

naphthalene ($K = 0.7-1.9$).¹⁵

To ensure that the observed T_1-T_n absorption spectra have the same origin at the different temperatures, the complete spectrum was recorded at 203 K. The only observed low-temperature change of the spectrum was a slight red shift (8 nm).

A summary of the thermodynamics is shown in Figure 7 (for ground-state and singlet-state energies see ref 7).

Comparison with Diphenylbutadiene Isomerization.¹⁶ The results presented in this paper are generally in accordance with those given by Yee et al. for the sensitized Z/E photoisomerization of 1,4-diphenylbutadiene. However, in their model bimolecular quenching of the excited triplet was suggested to give both E,E and (to a small extent) Z,E isomer, which is not necessary for our system. Although irradiation of ZZ with azulene present gives some ZE together with EE , the only product that is formed in quenched decay is EE . The unimolecular decay from the perpendicular triplet, ${}^3E_p^*$, is fast enough to compete with bimolecular quenching, and thus some ZE must be formed. The expected ratio between EE and ZE should be given by eq 9. From

$$[EE]/[ZE] = (k_{qAz}[Az] + (1 - \alpha)k_{Ep}K) / (\alpha k_{Ep}K) \quad (9)$$

this equation, with the experimentally obtained values of, k_{qAz} , $k_{Ep}K$, and α , the ratio is calculated as 59:1 at $[Az] = 1.8$ mM, which is in fair agreement with that experimentally observed, 68:1. If quenched decay occurred from ${}^3ZE^*$, a concentration dependence for the isomerization of EE would be expected. This is not observed.

It is remarkable to note that the excited triplet-state energy surfaces for diphenylbutadiene and for the investigated p -styrylstilbene are very similar, while the excited singlet-state energy surfaces are different. The singlet-state isomerization mechanism for diphenylbutadiene resembles an ordinary diabatic mechanism,

while for the p -styrylstilbene the mechanism is adiabatic (compare ref 7).

Conclusions and Outlook

We have previously shown that the singlet-state Z/E isomerization mechanism of p -styrylstilbene is different from the accepted diabatic one for stilbene Z/E isomerization. Here we have shown that also the triplet-state mechanism differs. Several possibilities of changing the commonly encountered diabatic mechanism to an adiabatic mechanism exist. As previously shown by Tokumaru and co-workers⁵ and later by Sandros and Becker,⁶ exchanging one of the benzene rings in stilbene for an anthryl group changes the Z/E photoisomerization mechanism from diabatic to adiabatic. The selection between a triplet-state diabatic and adiabatic mechanism for styryl arenes is stated to depend on the triplet energy of the arene.¹⁷ Therefore, we will investigate the effect of exchanging the central 1,4-phenylene, in the title molecule, for a 1,4-naphthylene, a 9,10-anthrylene, and a 4,4'-biphenylene, to see if this selection rule, between two-way and one-way isomerization, can be extended to bisstyryl aromatics or more precisely to see if any of the Z,Z isomers of these molecules show only a 2-fold but no single isomerization. The effect of extended conjugation on the mechanism, which seems to be important already in styrylstilbenes, will be pursued further simply by extending the conjugated chain from styrylstilbenes to bisstyrylstilbenes and so on.

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(15) Görner, H.; Eaker, D. W.; Saltiel, J. J. *Am. Chem. Soc.* **1981**, *103*, 7164.

(16) Yee, W. A.; Hug, S. J.; Kliger, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 2164.

(17) Arai, T.; Karatsu, T.; Misawa, H.; Kuriyama, Y.; Okamoto, H.; Hiresaki, T.; Furuuchi, H.; Zeng, H.; Sakuragi, H.; Tokumaru, K. *Pure Appl. Chem.* **1988**, *60*, 989. See also refs 5 and 6.

Further Evidence for Radical-Controlled Oscillations in the Belousov-Zhabotinskii Reaction: Large Effects of Ultraviolet Light and Silver Ions

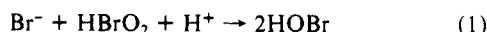
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We have performed experiments on the Belousov-Zhabotinskii reaction perturbed by ultraviolet light and by silver ions, and over a range of sulfuric acid concentrations, the reaction shows a large sensitivity to these perturbations. Our results support Försterling and Noszticzius' theory of malonyl radicals as a second control intermediate. Results of perturbation by both ultraviolet light and silver ions at the same time, however, are not adequately explained by either malonyl radical control or bromide control (or both) and suggest a third control intermediate such as bromomalonyl radicals.

