# Reaction of Bromous Acid with Bromide in the Presence of Silver Ions

H. D. Försterling and H. Schreiber
Fachbereich Physikalische Chemie, Philipps-Universität Marburg

Z. Naturforsch. **43a**, 956–960 (1988); received August 8, 1988

The reaction $HBrO_2 + Br^- + H^+ \rightarrow 2\,HOBr$, which is the most important control reaction in the Belousov-Zhabotinsky (BZ) system, is investigated in competition to the AgBr precipitation reaction $Ag^+ + Br^- \rightarrow AgBr$. It turns out that the bromite-bromide reaction starts even in the presence of $Ag^+$ in high concentration; the rate of consumption of bromite by bromide, however, is slowed down significantly if silver ions are present in the system. The experiments reveal that the AgBr precipitation reaction proceeds in a series of several steps, starting with a fast equilibrium. This way different experimental results on the influence of silver ions on the kinetics of the BZ reaction may now be better understood.

*Keywords*: Belousov-Zhabotinsky Reaction, Bromous Acid, Bromide, Silver Bromide.

## Introduction

There is a current controversy about the influence of the AgBr precipitation reaction

$$Br^- + Ag^+ \rightarrow AgBr \tag{R1}$$

on the oscillations of a Belousov-Zhabotinsky (BZ) system. The problem arose with the observation of Noszticzius [1] that a BZ oscillator works even in the presence of an excess of silver ions although no potential change of a bromide sensitive electrode can be detected. This result cannot be explained within the theory of Field, Körös, and Noyes (FKN) [2], if $Br^-$ is removed fast by the $Ag^+$ present in the system; in this case it is expected that the control reaction

$$Br^- + HBrO_2 + H^+ \rightarrow 2\,HOBr \tag{R2}$$

cannot start, and no oscillations should occur. Recently Schwitters and Ruoff [3] proposed that (R1) may be not as fast as assumed so far; calculations based on the Oregonator model (with (R1) included) led to oscillations if $k_1 = 1 \times 10^4\ M^{-1}\,s^{-1}$ was assumed. In the meantime, electrochemical experiments on (R1) performed by Noszticzius et al. [4, 5] indicated that $k_1$ must be at least $5 \times 10^7\ M^{-1}\,s^{-1}$. On the other hand, electrochemical experiments by Varga and Körös [6] and by Ruoff et al. [7] resulted in a low value of $k_1$ ($k_1 < 1 \times 10^4\ M^{-1}\,s^{-1}$). Khirshagar, Field, and Györgyi [8] were able to show by spectroscopic experiments that the AgBr precipitation process is much more complex than assumed so far, and that (R1) is initiated by a nearly diffusion controlled step. A critical discussion of the different points of view is given by Noyes et al. [9].

In our experiment we investigate the competition of (R1) and (R2) directly. A solution of NaBr is injected into a solution containing $HBrO_2$ and $AgNO_3$ simultaneously (reaction medium 1 M sulfuric acid). HOBr is expected as a reaction product according to (R2), which forms $Br_2$ in a consecutive reaction:

$$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O. \tag{R3}$$

Since (R3) is fast [10], (R2) and (R3) may be combined leading to the overall reaction

$$3\,Br^- + HBrO_2 + 3\,H^+ \rightarrow 2\,Br_2 + 2\,H_2O. \tag{R4}$$

In the presence of $Ag^+$, part of the bromide will react according to (R1) resulting in a $Br_2/Br^-$ ratio lower than the value 2/3 expected from (R4).

