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Mechanistic Investigations of the BZ Reaction with Oxalic Acid Substrate. I. The Oscillatory Parameter Region and Rate Constants Measured for the Reactions of HOBr, $HBrO_2$, and Acidic BrO_3^- with Oxalic Acid

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This paper is the first part of a study reinvestigating the mechanism of the Belousov−Zhabotinsky (BZ) reaction of oxalic acid, which is the simplest organic substrate for a BZ oscillator. New experiments are performed to find the oscillatory region in 1 M sulfuric acid at 20 °C. The removal rate of the end product bromine by an inert gas stream is a critical parameter here: oscillations can be observed only in a window of that parameter. The "rate constant" for the physical removal of bromine is measured as a function of the gas flow rate and reactor volume; furthermore, the rate constants of three component reactions important in this system are also determined. These are oxygen atom transfer reactions to the oxalic acid substrate from Br(I) (hypobromous acid), from Br(III) (bromous acid), and from Br(V) (acidic bromate) compounds. In these second-order reactions, the partial order of each oxybromine species is 1. The measured rate constants are $k_I = 17 \pm 2\ M^{-1}\ s^{-1}$, $k_{III} = 4.2 \pm 0.5\ M^{-1}\ s^{-1}$, and $k_V = (7.47 \pm 0.1) \times 10^{-4}\ M^{-1}\ s^{-1}$. In the case of the HOBr−oxalic acid reaction, however, an additional parallel reaction route was found that has importance at higher HOBr concentrations. In the mechanism of that new route, the active species is Br_2O, and the reaction order is not 1 but 2 with respect to HOBr. The rate constant of this parallel reaction is $k_I^{(2)} = (1.2 \pm 0.2) \times 10^5\ M^{-2}\ s^{-1}$. The *k* values measured here are compared with those reported earlier. A comparison of experimental results with computer simulations shows that free radicals play a negligible role or no role in the mechanism of the oxygen atom transfer reactions studied here.

1. Introduction

This introduction discusses the preliminaries, motivations, and main objectives of a research program the first part of which is reported here.

1.1. Oxalic Acid in the Classical BZ Reaction. The classical version of the Belousov−Zhabotinsky[1] (BZ) reaction, the cerium ion catalyzed oxidation and bromination of malonic acid by acidic bromate, is the most studied chemical oscillator. This is because of the rich nonlinear temporal and spatial phenomena exhibited by this special system under various experimental conditions.[2−6] Thus, ever since it became widely known, there has been intense research to reveal the exact mechanism of the reaction.[7−12] Despite these efforts, some important details of the mechanism are still not known. This is due to the great number of possible organic molecular and especially radical intermediates[13−16] that can appear when the substrate is malonic acid. The Marburg−Budapest−Missoula (MBM) mechanism suggested recently[12] tried to incorporate all of the available information about the organic intermediates, but some open questions still remained. One is the role of oxalic acid in the mechanism as it was found that, both in the induction period[17] and in the oscillatory regime itself,[12] some oxalic acid intermediate is present in the reaction mixture.

1.2. Effect of Oxalic Acid on the Classical BZ Reaction. A main question is whether oxalic acid has a significant impact on the dynamics. Looking for an answer, we perturbed the BZ reaction by adding some oxalic acid to the system. As in a recent paper[18] we studied the effect of methanol on the BZ reaction, it was reasonable to compare the effect of the two perturbants and to perform perturbation experiments with the same BZ system but applying oxalic acid instead of methanol. (BZ systems are rather sensitive to methanol perturbations. This is because that perturbant reacts with acidic bromate in a direct reaction to yield bromous acid, which is the autocatalytic intermediate of the BZ reaction.) Preliminary results suggested that oxalic acid can be an even more effective perturbant than methanol and that its direct reaction with acidic bromate is most probably also faster than that of the other perturbant. Unlike methanol, however, oxalic acid in a BZ system can participate in other significant reactions as well. Thus, if we want to understand the role of oxalic acid in the classical BZ reaction, it is a prerequisite to determine all of its significant reactions in a BZ system. To this end, however, the best possible test base is not the classical BZ system with all of the complex organic chemistry of malonic acid but the more simple BZ oscillator with oxalic acid substrate.

1.3. Previous Research with Oxalic Acid Oscillators. The BZ reaction of oxalic acid is well-known;[19,20] it was discovered[19] as early as 1979. Oscillations with this substrate can be observed when a stream of inert gas (such as N_2 or H_2) is bubbled through the reaction mixture. The role of this inert gas stream is to remove the dissolved Br_2 produced in the reaction. In this way, semibatch experiments (applying a batch reactor with product removal) were performed in which the flow rate of the inert

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gas stream played the role of a dynamical parameter.[21] Gáspár and Galambosi[22] performed CSTR experiments without any gas stream: in that case, it was the liquid flow of the CSTR that removed the produced bromine. Another possibility for bromine removal is to apply a second substrate in addition to oxalic acid, such as acetone, that can be brominated.[23] Such mixed-substrate systems can exhibit various interesting dynamical phenomena already in a batch reactor and have been studied by many authors (see, e.g., refs 24−27).

1.4. Earlier Model Calculations. Despite the relative simplicity of the oxalic acid substrate system, only a few model calculations are available in the literature.[22,28−33] The first attempt was made by Bódiss and Field,[28] who suggested that the system is a so-called bromine-hydrolysis-controlled (BHC) oscillator. According to this model, the source of bromide ions is the hydrolysis of bromine. (Bromide ion is the control intermediate of the BZ reaction. When the substrate is malonic acid, then—in the classical models[7,8]—the source of the bromide ions is a reaction between Ce^{4+} and bromomalonic acid. If the substrate is oxalic acid, the bromide source should be of a different type, as no brominated organic intermediate can appear in that case.) A BHC-type Oregonator[8] model was applied by Gáspár and Galambosi[22] as well to rationalize the results of their CSTR experiments. The idea of bromine hydrolysis control was also applied by Field and Boyd (FB)[29] in the simulation of the oxalic acid−acetone mixed-substrate oscillator. An additional new feature of this model is the important role attributed to the carboxyl radical. The main source of this radical is a reaction between Ce^{4+} and oxalic acid. It is presumed that carboxyl radical can react with hypobromous acid to give a bromine atom and inert products. In the next step, this bromine atom can react further with oxalic acid to give again a carboxyl radical together with a bromide ion and more inert products. In other words, a bromide-producing chain reaction can appear in this way, which is an additional bromide source in the FB model. Bromine hydrolysis and the same bromide-producing chain reaction can also be found in the model of Sasaki[30]. Gáspár, Noszticzius, and Farkas[31] created a model in which an inflow of the autocatalytic bromous acid was added. That inflow was generated by a direct reaction between acidic bromate and oxalic acid. All of these models were reviewed critically by Ševčik and Hlaváčová,[32] who also suggested a new model with an optimum combination of the above reactions and rate constants.[33] However, it was a general conclusion of these studies that, although all of the various models were able to oscillate in certain parameter ranges, they all had difficulties in explaining some of the experiments.