Introduction

The possibility of non-bromide-controlled oscillations in the Belousov-Zhabotinskii reaction has been controversial for more than 10 years.¹ The original FKN mechanism² explained the oscillations in terms of a delayed negative feedback loop which inhibits the autocatalytic production of bromous acid, $HBrO_2$. The heart of the negative feedback loop is the reaction



Since oscillations continue in the presence of silver ions,³ it is necessary to assume either that the precipitation of silver bromide does not occur fast enough to interfere with reaction 1 or that a second negative feedback loop exists.

Försterling and Noszticzius⁴ recently proposed a second control loop

(1) Noyes, R. M.; Field, R. J.; Försterling, H. D.; Körös, E.; Ruoff, P. J. *Phys. Chem.* **1989**, *93*, 270.

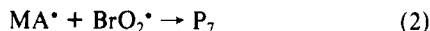
(2) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

(3) Noszticzius, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3660.

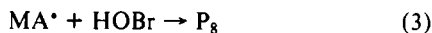
(4) Försterling, H. D.; Noszticzius, Z. *J. Phys. Chem.* **1989**, *93*, 2740.

* To whom correspondence should be addressed.

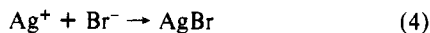
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where P_7 is presumed to be inert. They also reported another reaction which could play a significant role in the Belousov-Zhabotinskii system



where they speculated that P_8 might be bromide. On the other hand, Kshirsagar, Field, and Györgyi⁵ suggested that silver-perturbed oscillations could be adequately explained by bromide control. They studied the silver bromide precipitation reaction spectroscopically and concluded that their results were consistent with bromide removal equivalent to a rate constant of $\approx 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction



Ruoff⁶ had previously demonstrated that, in an Oregonator model, such a low rate constant would allow bromide control in the presence of silver perturbation. The value of the rate constant is still in dispute, however.⁷

Ionizing radiation has been shown⁸ to produce malonyl radicals, MA^\bullet , from malonic acid. Several studies⁹⁻¹¹ have demonstrated effects of irradiation on the dynamics of Belousov-Zhabotinskii systems. We have performed further experiments using silver ions to inhibit the bromide control loop and ultraviolet light to enhance the production of organic free radicals.

Experimental Section

Materials. All chemicals were reagent grade, and all solutions were prepared from distilled, deionized water. Sulfuric acid (H_2SO_4 , Baker), sodium bromide (NaBr , MCB), silver nitrate (AgNO_3 , Baker), and cerous sulfate ($\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, GFS) were used without further purification. Potassium bromate (KBrO_3 , Baker) was recrystallized twice from distilled, deionized water. Malonic acid ($\text{CH}_2(\text{COOH})_2$, Eastern Chemical) was recrystallized three times from acetone/chloroform and ethyl acetate.¹²

Electrochemical Experiments. All experiments were done in batch at laboratory temperature, $23 \pm 1^\circ \text{C}$, in ambient light. Magnetic stirring was provided. The reference was a double-junction Sensorex silver-silver chloride electrode. The overall redox potential was measured with a bright platinum electrode, and the bromide or silver ion concentration was measured with a silver-silver bromide electrode made in our laboratory, according to the procedure in ref 13. The potential of the silver bromide electrode at the AgBr solubility limit was $200 \pm 5 \text{ mV}$ in our experiments. We determined this value by calculating the mean of the electrode potentials measured in 10^{-5} M AgNO_3 and 10^{-5} M NaBr .