In order to obtain a simple kinetic behavior, $HBrO_2$ and $AgNO_3$ are applied in excess compared to NaBr. This way $[HBrO_2]$ and $[Ag^+]$ are kept nearly constant, and (R1), (R2) can be treated as first order reactions.

$$d[Br^-]/dt = -(k_1' + 3k_2')\,[Br^-]$$

$$\text{((R3) included)}, \tag{1}$$

$$[Br^-] = [Br^-]_0 \exp[-(k_1' + 3k_2')\,t], \tag{2}$$

$$d[Br_2]/dt = 2k_2'\,[Br^-], \tag{3}$$

$$[Br_2] = [Br^-]_0 [1 - \exp[-(k_1' + 3k_2')\,t]] \times 2k_2'/(k_1' + 3k_2'), \tag{4}$$

($k_1' = k_1\,[Ag^+]_0$; $k_2' = k_2\,[HBrO_2]_0$; $[Ag^+]_0$, $[HBrO_2]_0$, $[Br^-]_0$ = initial concentrations).

---

Reprint requests to Prof. Dr. H. D. Försterling, Physikalische Chemie, Fb 14, Universität Marburg, Hans-Meerwein-Str., D-3550 Marburg/L, FRG.

0932-0784 / 88 / 1100-0956 $ 01.30/0. – Please order a reprint rather than making your own copy.

For $t \to \infty$ we obtain ($[Br_2]_\infty$ = bromine concentration after the completion of (R1), (R2), (R3)):

$$[Br_2]_\infty = [Br^-]_0\, 2k'_2/(k'_1 + 3k'_2). \quad (5)$$

## Experiments

$H_2SO_4$ (96%), NaBr and $AgNO_3$ (all Fluka pa. grade) were used without further purification. $NaBrO_2$ was prepared following the procedure of Noszticzius et al. [11]. All experiments were performed at room temperature (22–24 °C). Solutions of $NaBrO_2$ (in 0.02 M NaOH) and of NaBr (in 1 M $H_2SO_4$) were subsequently injected into a solution containing $AgNO_3$ (in 1 M $H_2SO_4$) at different initial concentrations. The formation of $Br_2$ was detected by its absorbance at 401 nm using the dual wavelength technique [12]. A difficulty with this experiment is the disproportionation of the $HBrO_2$ formed immediately after the injection of $NaBrO_2$ into 1 M $H_2SO_4$:

$$2\,HBrO_2 \rightarrow HOBr + HBrO_3 \quad (R5)$$

with $k_5 = 3000\,M^{-1}\,s^{-1}$ [13]. In order to avoid a fast decay of $HBrO_2$ before the addition of NaBr, a low concentration $[HBrO_2]_0 = 1 \times 10^{-5}$ M, which is also a typical value for the BZ system, was chosen; at this concentration the half-life of $HBrO_2$ is about 30 s, long enough compared to the delay of about 2 s before the NaBr-injection. The initial concentration of NaBr was $1 \times 10^{-5}$ M, hence only 1/3 of the $HBrO_2$ disappears according to (R2) and (R3), and (R2) may be approximately treated as a first order reaction.

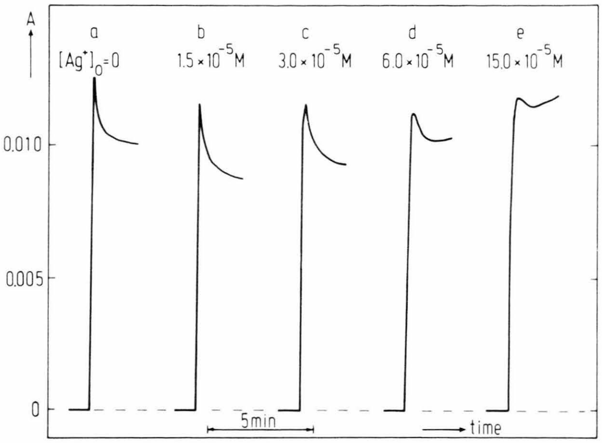

Fig. 1. Injections of 640 µl 0.0021 M $NaBrO_2$ (solved in 0.02 M NaOH) and of 136 µl 0.01 M NaBr (solved in 1 M $H_2SO_4$) into 136 ml 1 M $H_2SO_4$ (resulting initial concentrations $[HBrO_2]_0 = 9.88 \times 10^{-6}$ M, $[Br^-]_0 = 1 \times 10^{-5}$ M) containing different initial concentrations of $AgNO_3$: $[AgNO_3]_0 =$ 0, 1.5, 3.0, 6.0, 15.0 $\times 10^{-5}$ M for curves a–e. The absorbance $A$ is measured at 401 nm (dual wavelength technique, reference wavelength 601 nm, optical path length 10.8 cm). The experiments were performed at room temperature (22–24 °C).