1.5. Reasons To Reinvestigate the Oxalic Acid Oscillator. In addition to the above-mentioned difficulties of the various models, there are other reasons that support the idea that it is worthwhile to reinvestigate the BZ system with oxalic acid substrate by performing new experiments and model calculations. The following arguments can be mentioned:

(i) Some of the earlier model calculations[22,28,29] were made with an old set of rate constants[2,7,8] that were later revised by Field and Försterling.[34] Some further changes have been made since then (see, e.g., the MBM mechanism[12]). Currently, however, most of the reactions and rate constants of the inorganic subset of the BZ reaction are well established, and these data can be applied in the modeling of the oxalic acid oscillator as well.

(ii) Most of these rate constants were measured in 1 M sulfuric acid and at 20 °C, whereas previous experiments with the oxalic acid oscillator were performed mainly in 1.5 M sulfuric acid and at laboratory temperature (around 25 °C). Thus, it seemed reasonable to repeat the oxalic acid experiments in 1 M sulfuric acid and at 20 °C before comparing the experimental observations with the model calculations.

(iii) As previously mentioned, oxalic acid and carboxyl radicals also play an important role in the classical BZ oscillator. Thus, additional information about the BZ oscillator with oxalic acid can promote a better understanding of the classical BZ system as well.

(iv) The mechanism of this simple BZ oscillator contains only two organic reactants, namely, oxalic acid and carboxyl radical, but the information available about the rate constants of their reactions with the bromine species is limited. Thus, collecting more data in this area is necessary. It was realized that collecting such data is possible because at least some of these reactions can be studied separately with CO_2 and potentiometric measurements.

1.6. Objectives of the Present Work. The objectives of the present work are four-fold:

(i) The first objective is to examine the BZ reaction of oxalic acid in a semibatch reactor with N_2 gas flow as a control parameter to find the oscillatory parameter region of the reaction in 1 M H_2SO_4 at 20 °C. To follow the chemical oscillations, the CO_2 measuring technique applied previously[18,35] was chosen. Advantages of this technique are that it is sensitive and stable and the measured CO_2 evolution rate is proportional to the rate of the oxalic acid consumption.

(ii) The second objective is to measure the bromine removal rate from the same semibatch reactor as a function of the N_2 gas flow in separate experiments to assign a "rate constant" for the physical removal of bromine.

(iii) The third objective is to study some component reactions of the oxalic acid oscillator separately in subsystems that do not contain all the reactants of the oscillating system. There are two groups of these specific reactions depending on the organic reagent, which can be (a) oxalic acid or (b) carboxyl radical.

(a) In the case of oxalic acid, we could study only its reactions with molecular oxybromine species of oxidation numbers +1, +3, and +5, that is, with HOBr, $HBrO_2$, and BrO_3^-. These are the following oxygen atom transfer reactions

$$(COOH)_2 + HOBr \rightarrow 2CO_2 + H_2O + H^+ + Br^- \qquad (R.I)$$

$$(COOH)_2 + HBrO_2 \rightarrow 2CO_2 + H_2O + HOBr \qquad (R.III)$$

$$(COOH)_2 + HBrO_3 \rightarrow 2CO_2 + H_2O + HBrO_2 \qquad (R.V)$$

Thus, our objective was to measure k_I, k_{III}, and k_V, the rate constants of the above reactions.

Remarks on Previous Results for These Rate Constants.

(I) k_I has been measured[36] already but only between pH 3 and pH 6, where the important reactive species was the hydrogen oxalate ion. Here, in 1 M sulfuric acid, most of the oxalic acid is in an undissociated form, and no data were available about the reactivity of this species.

(III) We are not aware of any previous attempt to measure or estimate k_{III}.

(V) Ševčik et al.[37] determined k_V by polarography at a constant ionic strength of 2 M. Here, we measure k_V at a different ionic strength in 1 M H_2SO_4 and also with a different technique based on sensitive CO_2 measurements.

(b) Experiments and model calculations on the various reactions of the carboxyl radicals will be reported in a subsequent paper.[38]

(iv) Finally, we want to perform model calculations for the full oscillating system with all of the available and newly collected rate constants and compare the results with the new experiments reported herein. The results of these simulations will also be presented in a subsequent publication.[38]

2. Experimental Section

2.1. Chemicals. Oxalic acid (Reanal p.a.), $Ce(SO_4)_2 \cdot 4H_2O$ (Merck, p.a.), $NaBrO_3$ (Fluka, puriss), NaBr (Merck, p.a.), malonic acid (Fluka, puriss), and H_2SO_4 (97%, J.T. Baker) were used as received. All solutions were prepared with doubly distilled water. Hypobromous acid and bromine solutions (see later) were prepared freshly.

2.1.1. Preparation of Hypobromous Acid. (This procedure is a simplified and improved version of an earlier recipe.[39]) Three milliliters of H_2O and 5 mL of 97% H_2SO_4 were mixed in a wide test tube and cooled to a few degrees below 0 °C in an ice−saltwater bath. Then, 2 mL of 2 M $NaBrO_3$ solution was added dropwise under continuous stirring with a glass rod. (During this procedure, a light pink color appears, probably indicating the presence of some bromic acid anhydride.) In the next step, the test tube with the mixture was placed into a beaker containing hot water (about 40−50 °C), and the stirring with the glass rod was continued. First, the pink color became deeper, and then a more intense brown color appeared together with small bubbles of oxygen. Then, the oxygen evolution started to grow autocatalytically. The stoichiometry of the main overall reaction is

$$HBrO_3 \rightarrow HOBr + O_2$$

As the rate of the oxygen evolution became intense, some cooling with the ice−water bath was applied periodically to prevent the formation of a high foam column. The end of the vigorous oxygen evolution period was marked by the appearance of elemental bromine in larger amounts. At this point, to avoid further decomposition of the produced hypobromous acid to bromine, the reaction was stopped by diluting the mixture with water to 50 mL. The byproduct elemental bromine was removed by sucking air through the solution with an aspirator. An intense bubbling of air was continued for 15 min. Then, 44 mL of H_2O was added to obtain an HOBr solution in ∼1 M sulfuric acid. An aliquot of the light yellow HOBr solution prepared in this way was titrated with 0.01 M KBr solution. In the potentiometric titration, the indicator electrode was a silver wire coated with a thin layer of silver bromide.[40] The concentration of the freshly prepared stock solution was around $(2.2-2.4) \times 10^{-2}$ M.

2.1.2. Preparation of Aqueous Bromine−Bromide Solution. $NaBrO_3$ (0.25 mmol, 37.7 mg) and NaBr (1.5 mmol, 154.3 mg) were dissolved in 25 mL of 1 M sulfuric acid. The final concentrations were $[Br_2] = 0.03$ M and $[Br^-] = 0.01$ M.

2.2. Experimental Procedures Associated with CO_2 Measurements. *2.2.1. Apparatus for CO_2 Measurements.* The CO_2 measuring instrument was similar to the one applied in our previous experiments.[18,35] A nitrogen carrier gas containing the CO_2 removed from the reactor was mixed with a hydrogen gas flow (flow rate = 40 mL/min), and then the CO_2 was converted to methane on a nickel catalyst. Finally, the methane concentration of the gas mixture was measured by a flame ionization detector (FID). Further details of the method and the apparatus can be found in ref 35.