The cerous sulfate, malonic acid, sulfuric acid, and silver nitrate (when used) were first mixed, and then nitrogen was bubbled through the solution for at least 5 min. The run was then started by injection of potassium bromate solution, which had previously been purged with nitrogen. Nitrogen was bubbled through the reaction mixture for the duration of the run, to prevent oxygen effects. The initial concentrations were $[\text{CH}_2(\text{COOH})_2]_0 = 0.1 \text{ M}$, $[\text{Ce}_2(\text{SO}_4)_3]_0 = 0.0005 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{AgNO}_3]_0 = 0.001 \text{ M}$ (when used), and $[\text{H}_2\text{SO}_4]_0 = \text{variable, } 0.4\text{--}1.0 \text{ M}$. The total volume of solution was 60 mL in each run.

(5) Kshirsagar, G.; Field, R. J.; Györgyi, L. *J. Phys. Chem.* **1988**, *92*, 2472.

(6) (a) Ruoff, P. *Chem. Phys. Lett.* **1982**, *92*, 239. (b) Ruoff, P. *Z. Naturforsch., A* **1983**, *38A*, 974. (c) Ruoff, P.; Schwitters, B. *J. Phys. Chem.* **1984**, *88*, 6424.

(7) Hayes, D.; Schmidt, K.; Meisel, D. *J. Phys. Chem.* **1989**, *93*, 6100.

(8) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 12, 4214.

(9) Vavilin, V. A.; Zhabotinskii, A. M.; Zaikin, A. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1968**, *42*, 1649.

(10) Körös, E.; Putirskaya, G.; Varga, M. A. *Chim. Scient. Hung.* **1982**, *110*, 295.

(11) Gaspar, V.; Bazsa, G.; Beck, M. T. *Z. Phys. Chem. (Leipzig)* **1983**, *264*, 43.

(12) Noszticzus, Z.; McCormick, W. D.; Swinney, H. L. *J. Phys. Chem.* **1987**, *91*, 5129.

(13) Noszticzus, Z.; Wittmann, M.; Stirling, P. In *Proceedings of the 4th Symposium on Ion-Selective Electrodes at Matrafüred*; Pungor, E., Ed.; Elsevier: Amsterdam, 1985; p 579.

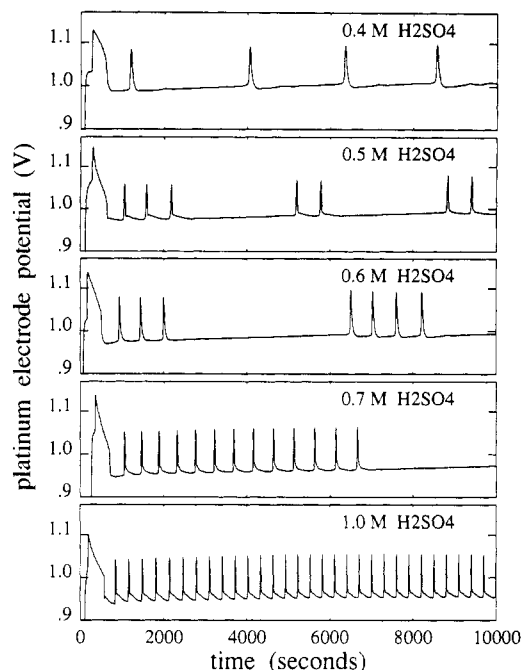


Figure 1. Unperturbed system. Platinum electrode potentials versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{H}_2\text{SO}_4]_0$ as indicated.

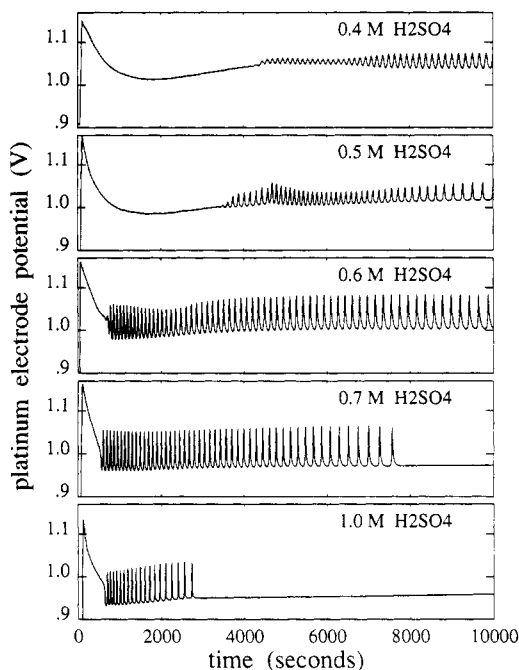


Figure 2. Silver ion perturbation. Platinum electrode potentials versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{AgNO}_3]_0 = 0.001 \text{ M}$, $[\text{H}_2\text{SO}_4]_0$ as indicated.