The absorbance change A in the absence of $AgNO_3$ is displayed in Fig. 1 (curve a). A fast rise to A = 0.0127 is observed. This value corresponds to a concentration $[Br_2] = 6.85 \times 10^{-6}$ M (optical path length 10.8 cm, extinction coefficient of $Br_2$ at 401 nm $\varepsilon = 172\,M^{-1}\,cm^{-1}$) in good agreement with the expected value $(2/3) \times 10^{-5}\,M = 6.66 \times 10^{-6}$ M. Within 5 min there is a slow decay of $A$ due to the reaction of excess $HBrO_2$ with $Br^-$ formed by (R-3); this decay is finished after the completion of the disproportionation reaction (R5). Essentially the same kinetics is observed if the experiment is repeated with $[Ag^+]_0 = 1.5 \times 10^{-5}$ M to $6.0 \times 10^{-5}$ M (Fig. 1, curves b–d). If $[Ag^+]_0$ is increased to $15 \times 10^{-5}$ M (Fig. 1, curve e), however, the absorbance $A$ increases again after the completion of (R2), (R3); this fact is due to the light scattering of AgBr particles formed during the experiment, indicating that the solubility product of AgBr is exceeded. At higher initial concentrations of $Ag^+$ the completion of (R2), (R3) cannot be followed in this series of experiments, since the light scattering effect dominates over the absorbance change due to $Br_2$.

It turned out that the light scattering effect can be reduced by using a lower NaBr initial concentration $[NaBr]_0 = 2.0 \times 10^{-6}$ M instead of $1 \times 10^{-5}$ M; moreover, the first order approximation in (1) to (5) is better justified in this case (less than 7% of the $HBrO_2$ is consumed by bromide). The results of a series of experiments starting with this lower bromide concentration are displayed in Figure 2. In the absence of $AgNO_3$, the maximum absorbance $A = 0.0024$ (corresponding to $[Br_2]_\infty = 1.3 \times 10^{-6}$ M) is obtained, followed by a slow decay again (Fig. 2, curve a). No light scattering is observed below $[Ag^+]_0 = 14.8 \times 10^{-4}$ M (Fig. 2, curves b–d). For comparison, the influence of light scattering on the absorbance $A$ was investigated separately. Into an $AgNO_3$-solution (concentration $1.5 \times 10^{-5}$ M) NaBr-solutions were injected. The response on added $Br^-$ ($[Br^-]$ = 7, 14, 21, 28, 35 $\times 10^{-7}$ M) is displayed in Fig. 3 (injections 1 to 5). The effect of light scattering in Fig. 2 (curve d) is comparable to case 3 in Fig. 3, indicating that a significant

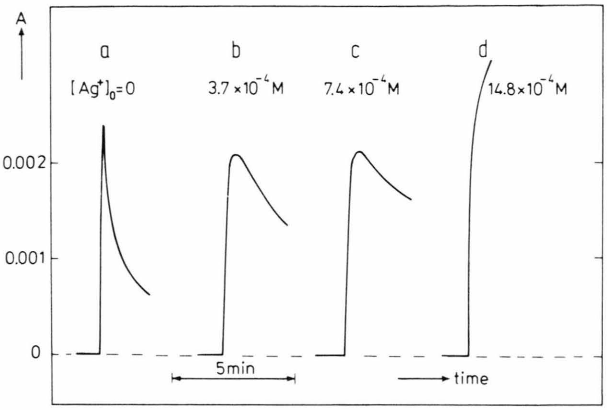

Fig. 2. Same experiment as in Fig. 1 with lower concentration of NaBr (injection of 54 µl 0.005 M NaBr; resulting initial concentrations $[HBrO_2]_0 = 9.88 \times 10^{-6}$ M, $[Br^-]_0 = 2 \times 10^{-6}$ M). $[Ag^+]_0 = 0$, 3.7, 7.4, $14.8 \times 10^{-4}$ M.