2.2.2. Calibration of the CO_2 Measuring Apparatus. The apparatus actually measures CO_2 flow rates. Thus, the calibration required a CO_2 source with a known output. Generation of CO_2 by electrolysis from an aqueous mixture of sulfuric and oxalic acids was applied for that purpose.[35] The electric current was controlled by an electronic current generator.

The sensitivity of the flame ionization detector depends on the H_2 and N_2 flow rates. Therefore, calibration was repeated for each flow rate applied in the experiments.

2.2.3. Reactor. A double-walled glass test tube (inner diameter = 7 mm, total volume = 5 mL) was used as the reactor. It was thermostated to 20 °C. The carrier gas was introduced via a narrow Teflon tubing (outer diameter = 1.7 mm, inner diameter = 0.8 mm) at the bottom of the reactor.

2.2.4. Injection of the Reactants into the Reactor. Role of the Carrier Gas. The reactants were injected using a plexiglass injector. A similar one was applied in a previous work[18] of our laboratory, but in that case, the reaction components were injected via a silicon rubber septum. Here, a piston valve was applied that could be opened by pushing the tip of the plastic syringe containing the reagent. In this way, the reactants could be injected into the nitrogen carrier gas without using a metallic needle. (We found that even trace amounts of metal ions from the needle can affect the reaction dynamics.) The gas stream played multiple roles here: it carried the liquid reactants to the reactor; created anaerobic conditions there; provided constant stirring of the reaction mixture; and most importantly, stripped the gaseous products from the reactor and carried the CO_2 to the measuring system.

2.2.5. CO_2 Measurements on the BZ Reaction. 2.2.5.1. Preparation of the Reaction Mixture. Components of the BZ reaction system were injected into the reactor in the following order: 0.35 mL of 120 mM $NaBrO_3$ solution (in water), 0.625 mL of 1.6 mM $Ce(SO_4)_2$ solution (in 2 M H_2SO_4), 0.55 mL of water, 0.075 mL of 10 M H_2SO_4. The mixture was bubbled with the carrier nitrogen gas for 0.5 min. Then, the reaction was started by injecting 0.4 mL of 0.1 M oxalic acid solution (in water). Thus, after mixing, the initial concentrations of the main reactants were 20 mM oxalic acid, 21 mM bromate, 0.5 mM Ce^{4+}, and 1 M sulfuric acid in a total volume of 2 mL.

2.2.5.2. CO_2 Measurements on Subsystems of the BZ Reaction. These measurements were performed in a similar way as in the case of an oscillating system, but in this case, we were interested in the initial rate of the reaction and not in its dynamics. The initial reaction rate was calculated by extrapolating the CO_2 evolution rate to time zero. The rate constants of the various component reactions were calculated from the initial reaction rates and component concentrations.

2.2.5.3. Measurement of the Oxalic Acid−Acidic Bromate Reaction. Components of the reaction were injected into the reactor in the following order: 0.5 mL of 120 mM $NaBrO_3$ solution in water, 0.8 mL of water, 0.2 mL of 10 M H_2SO_4. The reaction was then started by injecting 0.5 mL of 0.1 M oxalic acid in water. The initial concentrations in the reactor after mixing were therefore 30 mM bromate, 25 mM oxalic acid, and 1 M sulfuric acid in a total volume of 2 mL.

2.2.5.4. Experiment to Determine the Rate of the Oxalic Acid−Bromous Acid Reaction. Components of the reaction were injected into the reactor in the following order: 0.5 mL of 120 mM $NaBrO_3$ solution in water, 0.4 mL of water, 0.1 mL of 10 M H_2SO_4, 0.5 mL of 0.4 M malonic acid in 2 M sulfuric acid. The reaction was then started by injecting 0.5 mL of 0.1 M oxalic acid in water. The initial concentrations in the reactor after mixing were therefore 30 mM bromate, 25 mM oxalic acid, 100 mM malonic acid, and 1 M sulfuric acid in a total volume of 2 mL.

2.3. Experiments Applying Potentiometry. *2.3.1. Measurement of k_G, the "Rate Constant" for the Physical Removal of Bromine.* The reactor applied in these measurements had the same geometry as the one used in the BZ experiments. The only difference was that a platinum electrode and a Ag/AgBr electrode were mounted at the bottom of the reactor to monitor the bromine concentration of the mixture. A solution containing both bromine and bromide ($[Br_2] = 0.03$ M, $[Br^-] = 0.01$ M) in 1 M sulfuric acid (total volume = 1, 2, or 4 mL) was pipetted into the reactor. Then, the reactor was closed, and a constant flow (20, 30, 40, or 50 mL/min) of the nitrogen carrier gas was applied. Removal of the bromine was indicated by the continuously dropping potential of the Pt electrode. The Nernstian voltage, ϵ, measured between the two electrodes at 20 °C can be expressed as

$$\epsilon = \epsilon_0 + 12.6 \text{ mV} \ln([Br_2]/[Br_2]_0)$$

where ϵ_0 is the voltage at the start of the bromine removal. (Because the bromide concentration does not change in the course of this experiment, its value can be incorporated into the constant term.) At fixed conditions, the removal rate of bromine is proportional to its actual concentration in the aqueous phase

$$d[Br_2]/dt = -k_G[Br_2]$$

where the rate constant k_G depends on the gas flow and on the liquid volume. The solution of the above first-order homogeneous linear differential equation is

$$[Br_2] = [Br_2]_0 \exp(-k_G t)$$

Thus, the rate of the potential change can be expressed as

$$d\epsilon/dt = -(12.6 \text{ mV})k_G$$

and k_G can be calculated from the measured slope of the voltage vs time diagram.

2.3.2. Measuring the Rate of the Hypobromous Acid−Oxalic Acid Reaction. A magnetically stirred 50-mL beaker with a thermostated jacket was used as the reactor. The hypobromous acid concentration was monitored by a special Ag/AgBr electrode (silver wire electrode coated with AgBr melt[40]). In strongly acidic solutions, HOBr gives a close-to-Nernstian potential response because of its corrosive reaction with the electrode material.[39] In the present case, the electrode response for HOBr was (59 ± 2) mV/decade in the concentration range of our experiments, which agrees well within the experimental error with the theoretical sensitivity of 58.1 mV/decade valid at 20 °C. Thus, that theoretical value was applied in our further calculations. A Ag/AgCl reference electrode was used in a solution containing both KCl and H_2SO_4 at 1 M concentrations. The reference electrode was connected to the reactor via a salt bridge filled with 1 M H_2SO_4. (The presence of the sulfuric acid both in the reference solution and in the salt bridge helped to keep the otherwise somewhat unstable liquid−liquid junction potentials at a low value. The absolute potential was not important in this experiment.) The voltage, ϵ, of the above galvanic cell thermostated to 20 °C can be expressed as

$$\epsilon = \epsilon_0 + 25.2 \text{ mV} \ln([HOBr]/[HOBr]_0)$$

where ϵ_0 is the voltage at the start of the experiment.