Spectroscopic Experiments. Light absorbances at 318 nm (λ_{max} for the Ce^{4+} ion) were measured in a Hewlett-Packard 8452A diode array spectrophotometer. The path length was 1 cm. Absorption by water was used as a reference. The experimental conditions were the same as in the electrochemistry experiments, except that the total volume of solution was 3 mL for each run. The spectrophotometer illuminates the sample with the full spectrum of light from a deuterium lamp, from 190 to 820 nm.

Results

Figures 1–4 show platinum electrode potentials and light absorbances versus time for experiments with and without silver, and with varying initial concentrations of sulfuric acid. The

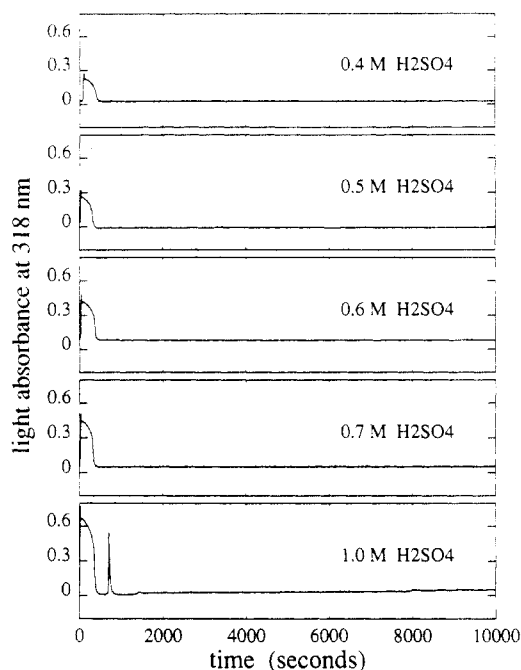


Figure 3. Ultraviolet light perturbation. Light absorbance versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{H}_2\text{SO}_4]_0$ as indicated.

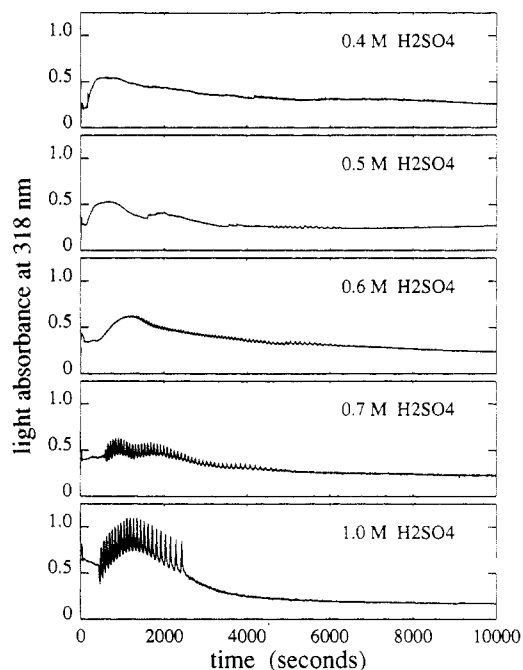


Figure 4. Perturbation by both silver ions and ultraviolet light. Light absorbance versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{AgNO}_3]_0 = 0.001 \text{ M}$, $[\text{H}_2\text{SO}_4]_0$ as indicated.

spectroscopic results for the experiments with silver are noisy, and the baselines are not flat, because of light scattering from the silver bromide precipitate. For the spectrophotometric runs without silver, the baseline is not always at zero because the reference was scanned in a different cell from the sample. The data of Figure 3 should be interpreted only as showing the absence of oscillations, not as demonstrating different final Ce^{4+} concentrations.

Figure 5 illustrates the platinum and silver–silver bromide electrode potential oscillations for a typical run without silver. Here the scale is changed to show data out to 50 000 s. Figure 6 shows the corresponding data for a run with silver perturbation.