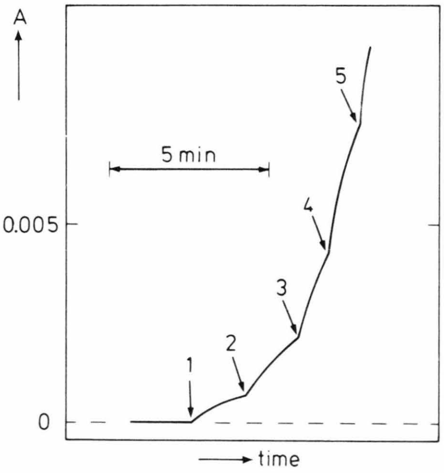

Fig. 3. Change of the absorbance $A$ at 401 nm due to the light scattering of AgBr particles. At points 1 to 5 100 µl of a 0.001 M NaBr solution were injected into 136 ml of 1 M $H_2SO_4$ containing $AgNO_3$ ($[Ag^+]_0 = 1.5 \times 10^{-5}$ M) resulting in bromide concentrations of 7, 14, 21, 28, $35 \times 10^{-7}$ M.

fraction of injected $Br^-$ has reacted via (R1). On the other hand, no light scattering effect is to be seen in curves b–c of Figure 2. From this result we conclude that the contribution of $k'_1$ in (5) is small compared to $3k'_2$ for $[HBrO_2]_0 = 1 \times 10^{-5}$ M and $[Ag^+]_0 = 7.4 \times 10^{-4}$ M.

Hence

$$k_1 < (3k_2 \times 10^{-5}\,\mathrm{M})/(7.4 \times 10^{-4}\,\mathrm{M}) = 0.04\,k_2 .$$

$k_2 = 7 \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$ was measured by Ariese and Nagy [14] for reaction (R2) in 1 M $H_2SO_4$. This way we obtain $k_1 < 3 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$.

## Discussion

From our experiments it is evident that at $[HBrO_2]_0 = 1 \times 10^{-5}$ M the control reaction (R2) is not inhibited by the AgBr precipitation reaction (R1) even at $[Ag^+]_0 = 7.4 \times 10^{-4}$ M. The derived value $k_1 < 3 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$ seems to be in good agreement with the results of Varga and Körös [6], and Ruoff et al. [7], but in disagreement with the high value $5 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}$ obtained by Noszticzius et al. [4, 5] and with the diffusion controlled value $k_1 = 1 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ estimated by Kshirsagar, Field and Györgyi [8] for the initial step of (R1).

A closer inspection of our experiments, however, reveals that the situation is more complex than assumed in deriving (1) to (5). First, the concentrations $[Br_2]_\infty$ obtained in Figs. 1 and 2 are 10–20% lower in the presence of silver ions (Fig. 1, curves b–d; Fig. 2, curves b–c) although no light scattering due to AgBr particles is to be observed. Secondly, the rise time of the absorbance $A$ increases significantly with increasing $[Ag^+]_0$. This effect is shown in more detail in Figure 4. In the absence of $Ag^+$ (Fig. 4, curve a) the maximum value of $A$ is reached after 3 s (due to the time constant of 0.5 s of the measuring system and to the process of mixing). With added $AgNO_3$ (Fig. 4, curve d) 15 s are required before the maximum value is reached. Both observations indicate that there must be a fast reaction of $Br^-$ with $Ag^+$ immediately after the injection of NaBr; this reaction must be reversible, and the rate of $Br_2$-formation must be connected with the removal of $Br^-$ from the primary reaction product. Anyway, the reversibility of the AgBr formation can easily be shown by adding $HBrO_2$ to a system already containing some AgBr sol; the light scattering disappears completely, and the final absorbance is due to $Br_2$.