First, 39.2 mL of 1 M H_2SO_4 was pipetted into the reactor, and then 0.5 mL of freshly prepared HOBr solution (19−22 mM in 1 M H_2SO_4) was added under continuous stirring. After 5 min, when the measured potential reached a steady value, the reaction was started by injecting 0.3 mL of 40 mM oxalic acid (in 1 M H_2SO_4) into the reactor. The initial concentrations were as follows: $[HOBr]_0 = 0.24{-}0.27$ mM, $[OA]_0 = 0.3$ mM, $[H_2SO_4]_0 = 1$ M.

According to the recorded potentiometric traces, two different mechanisms are active in the HOBr oxalic acid reaction: one in which the reaction order with respect to HOBr is 1 and another in which that order is 2. To determine the rate constants of the two parallel processes, the potentiometric curves were evaluated by a special curve-fitting method described in the Appendix.

In the experiments discussed above, oxalic acid was applied in a relatively low initial concentration; it was in only a slight stoichiometric excess over the initial hypobromous acid amount. In such dilute solutions, the rate of the reaction was slow enough to be followed with our AgBr electrode, whose potential otherwise responded with some delay to rapid changes in the HOBr concentration. We found, however, that any error due to such a delayed electrode response was negligible when the rate of the electrode potential change was kept below 0.5 mV/s.

3. Results and Discussion

3.1. BZ Reaction of Oxalic Acid in a Semibatch Reactor with Selective Bromine Removal. To study the BZ reaction with oxalic acid substrate in a semibatch reactor, the same initial conditions were applied in each experiment as indicated in the caption of Figure 1.

The variable control parameter was the nitrogen gas flow that removed the volatile endproducts (CO_2 and Br_2) from the aqueous phase of the reaction mixture. As Br_2 can participate in various reactions (see later) that slow the overall rate of the reaction, its removal rate affects the reaction dynamics significantly. A slower flow of the carrier gas or a higher reaction volume results in slower bromine removal associated with a higher steady-state bromine concentration in the reactor and with a slower overall reaction. This is the case in Figure 1a, where the total reaction time is about 11 000 s. The first peak after the start of the reaction is not an “oscillation”; it is due only to the reduction of the initial Ce^{4+} by oxalic acid. That single peak is followed by a long induction period (more than 8000 s) during which the Ce^{4+} concentration and the rate of CO_2 evolution are low. After the induction period, a relatively short oscillatory regime with five slow oscillations occurs. In Figure 1b, the rate of bromine removal is increased by a factor of ∼2 (5.7/3.1 = 1.84) compared to that in Figure 1a, and this shortens the overall reaction time by a factor of ∼1.6 (11 000/7000 = 1.57), the time period of the oscillations by a factor of ∼1.4 (380/280), and especially the induction period by a factor of ∼2.6 (8600/3300). The oscillatory regime is now longer and contains twice as many oscillations. In addition, the amplitude is also approximately doubled. When the gas flow is again increased by a factor of 2 (see Figure 1c), the shrinking induction time disappears completely, and the other tendencies continue: both the time period of the oscillations and the overall reaction time become shorter. The last peak, however, develops a shoulder and becomes much wider than the previous ones. As the gas flow rate is increased further, the oscillatory regime shrinks, but the width of the last peak with the shoulder does not change significantly (it grows slightly). When the bromine removal rate reaches a critical interval ($21 \text{ s}^{-1} < k_G < 24 \text{ s}^{-1}$), the oscillatory region rapidly shrinks and finally disappears (Figure 1d−f). Observe that small-amplitude oscillations appear on the top of the shoulder as the regime of the large-amplitude oscillations shrinks, indicating a supercritical Hopf-bifurcation-like scenario.

3.2. Rate Constant of Bromine Decay as a Function of the Stripping Gas Flow. The physical removal of bromine by the nitrogen carrier gas can be regarded as a first-order chemical reaction [$Br_2(aq) \rightarrow Br_2(gas)$], as its rate is proportional to the bromine concentration in the aqueous phase. This was verified by measuring the potential of a platinum electrode vs a Ag/

