 400–500-nm region via the allowed transition from the $^1A_g^-$ ground state (S_0) to the $^1B_u^+$ excited state (S_2). Rapid internal conversion occurs subsequently from S_2 to the $2^1A_g^-$ excited state (S_1) with a time constant of <1 ps. Optical transitions between S_1 and S_0 are symmetry-forbidden, and the lifetime of S_1 is ≈10 ps in organic solvents.[3-5] It has been suggested that the singlet–singlet energy transfer from carotenoid to Chl (or Bchl) takes place from S_1 and not from S_2.[6-8] To more fully elucidate the energy-transfer mechanism, a detailed understanding of the photochemical properties and structures of S_1 excited states in a variety of carotenoids is necessary.

Chemically, carotenoids belong to the polyene group that includes retinals. The vibrational frequencies of S_1 in the shorter polyenes (i.e., the number of conjugated C=C bonds $N \leq 8$) have been studied by high-resolution fluorescence excitation spectra in polycrystalline matrices at liquid helium temperature.[9-13] In

these polyenes, the strongest C=C stretching band is found at much higher frequencies in S_1 (≥1700 cm⁻¹) than in S_0 (1500–1600 cm⁻¹). Recently, picosecond time-resolved resonance Raman (PTR³) spectra of some carotenoids also have revealed the same type of large frequency differences in the C=C stretching mode between S_0 and S_1.[14-19] These frequency differences have

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