In order to explain their experimental results, Kshirsagar, Field and Györgyi [8] discuss a fast starting reaction

$$Ag + Br^- \rightarrow (AgBr)_p \qquad \text{(R1 a)}$$

in which ion pairs $(AgBr)_p$ are formed; this reaction is followed by a slow consecutive reaction forming AgBr sol. They attribute a high rate constant $k_{1a} = 1 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ to the formation of $(AgBr)_p$ and they assume that $HBrO_2$ reacts with $(AgBr)_p$ at the same rate as with bromide. Regarding a slow back reaction ($k_{-1a} = 10\ \mathrm{s^{-1}}$) they obtain an extremely low bromide concentration (which cannot be monitored

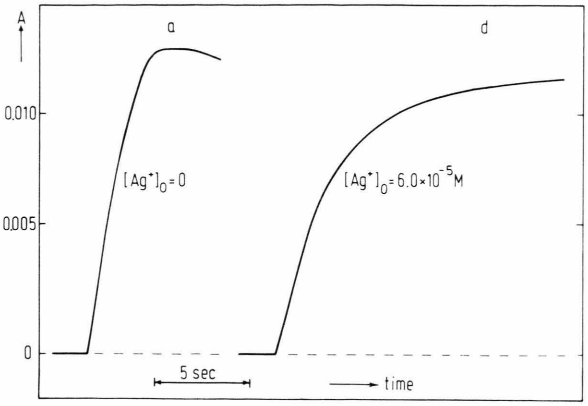

Fig. 4. Curves a and d from Fig. 1, time scale expanded by a factor of 60.

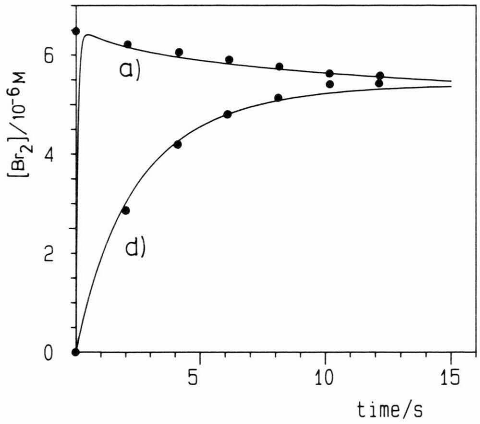

Fig. 5. Comparison of measured (dots) and calculated (solid lines) bromine concentrations as a function of time in cases a) and d) of Figure 4. The experimental curve a) was extrapolated to $t = 0$. Both experimental curves were corrected by a factor of 0.9 as outlined in the text. The concentration was calculated from the absorbance $A$ by using $d = 10.8$ cm for the optical path length and $\varepsilon = 172\ \mathrm{M^{-1}\,cm^{-1}}$ for the extinction coefficient of bromine.

The rate constants used in the calculations are:

$k_{1a} = 1 \times 10^{9}\ \mathrm{M^{-1}\,s^{-1}}$, $k_{-1a} = 1200\ \mathrm{s^{-1}}$,
$k_{2} = 5 \times 10^{5}\ \mathrm{M^{-1}\,s^{-1}}$, $k_{-2} = 2 \times 10^{-5}\ \mathrm{s^{-1}}$,
$k_{3} = 8 \times 10^{9}\ \mathrm{M^{-1}\,s^{-1}}$, $k_{-3} = 110\ \mathrm{s^{-1}}$,
$k_{5} = 3000\ \mathrm{M^{-1}\,s^{-1}}$, $k_{-5} = 1 \times 10^{-8}\ \mathrm{M^{-1}\,s^{-1}}$.

The initial conditions are the same as given in Fig. 1 ($[\mathrm{Br^-}]_0 = [\mathrm{HBrO_2}]_0 = 1 \times 10^{-5}$ M, $[\mathrm{Ag^+}]_0 = 0$ in case a) and $[\mathrm{Ag^+}]_0 = 6 \times 10^{-5}$ M in case d)). The set of differential equations was solved numerically by using Gear's method.

by a bromide sensitive electrode, as was found in the experiment of Noszticzius [1]); this way the bromide control of the BZ reaction is replaced by a $(\mathrm{AgBr})_p$ control.