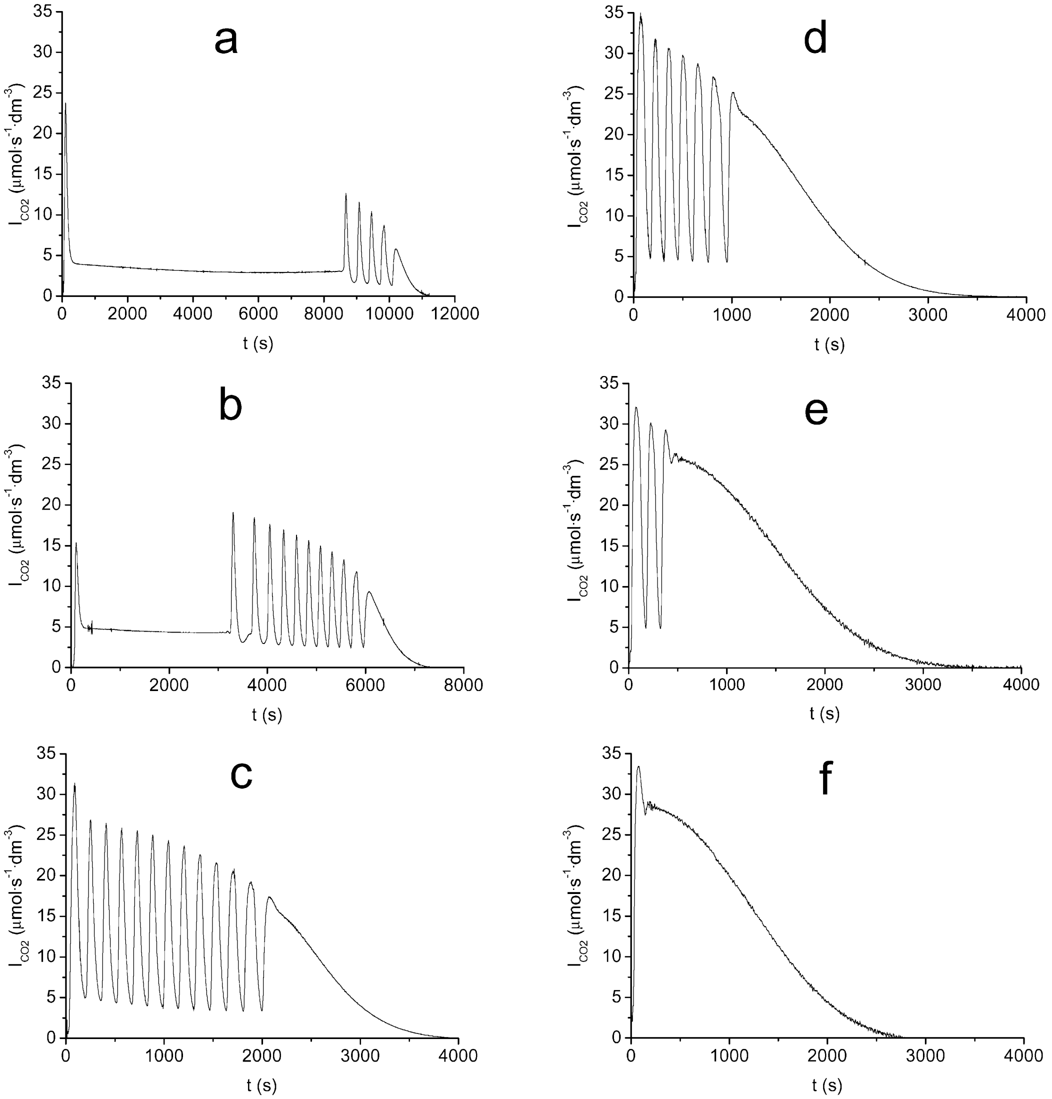

Figure 1. Dynamics of the BZ reaction with oxalic acid in a semibatch reactor as a function of the bromine removal rate. Initial concentrations: $[NaBrO_3]_0 = 21$ mM, $[OA]_0 = 20$ mM, $[Ce(SO_4)_2] = 0.5$ mM, $[H_2SO_4] = 1$ M. The thermostated temperature was 20 °C in all experiments. The reaction volume and the nitrogen carrier gas velocity were changed to vary k_G, the bromine removal rate. The k_G values were calculated from the plots of Figure 2. (a) Reaction volume $V = 4$ mL, flow rate of carrier gas $w = 20$ mL/min, $k_G = 3.1 \times 10^{-3}$ s^{-1}, time period of oscillations $\tau = 380$ s. (b) $V = 2$ mL, $w = 20$ mL/min, $k_G = 5.7 \times 10^{-3}$ s^{-1}, $\tau = 280$ s. (c) $V = 2$ mL, $w = 40$ mL/min, $k_G = 11.4 \times 10^{-3}$ s^{-1}, $\tau = 165$ s. (d) $V = 2$ mL, $w = 60$ mL/min, $k_G = 17.2 \times 10^{-3}$ s^{-1}, $\tau = 160$ s. (e) $V = 1$ mL, $w = 50$ mL/min, $k_G = 18.9 \times 10^{-3}$ s^{-1}, $\tau = 150$ s. (f) $V = 1$ mL, $w = 55$ mL/min, $k_G = 20.8 \times 10^{-3}$ s^{-1}.

AgBr electrode. The reactor was filled with a 1 M sulfuric acid solution (1, 2, or 4 mL, as in the BZ experiments) also containing bromide ($[Br^-] = 0.01$ M) and bromine ($[Br_2]_0 = 0.001$ M). The potentiometric trace recorded while the bromine was stripped by the gas flow was a straight line, thus confirming that the assumption of the first-order decay is valid. k_G, the rate constant of the bromine decay process, was calculated from the slope of the potentiometric trace as discussed in the Experimental Section. Figure 2 displays the results.

3.3. Mechanism of and Rate Constants for the Hypobromous Acid−Oxalic Acid Reaction. The rate constant of R.I, the reaction between hypobromous and oxalic acids, has been measured by several authors. The most recent work was published by Smith[36] in 1972. He performed batch experiments in buffered solutions containing oxalic acid, bromine, and bromide and monitored the bromine concentration by measuring the potential of a bright platinum electrode. The pH of the buffered solutions was between 3 and 6. In this pH range, it was found that the active species is the hydrogen oxalate ion and the contribution of the reaction between hypobromous acid and oxalate ion is negligible. Smith could describe the consumption of bromine in his experiments with the following rate law

$$d[Br_2]_A/dt = -k_{HOA}[HOA^-][HOBr]$$

where $[Br_2]_A$ is the analytical bromine concentration (a value that can be determined, for example, by titration and that, in his case, also included bromine bound in tribromide ion) and $[HOA^-]$ is the concentration of hydrogen oxalate ion. According to Smith, $k_{HOA} = 230$ M^{-1} s^{-1} at 20 °C.

In the oscillatory BZ reaction of oxalic acid, the sulfuric acid concentration is 1 M ($[H^+] = 1.29$ M); thus, we wanted to investigate the oxalic acid−hypobromous acid reaction in such a medium. This hydrogen ion concentration, however, is much higher than the one applied by Smith. Therefore, in this case, most of the oxalic acid is in acid form, and only a small fraction of the added oxalic acid, with concentration $[OA]_A$, is in the

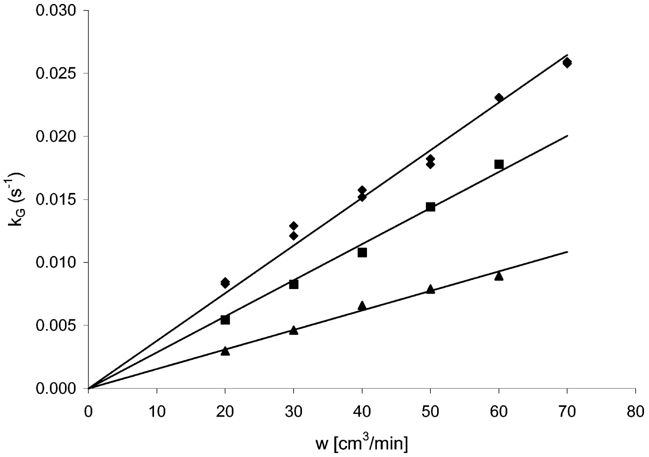

Figure 2. k_G, the rate constant of the physical removal of bromine from the aqueous phase, as a function of the nitrogen gas flow rate, w, bubbling through the liquid ($d[Br_2]/dt = -k_G[Br_2]$, where $[Br_2]$ is the concentration of dissolved bromine). k_G depends on the volume V of the aqueous phase as well. ♦ $V = 1$ mL, $k_G \approx 3.78 \times 10^{-4}$ s^{-1}·w/mL/min. ■ $V = 2$ mL, $k_G \approx 2.86 \times 10^{-4}$ s^{-1}·w/mL/min. ▲ $V = 4$ mL, $k_G \approx 1.55 \times 10^{-4}$ s^{-1}·w/mL/min.

hydrogen oxalate form

$$[OA]_A = [OA] + [HOA^-]$$

This fraction, θ, can be expressed as

$$\theta = [HOA^-]/[OA]_A = 1/(1 + [H^+]/K_1)$$

where K_1 is the first dissociation constant of oxalic acid. According to a reference table,[41] $K_1 = 2.4 \times 10^{-2}$ M at 20 °C. Applying this value and the actual hydrogen ion concentration of 1.29 M, $\theta = 1.83 \times 10^{-2}$. Thus, assuming that it is exclusively the hydrogen oxalate ion that can react with the hypobromous acid and that any contribution from the undissociated oxalic acid itself can be neglected, the rate law found by Smith can be extrapolated to

$$d[HOBr]/dt = -k_{HOA}[HOA^-][HOBr] = -k_{HOA}\theta[OA]_A[HOBr]$$

According to the above formula, $k_I = k_{HOA}\theta$, that is, k_I should be 4.2 M^{-1} s^{-1} in 1 M sulfuric acid.