Figure 7 shows AgBr electrode potentials versus time up to 30 000 s for the silver perturbation runs. The potential drops

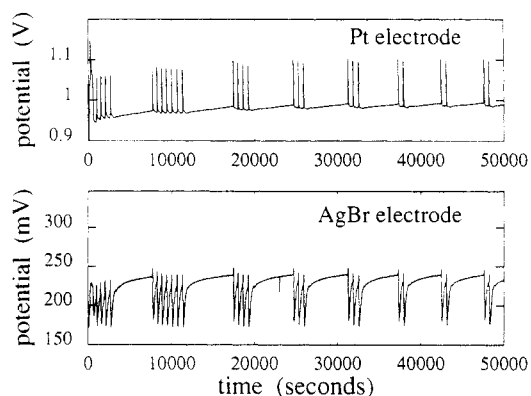


Figure 5. Unperturbed system. Platinum and silver bromide potentials versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.6 \text{ M}$.

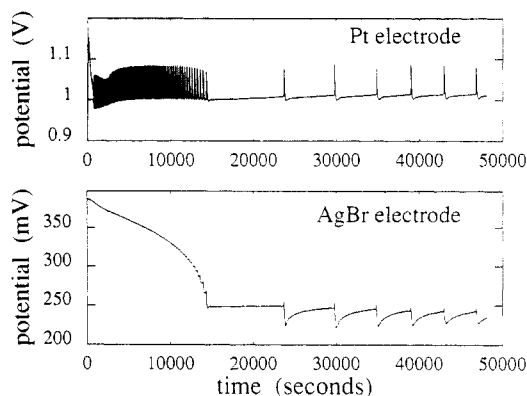


Figure 6. Silver ion perturbation. Platinum and silver bromide potentials versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{AgNO}_3]_0 = 0.001 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.6 \text{ M}$.

precipitously to about 250 mV when the silver has been consumed. At this point, $1 \times 10^{-3} \text{ M}$ bromide has been produced, in addition to the amount of bromide consumed in the competing reactions of the regular Belousov–Zhabotinskii system. We see in Figure 7 that the rate of bromide production changes dramatically with $[\text{H}_2\text{SO}_4]_0$, but the period of oscillations (as seen in Figure 2) is approximately constant.

We will discuss these results in terms of the malonyl radical reactions reported by Försterling and Noszticzius⁴ and the purely bromide-controlled model reviewed by Noyes et al.¹

Discussion

Bromide-Controlled Model. The idea of the bromide-controlled model for oscillations in the presence of silver ions is that the main effect of the precipitation reaction is to speed up the oscillations. In a typical oscillatory solution, the Belousov–Zhabotinskii reaction spends most of its time in the bromide consumption phase. If a reaction removes bromide at a rate comparable to the rate of removal by the usual Belousov–Zhabotinskii reactions, then this additional reaction will shorten the bromide consumption phase and accelerate the beginning of the next cycle. The result is an increase in oscillation frequency.

In Noszticzius' original experiment,³ addition of silver ions did increase the frequency of Belousov–Zhabotinskii oscillations. Noszticzius assumed that the precipitation of silver bromide (reaction 4) was essentially instantaneous, so that reaction 1 could not occur to any appreciable extent. With this assumption, bromide control was impossible and a second control mechanism had to be postulated.

Most of the controversy about the possibility of non-bromide-controlled oscillations¹ concerns the rate of bromide removal by reaction 4. However, regardless of the assumed rate constant, we do not expect this model to predict a change from