Following these assumptions, the removal of $\mathrm{HBrO_2}$ by added bromide in our experiments is expected to be as fast as in the absence of $\mathrm{Ag^+}$. This conclusion is in contrast to our observation that the formation of $\mathrm{Br_2}$ is much slower in the presence of silver ions (Figure 4). A reasonable explanation of our results would be to treat (R1 a) as an equilibrium with a much higher value $k_{-1a}$ attributed to (R-1a) than assumed by Kishargar, Field and Györgyi [8]. This way $\mathrm{Br^-}$ may reach a higher level (high enough for (R2) to proceed at a reasonable rate, but low enough that $\mathrm{Br^-}$ cannot be detected by a bromide sensitive electrode). In this approach the BZ reaction would be still bromide controlled (although the net rate of (R2) would be reduced by the lower bromide concentration in the presence of silver ions), and it is not needed to assume a fast reaction of $(\mathrm{AgBr})_p$ with $\mathrm{HBrO_2}$.

In order to check our hypothesis, the experimental curves in Fig. 4 were compared to numerical calculations. There is one difficulty with curve a) in Fig. 4, since the time period up to 3 s cannot be measured because of the long rise time of the measuring system. Assuming that the slope of $A$ is similar at $t = 0 \div 3$ s as in the time period after reaching the maximum value, curve a) was extrapolated to $t = 0$; this way we obtain $A(t = 0) = 0.0139$. This is 10% more than expected for the formation of $0.666 \times 10^{-5}$ M $\mathrm{Br_2}$ (see experimental part). This deviation may be due to some bromide or NaOBr impurities in the $\mathrm{NaBrO_2}$ sample, but we think it is not a central problem within our considerations; for better comparison with calculated curves (on the basis of the same initial conditions as in the experiment), however, the $\mathrm{Br_2}$ concentration calculated from the measured absorbance $A$ was decreased by a factor of 0.90 as well in case a) as in case d) of Figure 4. First, numerical calculations were done for curve a) on the basis of (R2), (R3) and (R5). The rate constants used were the same as given by Field and Försterling [13] except $k_2$. With $k_2 = 7 \times 10^{5}\ \mathrm{M^{-1}\,s^{-1}}$ as measured by Ariese and Nagy [14] the decay of $[\mathrm{Br_2}]$ was found to be too fast, but experiment was in accordance with theory with $k_2 = 5 \times 10^{5}\ \mathrm{M^{-1}\,s^{-1}}$ (Fig. 5, curve a). Apparently, a more accurate estimation of $k_2$ is needed, but anyway the value $3 \times 10^{6}\ \mathrm{M^{-1}\,s^{-1}}$ as proposed in [13] seems to be too high. From measurements on the reaction of bromate with bromine Kshirsagar and Field [15] conclude that $k_{-3}$, the rate constant for the dissociation of $\mathrm{Br_2}$, must be much smaller than assumed so far for sulfuric acid reaction medium. Of course, a change of $k_{-3}$ would change the results of our calculations significantly; a direct estimation of $k_{-3}$, which is just in progress, does not support this hypothesis, however [16].

In the calculation of curve d) reaction (R1 a) was added; $k_{1a} = 1 \times 10^9\,M^{-1}\,s^{-1}$ was used as proposed in [8], but $k_{-1a}$ was increased from $10\,s^{-1}$ to $1200\,s^{-1}$. With these values theory and experiment agree very well (Fig. 5, curve d). Moreover, it is to be seen from Fig. 5 that the maximum value obtained for $[Br_2]$ must be smaller in the presence of $Ag^+$ (as can also be seen in Figs. 1 and 2), because $Br_2$ is removed according to (R-3) and (R2) for a longer time period before the maximum of the curve is reached.