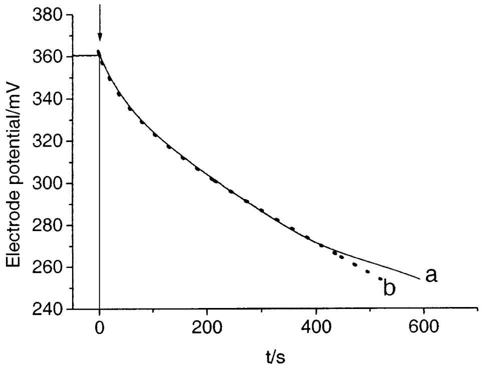

Figure 3. Potential of a special Ag/AgBr electrode (silver wire coated with AgBr; see the Experimental Section) as a function of time. The electrode in this case works as a hypobromous acid selective electrode (see text for explanation). Initial concentrations: $[HOBr]_0 = 0.27$ mM, $[OA]_0 = 0.3$ mM, $[H_2SO_4]_0 = 1$ M. Temperature = 20 °C. Oxalic acid was added as the last component at the moment indicated by an arrow. Curve a, experiment; curve b, theory calculated with $k_I = 17$ M^{-1} s^{-1} and $k_I^{(2)} = 120\,000$ M^{-2} s^{-1}. The method of calculation is described in the Appendix.

On the basis of Smith's results, we expected that the HOBr−oxalic acid reaction is pseudo-first-order if oxalic acid is in excess. In that case, during the HOBr−oxalic acid reaction, the potential of a AgBr electrode should decrease linearly. (This is because the hypobromous acid concentration should decrease exponentially in a pseudo-first-order reaction and the electrode potential depends on the logarithm of the HOBr concentration.) The slope ($tg\alpha$) of such an electrode potential vs time diagram would be

$$tg\alpha \approx -(25.2\ \text{mV})2k_I[OA]_0$$

assuming that the oxalic acid concentration remains essentially constant. (This can be a good approximation if oxalic acid is applied in excess or if only the initial slope is considered. The factor of 2 is due to the fast consecutive reaction of the produced bromide ion with a second hypobromous acid molecule.) Originally, we planned to calculate k_I from the above formula. In the real experiments, however, we found that the potential vs time diagrams were not straight lines (see Figure 3) and even the initial slope was not constant but rather depended on the initial HOBr concentration. At this point, it became evident that a new rate law consistent with the experiments should be found. In fact, assuming an additional parallel reaction between HOBr and oxalic acid, we could obtain a different rate law that was able to describe our observations. The suggested rate law has two terms

$$r_I = r_I^{(1)} + r_I^{(2)}$$

where r_I is the rate of the total HOBr consumption and its two terms are given by

$$r_I^{(1)} = 2k_I[OA][HOBr] \quad \text{and} \quad r_I^{(2)} = 2k_I^{(2)}[OA][HOBr]^2$$

As can be seen in the new additional term, the reaction order with respect to HOBr is not 1 but 2, so this parallel reaction should have a different mechanism. As a termolecular mechanism is not a very probable explanation for the new rate law, it is more realistic to assume a preequilibrium involving two HOBr molecules, i.e.

$$2HOBr \leftrightarrow Br_2O + H_2O$$

The bromine monoxide produced in the above preequilibrium can react with oxalic acid to give elemental bromine and another water molecule

$$Br_2O + (COOH)_2 \rightarrow Br_2 + 2CO_2 + H_2O$$

Although the mechanism, and consequently the rate law, of the above additional reaction route is different, its resulting stoichiometry

$$2HOBr + (COOH)_2 \rightarrow Br_2 + 2CO_2 + 2H_2O$$

is the same as what can be observed in a reaction sequence in which the first step is bromide production in reaction R.I, followed by the reaction of the resulting bromide ion with another HOBr.

As Figure 3 shows, the nonlinear AgBr electrode potential vs time curve recorded in the course of a HOBr−oxalic acid reaction can be fitted well with the above hypothesis: the experimental (curve a) and the theoretical (curve b) potential−

time diagrams are in a good agreement if the k_I and $k_I^{(2)}$ values are chosen properly. On the basis of seven parallel experiments, we found $k_I = 17 \pm 2\ M^{-1}\ s^{-1}$ and $k_I^{(2)} = (1.2 \pm 0.2) \times 10^5\ M^{-2}\ s^{-1}$. At lower HOBr concentrations (below 10^{-6} M), such as in the experiments of Smith,[36] the contribution of the newly observed term to the rate of the HOBr−oxalic acid reaction is negligible.

Nevertheless, the rate constant of the term that is first-order with respect to HOBr is not 4.2 $M^{-1}\ s^{-1}$, as could be expected from an extrapolation of Smith's results, but rather is about four times larger. This result suggests that the reaction of the undissociated oxalic acid with the hypobromous acid cannot be neglected in a 1 M sulfuric acid solution. Assuming a similar rate law between OA and HOBr with a rate constant of k_{OA}, the overall rate constant can be expressed as

$$k_I = k_{HOA}\theta + k_{OA}(1 - \theta)$$

which gives $k_{OA} = 13 \pm 2\ M^{-1}\ s^{-1}$. Thus, although k_{OA} is about 20 times smaller than k_{HOA}, its contribution cannot be neglected when θ is small.

3.4. Determination of k_V. CO_2 Evolution in the Reaction of Acidic Bromate with Oxalic Acid. As shown in Figure 4, the initial CO_2 evolution rate is 2.8 μmol $s^{-1}\ dm^{-3}$ in experiment a. This carbon dioxide is coming from reactions of oxalic acid with three different oxybromine species: acidic bromate, bromous acid, and hypobromous acid. In each reaction, one oxygen atom is transferred from the oxybromine species to the oxalic acid

$$H^+ + BrO_3^- + (COOH)_2 \rightarrow HBrO_2 + 2CO_2 + H_2O \quad (R.V)$$

$$HBrO_2 + (COOH)_2 \rightarrow HOBr + 2CO_2 + H_2O \quad (R.III)$$

$$HOBr + (COOH)_2 \rightarrow H^+ + Br^- + 2CO_2 + H_2O \quad (R.I)$$

(The Roman numeral denoting each reaction was chosen according to the oxidation number of the oxybromine species participating in that reaction.) Bromide (oxidation number −1) can also react with the above three oxybromine species

$$H^+ + BrO_3^- + Br^- + H^+ \rightarrow HBrO_2 + HOBr \quad (R.V\text{-}1)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \quad (R.III\text{-}1)$$

$$HOBr + Br^- + H^+ \leftrightarrow Br_2 + H_2O \quad (R.I\text{-}1)$$

and hydrolysis of bromine, the reverse of the last reaction, can also occur. The rate constants of the last three reactions are known,[12] together with the rate constant of the disproportionation of bromous acid

$$2HBrO_2 \rightarrow HOBr + H^+ + BrO_3^- \quad (R.d)$$

k_I was already determined in a previous section, but k_V and k_{III} are not yet known; these values we want to calculate from the experimental data shown in Figure 4.