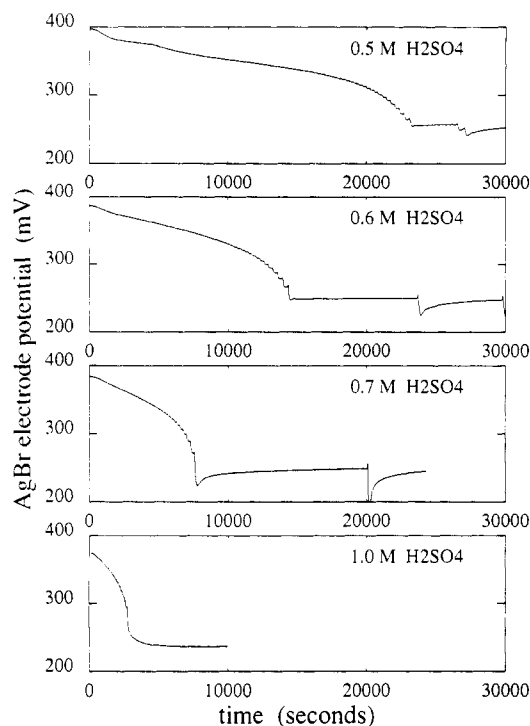


Figure 7. Silver ion perturbation. AgBr electrode potentials versus time for batch reactions with the following initial conditions: $[\text{malonic acid}]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{KBrO}_3]_0 = 0.015 \text{ M}$, $[\text{AgNO}_3]_0 = 0.001 \text{ M}$, $[\text{H}_2\text{SO}_4]_0$ as indicated. Note that the time scale is different from Figure 2.

the complex oscillations shown in Figure 5 to the simple ones shown in the first part of Figure 6 (before the silver is consumed), simply by the addition of a bromide-consuming reaction.

Without silver, we see in Figure 1 that the oscillations develop from very long period (about 2500 s) to shorter period (about 500 s) through a sequence of intermittently oscillating patterns as the concentration of sulfuric acid increases. With silver, the oscillations are all about the same period, regardless of sulfuric acid concentration, and never show the complex pattern of long and short intervals in the reduced state. Further, by comparing Figures 2 and 7, we note that the rate of bromide production has little effect on the period of oscillations. In fact, for initial sulfuric acid concentrations from 0.6 to 1.0 M, the initial period of oscillations is constant at 91 s while the time required to produce $1 \times 10^{-3} \text{ M}$ bromide decreases by an order of magnitude.

It appears more likely that the oscillations of Figure 2 are controlled by a negative feedback loop other than bromide, while the more complicated oscillations in Figure 1 are controlled by competing bromide and non-bromide feedback loops.

Malonyl Radical Reactions. Reaction 2 should inhibit the autocatalytic reaction and therefore drive the system toward the reduced state. If reaction 3 produces bromide, it should have the same effect. Ultraviolet light may be expected to enhance the production of malonyl radicals and therefore increase the amount of time the system spends in the reduced state. This effect is dramatically evident in Figures 1 and 3.

The situation when silver ions are present is more complicated. Ultraviolet light inhibits oscillations at low sulfuric acid concentrations but speeds them up somewhat at higher concentrations. The increase in frequency caused by light cannot be explained by any of the reactions considered so far.

Possible Role of Bromomalonyl Radicals. When silver ions are added, the induction time before the onset of oscillations is a strong function of sulfuric acid concentration. In contrast, sulfuric acid concentration has no significant effect on the induction time in the absence of silver. The induction time has been attributed¹⁴ to the production of bromomalonic acid. If a certain concentration of bromomalonic acid is necessary to initiate oscillations, then the dependence of induction time on $[\text{H}_2\text{SO}_4]_0$ should be as in Figure 2, since the reactions producing bromine² consume H^+ . But why should bromomalonic acid be necessary? Field et al.² assumed it is the source of bromide. However, Varga, Györgyi, and Körös have demonstrated by isotopic labeling techniques¹⁵ that the main source of bromide is the bromate, not the bromomalonic acid. Furthermore, we see that, in the absence of silver, the induction time is independent of H^+ .

What then is the role of bromomalonic acid? Our results indicate that it is especially important in the absence of bromide. Thus, it may provide a control mechanism to inhibit the autocatalytic production of HBrO_2 , independent of the bromide negative feedback loop. By analogy with Försterling and Noszticzius' results,⁴ we suspect that bromomalonyl radicals consume BrO_2^* radicals. However, this is not sufficient to explain the increase in frequency when ultraviolet light perturbation is added to the silver perturbation. Further experiments are in progress to explore the role of bromomalonic acid.

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(14) Burger, M.; Körös, E. *J. Phys. Chem.* **1980**, *84*, 496.

(15) Varga, M.; Györgyi, L.; Körös, E. *J. Am. Chem. Soc.* **1985**, *107*, 4780.