## Conclusions

We have proved by our experiments that there must be a fast reversible primary step in the reaction of silver ions with bromide (equilibrium (R1a)) as was already found by Khirshagar, Field, and Györgyi [8]. This equilibrium, however, must be shifted much more to the left hand side than assumed in [8]. Our results indicate that $HBrO_2$ is directly removed by $Br^-$, and in order to explain our experiments it is not necessary at all to postulate a fast reaction of $(AgBr)_p$ with $HBrO_2$. Our hypothesis is supported by direct measurements of the rate constant $k_{1a}$ by Schmidt, Patel and Meisel [17] in a reaction medium of $1 \times 10^{-4}\,M$ perchloric acid. They find $k_{1a} = 1.3 \times 10^{10}\,M^{-1}\,s^{-1}$, which value is larger by one order of magnitude than assumed in our calculations. From a value of the equilibrium constant they deduce $k_{-1a} = 4.6 \times 10^5\,s^{-1}$, leading to a $k_{1a}/k_{-1a}$ ratio $3 \times 10^4\,M^{-1}$ compared to $8 \times 10^5\,M^{-1}$ as used in our calculations; there is still a difference of one order of magnitude, which, however, may be due to the different reaction media.

Of course, theories explaining silver ion disturbed oscillations in the BZ system should be in agreement with the experimental facts presented here. Khirshagar, Field, and Györgyi [8] were able to get oscillations within an extended Oregonator model including their basic assumptions. On the other hand, we were not able to see oscillations in a similar procedure if our basic assumptions (which are compatible with our direct experiments) are introduced into the same model. Maybe the situation regarding the silver ion effect is still more complicated than assumed so far. Another possibility would be that the BZ system is not exclusively bromide controlled. A second control intermediate might be the malonyl radical, as could be proven by Försterling and Noszticzius [18], which is not included in the silver ion disturbed Oregonator model so far.

### *Acknowledgements*

The authors wish to thank the Stiftung Volkswagenwerk, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

[1] Z. Noszticzius, J. Amer. Chem. Soc. **101,** 3660 (1979).
[2] R. J. Field, E. Körös, and R. M. Noyes, J. Amer. Chem. Soc. **94,** 8649 (1972).
[3] B. Schwitters and P. Ruoff, J. Phys. Chem. **90,** 2497 (1986).
[4] Z. Noszticzius and W. D. McCormick, J. Phys. Chem. **91,** 4430 (1987); – Z. Noszticzius and W. D. McCormick, J. Phys. Chem. **92,** 374 (1988).
[5] Z. Noszticzius, W. D. McCormick, H. L. Swinney, and Z. A. Schelly, Acta Polytechn. Scand. Ch **178,** 57 (1987).
[6] M. Varga and E. Körös, J. Phys. Chem. **90,** 4373 (1986).
[7] P. Ruoff, M. Varga, and E. Körös, J. Phys. Chem. **91,** 4431 (1987).
[8] G. Kshirsagar, R. J. Field, and L. Györgyi, J. Phys Chem. **92,** 2472 (1988).
[9] R. M. Noyes, R. J. Field, H. D. Försterling, E. Körös, and P. Ruoff, J. Phys. Chem. **92,** submitted.
[10] M. Eigen and K. Kustin, J. Amer. Chem. Soc. **84,** 1355 (1962).
[11] Z. Noszticzius, E. Noszticzius, and Z. A. Schelly, J. Chem. Phys. **87,** 510 (1983).
[12] H. D. Försterling, H. Schreiber, and W. Zittlau, Z. Naturforsch. **33a,** 1552 (1978).
[13] R. J. Field and H. D. Försterling, J. Phys. Chem. **90,** 5400 (1986).
[14] F. Ariese and Z. Nagy, J. Phys. Chem. **90,** 1496 (1986).
[15] G. Kshirsagar and R. J. Field, J. Phys. Chem., submitted.
[16] H. D. Försterling, S. Muranyi, and H. Schreiber, in preparation.
[17] K. H. Schmidt, R. Patel, and D. Meisel, J. Amer. Chem. Soc., **110,** 4882 (1988); D. Meisel, to be published.
[18] H. D. Försterling and Z. Noszticzius, J. Phys. Chem, submitted.