In experiment a, the final product is elemental bromine, which is stripped from the reaction mixture by bubbling nitrogen through it. In this case, the overall process (P1) can be described with the following stoichiometry

$$HBrO_3 + 2.5(COOH)_2 \rightarrow 0.5Br_2 + 5CO_2 + 3H_2O \quad (P1)$$

Note that the change in the oxidation number of bromine is equal to the number of CO_2 molecules produced.

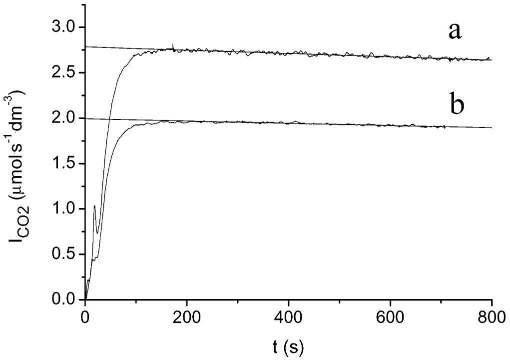

Figure 4. Carbon dioxide evolution rate (μmol of CO_2/s in 1-dm^3 reactor volume) vs time. Initial concentrations in the experiment giving curve a: $[(COOH)_2]_0 = 0.025$ M, $[NaBrO_3]_0 = 0.030$ M, $[H_2SO_4]_0 = 1$ M. In experiment b, oxalic acid, sodium bromate, and sulfuric acid were applied in the same initial concentrations, but in addition, malonic acid was also present at a concentration of 0.1 M. Initial rate of CO_2 evolution (extrapolated back to zero time): 2.8 μmol of $CO_2\ s^{-1}\ dm^{-3}$ in experiment a and 1.99 μmol of $CO_2\ s^{-1}\ dm^{-3}$ in experiment b. The nitrogen gas flow rate was 40 mL/min.

The rate-determining step of process P1 is R.V. This conclusion was corroborated by computer simulations, which also showed that (i) the rate of disproportionation of bromous acid is negligible because, under these conditions, bromous acid reacts mainly with bromide in reaction R.III-1, and (ii) the rate of bromous and hypobromous acid production in reaction R.V-1 is also negligible compared to the rate of bromous acid production in reaction R.V.

Thus, the rate of the CO_2 evolution, I_{CO_2}, is 5 times higher (according to computer simulations, this factor is 5.02) than the rate of reaction R.V. According to this relationship, k_V can be calculated as

$$k_V = I_{CO_2}(0)/(5[BrO_3^-]_0[(COOH)_2]_0)$$

where $I_{CO_2}(0)$ is the initial carbon dioxide evolution rate extrapolated back to time zero. The above formula assumes a bilinear dependence of $I_{CO_2}(0)$ on both the bromate and oxalic acid concentrations, which was checked experimentally. Substituting our data into the formula gives $k_V = 7.47 \times 10^{-4}\ M^{-1}\ s^{-1}$. This is in a good agreement with the result of Ševčik et al.[37] An interpolation of their data gives $7.4 \times 10^{-4}\ M^{-1}\ s^{-1}$. The only difference in the applied experimental conditions is the ionic strength, which was increased to 2 M in their experiments by the addition of sodium sulfate to the solution. The ionic strength in our experiments was only 1.60 (this is due mainly to the 1 M sulfuric acid solution, where the hydrogen ion concentration is[12] 1.29 M). Thus, we can conclude that the ionic strength has no sinificant impact on reaction R.V in this concentration range.

3.5. Determination of k_{III}. The Oxalic Acid−Bromate Reaction in the Presence of Malonic Acid. When malonic acid is also present, most of the hypobromous acid reacts with this compound to give bromomalonic acid

$$HOBr + MA \rightarrow BrMA + H_2O \quad (R.b)$$

If the now-suppressed bromine formation is neglected, the overall stoichiometry is

$$H^+ + BrO_3^- + 2(COOH)_2 + MA \rightarrow 4CO_2 + 3H_2O + BrMA \quad (P2)$$

Here, the number of CO_2 molecules produced is again equal to the decrease in the oxidation number of bromine, which is now 4. Thus, if we disregard reaction R.d, the disproportionation of bromous acid, then the rate of CO_2 evolution in case b of Figure 4 should be 80% compared to that of case a; as the rate-determining first step, reaction R.V would generate now 4 CO_2 molecules instead of 5. On the other hand, if the disproportionation of bromous acid is much faster than reactions R.III and R.III-1, then the rate of CO_2 evolution in the presence of malonic acid could drop further to only 40% of the original rate following the stoichiometry of process P3

$$\mathrm{H^+ + BrO_3^- + (COOH)_2 + 0.5MA \rightarrow 2CO_2 + 1.5H_2O + 0.5H^+ + 0.5BrO_3^- + 0.5BrMA} \quad \text{(P3)}$$

As the rate-determining first step, reaction R.V would generate only 2 CO_2 molecules in this case. Our result, $1.99/2.80 = 71\%$, is between these two limits, indicating that the disproportionation of bromous acid is slower than its reaction with oxalic acid; nevertheless, this process cannot be neglected. The competition of reactions R.III and R.d, which proceed with comparable rates, provides an opportunity to determine the unknown rate constant k_{III} because k_{d} is known. According to computer simulations including all possible reactions,[38] a k_{III} value of 4.2 $M^{-1}\ s^{-1}$ is compatible with the measured 71% result.

A rough estimate (which neglects any reaction of oxalic acid with HOBr and consecutive reactions of bromide produced in this way) can be also obtained assuming a steady state

$$r_{\mathrm{V}} = 2r_{\mathrm{d}} + r_{\mathrm{III}}$$

where $r_{\mathrm{V}} = k_{\mathrm{V}}[\mathrm{BrO_3^-}][\mathrm{OA}]$, the rate of reaction R.V; $r_{\mathrm{d}} = k_{\mathrm{d}}[\mathrm{HBrO_2}]^2$; and $r_{\mathrm{III}} = k_{\mathrm{III}}[\mathrm{HBrO_2}][\mathrm{OA}]$. Moreover, we know that, in the absence of malonic acid, $I_{\mathrm{CO_2}}(\mathrm{ref})$, the CO_2 evolution rate in this reference experiment, is

$$I_{\mathrm{CO_2}}(\mathrm{ref}) = 5r_{\mathrm{V}}$$

whereas in the presence of malonic acid, $I_{\mathrm{CO_2}}$ is smaller, namely

$$I_{\mathrm{CO_2}} = 2r_{\mathrm{V}} + 2r_{\mathrm{III}}$$

Using these relationships, our experimental data, and rate constants known from the literature,[42] k_{III} can be estimated with the following formula

$$k_{\mathrm{III}} \approx (R - 1)\{(2k_{\mathrm{d}}k_{\mathrm{V}}[\mathrm{BrO_3^-}])/(2 - R)[\mathrm{OA}]\}^{1/2}$$

where $R = 5I_{\mathrm{CO_2}}/2I_{\mathrm{CO_2}}(\mathrm{ref})$. Substituting the numerical values, we obtain $k_{\mathrm{III}} \approx 4.6\ M^{-1}\ s^{-1}$, a result that is not too far from the more precise result of the model calculations including all reactions.

