Stoichiometry of Bromide Production from Ceric Oxidation of Bromomalonic Acid in the Belousov-Zhabotinskii Reaction

Horst-Dieter Försterling* and Linda Stuk

Fachbereich Physikalische Chemie, Philipps-Universität, D-3550 Marburg, Germany

Alexander Barr and William D. McCormick

Center for Nonlinear Dynamics and Department of Physics, The University of Texas at Austin, Austin, Texas 78712

Received: November 3, 1992

We investigated the number of Ce^{4+} ions required to produce one Br^- ion in the oxidation of bromomalonic acid by Ce^{4+} under conditions appropriate to the oscillating Belousov-Zhabotinskii (BZ) reaction. We found a ratio of 1:1, in agreement with earlier results by Jwo and Noyes (J. Am. Chem. Soc. 1975, 97, 5422), in the presence of oxygen. With oxygen excluded from the system, we found a ratio of 2:1. The presence of malonic acid in the system had no effect on the bromide production, contrary to the assumption of recent theoretical models of the Belousov-Zhabotinskii reaction.

1. Introduction

The production of bromide from bromomalonic acid (BrMA, CHBr(COOH)₂) is an important part of the Belousov-Zhabotinskii (BZ) reaction. A detailed model of the BZ reaction was recently presented by Györgyi, Turányi, and Field.¹ Försterling and Stuk² concluded from ESR experiments that the GTF model overestimates the production of Br⁻ from a set of reactions including hydrogen abstraction from bromomalonic acid by malonyl radicals (*CH(COOH)₂). Adjusting the rate constants in the GTF model to incorporate these new results caused too low a rate of Br⁻ production during the induction period in several simulations.² That is, the corrected models predicted induction times much longer than the experimentally observed induction times.

The interpretation of the ESR experiments² has been questioned by Györgyi, Turányi, and Field in a recent manuscript.³ These ESR experiments measured only the concentration of malonyl radicals in a flow system containing MA, BrMA, Ce⁴⁺, and H₂-SO₄ as inputs. Therefore it is important to measure another result of the reaction, such as the stoichiometry of Br⁻ production from systems with the same initial conditions. The conclusions of ref 2 are also subject to the assumption that the synthesis of BrMA in the experiments yielded only BrMA, with no reactants consumed in the production of Br₂MA.

Jwo and Noyes⁴ previously measured Br⁻ production stoichiometry from aqueous solutions containing initially BrMA, Ce⁴⁺, H₂SO₄, and sometimes MA. These authors used a bromideselective electrode. For systems containing initially no MA, they found that the ratio [Ce⁴⁺]₀:[Br⁻]_f (where the subscript f indicates the final value) approached 1:1 as the ratio [BrMA]₀/[Ce⁴⁺]₀ increased. These experiments were done in the air (with no exclusion of oxygen). In modelling studies of CSTR experiments done in the presence of oxygen, Györgyi, Rempe, and Field⁵ and Györgyi and Field⁶ assumed that one Ce⁴⁺ plus one BrMA produce one Br⁻. For experiments with oxygen excluded, the model of Györgyi, Turányi, and Field (GTF)¹ predicts somewhat less Br⁻ production. The exact stoichiometry is described in the recent manuscript of Györgyi, Turányi, and Field.³

A further problem in the modelling of bromide production in the BZ system is the possible effect of malonic acid (MA, $CH_2(COOH)_2$), or malonyl radicals (MA[•], $CH(COOH)_2$). Jwo and Noyes⁴ found that the production of bromide from systems containing initially Ce⁴⁺, MA, and BrMA was more than one Brion per BrMA molecule oxidized by the cerium. Jwo and Noyes⁴ concluded that BrMA can be oxidized by malonyl radicals to bromomalonyl radicals, BrMA^{*}.

This paper tests two models of Br^- production in a subset of the BZ system containing no oxybromine species. The first, which we will call the simple theory, consists of the following five reactions:

$$Ce^{4+} + MA \rightarrow Ce^{3+} + H^+ + MA^*$$
 (R1)

$$Ce^{4+} + BrMA \rightarrow Ce^{3+} + H^+ + BrMA^{\circ}$$
 (R2)

$$2MA^{\bullet} + H_2O \rightarrow TTA + MA$$
 (R3)

$$2BrMA^{\bullet} + H_2O \rightarrow BrTTA + BrMA$$
 (R4)

$$BrTTA \rightarrow Br^- + H^+ + MOA$$
 (R5)

where BrMA[•] is the bromomalonyl radical, [•]BrCH(COOH)₂; TTA is tartronic acid, CHOH(COOH)₂; BrTTA is bromotartronic acid, CBrOH(COOH)₂; and MOA is mesoxalic acid, CO-(COOH)₂.