3.6. On the Possibility of Radical Reactions in the Oxalic Acid−Acidic Bromate System. When modeling oxygen transfer reactions R.I, R.III, and R.V, no radical intermediates were assumed. In some published works,[11,29] however, a radical mechanism has been suggested as a first step in the oxygen atom transfer process. For example, in the case of the hypobromous acid−oxalic acid reaction, bromine atom and carboxyl radical are proposed to be among the first products

$$\mathrm{HOBr + (COOH)_2 \rightarrow CO_2 + H_2O + \bullet Br + \bullet COOH} \quad \text{(FB1)}$$

according to a scheme by Field and Boyd[29] (ninth row of Table 1). If these freshly produced free radicals react with each other, then the result is reaction R.I. In that case, the rate of reaction R.I would be equal to the rate of the rate-determining first step (FB1), and there would be no significant difference between the two schemes. Nevertheless, because radical concentrations are very low, free radical−molecule reactions have a much higher probability than radical−radical reactions. This means that bromine atoms would react mainly with oxalic acid molecules (producing new carboxyl radicals), whereas carboxyl radicals would react primarily with HOBr (producing new bromine atoms). In this way, chain reactions would dominate in the oxygen atom transfer reactions. Although we cannot completely exclude such a possibility, we found it difficult to model the experimental observations in the acidic bromate−oxalic acid reaction based on the above radical hypothesis. Thus, we suggest that, even if FB1-type processes were to occur within the activated complex, the free radicals should react with each other there and only molecular products should escape.

In the course of the acidic bromate−oxalic acid reaction, the starting point of another possible radical chain reaction could be the bromine dioxide−oxalic acid reaction. Field and Boyd[29] found that this reaction was slow, with a second-order rate constant of less than 150 $M^{-1}\ s^{-1}$. According to our model calculations this limit is even smaller: assuming a rate constant of 10−20 $M^{-1}\ s^{-1}$ already causes observable deviations from the experimental results, and large deviations appear if the rate constant is raised to 100 $M^{-1}\ s^{-1}$. Consequently, this reaction will be neglected in the following work.

Thus, we can conclude that radical reactions do not play any significant role in the oxalic acid−acidic bromate reaction system in the absence of cerium ions. If cerium ions are present, however, then radical and radical chain reactions can occur. The experimental and computational study of these radical processes is the subject of our next paper.[38]

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Appendix

Calculation of the Rate Constants k_{I} and $k_{\mathrm{I}}^{(2)}$ by Applying the Integrated Rate Law of the HOBr−Oxalic Acid Reaction. Regarding the differential rate law for the HOBr−oxalic acid reaction and the component balance for HOBr in a batch reactor, we can obtain the following differential equation

$$\mathrm{d}x/\mathrm{d}t = -2k_{\mathrm{I}}xy - 2k_{\mathrm{I}}^{(2)}x^2y$$

where $x = [\mathrm{HOBr}]$ and $y = [\mathrm{OA}]$. This equation can be rewritten in the form

$$\mathrm{d}x/\mathrm{d}t = k_{\mathrm{I}}^{(2)}(a + x)(b + x)x$$

where $a = 2y_0 - x_0$ and $b = k_{\mathrm{I}}/k_{\mathrm{I}}^{(2)}$. (Here, the stoichiometry of the HOBr−oxalic acid reaction was also regarded, according to which $x - x_0 = 2(y - y_0)$, as one oxalic acid molecule consumes two hypobromous acid molecules.) The latter differential equation can be integrated in a closed form that is explicit for the time to give

$$t = -\frac{1}{ak_{\mathrm{I}}}\left[\ln\left(\frac{x}{x_0}\right) + \frac{b}{a - b}\ln\left(\frac{x + a}{x_0 + a}\right) + \frac{a}{a - b}\ln\left(\frac{x + b}{x_0 + b}\right)\right] \tag{1}$$

In this way, with given a, k_{I}, and $k_{\mathrm{I}}^{(2)}$ values, t vs x curves can

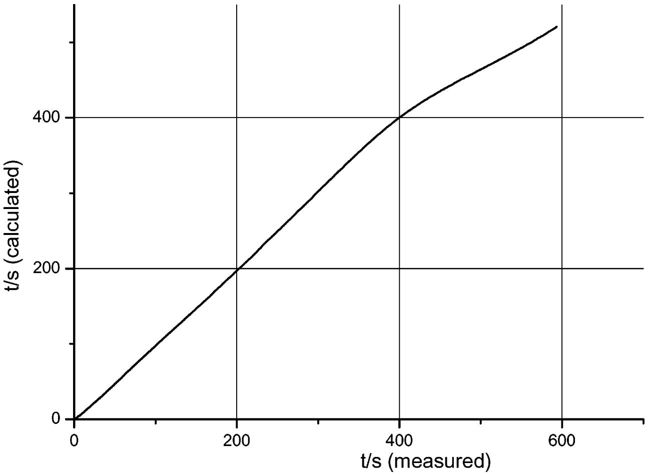

Figure 5. *t* (calculated) vs *t* (measured) for the experiment depicted in Figure 3.

be constructed. As x can be calculated from the measured electrode potential with the equation

$$x = x_0 \exp\left(\frac{\epsilon - \epsilon_0}{25.2\ \mathrm{mV}}\right) \qquad (2)$$

it is also possible to construct t vs ϵ diagrams, which can be compared with the experimental ϵ vs t diagrams, as shown in Figure 3. To find the optimum values for k_I and $k_\mathrm{I}^{(2)}$, however, we applied a different technique. For a given measured time of the experiment, we computed a so-called "calculated time" in the following way: First, from the measured potential, x was calculated according to eq 2; then, from this x value, a calculated time was obtained with eq 1. Then, these calculated times were depicted as a function of the measured time (see Figure 5). Optimal k_I and $k_\mathrm{I}^{(2)}$ values were chosen so as to give a straight line through the origin with a slope of unity in this plot. As Figure 5 shows, this could be achieved in the 0−400-s interval. (Above 400 s, the HOBr concentration decreased to a value such that the electrode response was no longer Nernstian.)

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(42) In the MBM mechanism, the disproportionation of bromous acid proceeds via the reaction of a protonated and a nonprotonated bromous acid. The rate constant of this reaction is $1.7 \times 10^{+5}$ $\mathrm{M^{-1}\ s^{-1}}$. If we assume a fast equilibrium for the protonation, then the concentration of the protonated bromous acid can be expressed as $2 \times 10^6[\mathrm{H^+}][\mathrm{HBrO_2}]/10^8 = 2.6 \times 10^{-2}[\mathrm{HBrO_2}]$. Thus, as a quasi-steady-state approximation, $k_\mathrm{d} \approx 1.7 \times 10^5 \times 2.6 \times 10^{-2} = 4.4 \times 10^3$ $\mathrm{M^{-1}\ s^{-1}}$.