The second model to be tested is the 80-equation model of Györgyi, Turányi, and Field.¹ The most important difference between the two models for systems containing initially only Ce⁴⁺, MA, BrMA, and H_2SO_4 is that the GTF model includes the following reactions, in addition to (R1)–(R5):

$$MA^{\bullet} + BrMA^{\bullet} + H_{2}O \rightarrow MA + BrTTA$$
 (R6)

$$MA^* + BrMA \rightarrow MA + BrMA^*$$
 (R7)

$$MA + BrMA^{\bullet} \rightarrow MA^{\bullet} + BrMA$$
 (R8)

Reaction R6 is the mixed disproportionation reaction of malonyl and bromomalonyl radicals. Reactions R7 and R8 are hydrogen abstraction, or radical transfer, reactions.

The rate constants for the reactions given in reactions R1-R8 are listed in Table I. Recently we have shown⁷ that the value for k_3 should be corrected to 4.2×10^8 M⁻¹ s⁻¹, but we use the older value⁸ throughout this paper to facilitate comparison with the GTF model¹ and with our earlier ESR paper.² We will note the differences in each calculation which would result from use of the newer rate constant.

0022-3654/93/2097-2623\$04.00/0 © 1993 American Chemical Society

^{*} To whom correspondence should be addressed.

 TABLE I:
 Rate Constants for Reactions R1-R8, from Ref 1

reaction	k
1	0.23 M ⁻¹ s ⁻¹
2	0.09 M ⁻¹ s ⁻¹
3	$3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
4	$1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
5	1.0 s ⁻¹
6	$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
7	$1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
8	$5.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$

The GTF model predicts significantly more Br^- production than does the simple model for systems with initial concentrations in the range of those used in ref 2. Thus a direct measurement of Br^- production should indicate whether the hydrogen abstraction reactions are significant compared to the radical disproportionation reactions of the simple theory.

2. Experimental Section

2.1. Materials. All chemicals were reagent grade. $KBrO_3$ was recrystallized twice from water, and the other reagents were used without further purification. All solutions were prepared from distilled, deionized water.

2.2. Preparation of Bromomalonic Acid. The bromomalonic acid was synthesized by two different methods. One is the Zhabotinskii method,⁹ which was used only to prepare mixtures of malonic acid and bromomalonic acid. In this case the malonic acid was brominated in 1 M H_2SO_4 according to the overall reaction:

$$3CH_2(COOH)_2 + BrO_3^- + 2Br^- + 3H^+ \rightarrow$$
$$3CHBr(COOH)_2 + 3H_2O \quad (Z1)$$

The important steps in the reaction are

$$BrO_3^- + 6H^+ + 5Br^- \rightarrow 3Br_2 + 3H_2O$$
 (Z1a)

 $Br_2 + CH_2(COOH)_2 \rightarrow$

$$CHBr(COOH), + H^+ + Br^- (Z1b)$$

A competing reaction is the bromination of BrMA:

Br₂ + CHBr(COOH)₂ → CBr₂(COOH)₂ + H⁺ + Br⁻ (Z2)

It is generally assumed that reaction Z2 can be neglected. The justification for this assumption will be examined in the next section and in section 3.1.

For the Zhabotinskii synthesis procedure, the malonic acid and bromate were mixed in 1 M H₂SO₄, and a solution of bromide in 1 M H₂SO₄ was added dropwise with stirring, at room temperature.

The other bromomalonic acid synthesis procedure was adapted from refs 2 and 10. A 5 mL sample of Br_2 (0.0976 mol) was dissolved in 30 mL of CCl₄. A 10.16 g sample of MA (0.0976 mol) was dissolved in 200 mL of diethyl ether. The MA/ether solution was placed in an ice bath with magnetic stirring, and the Br_2/CCl_4 solution was added dropwise. At the end of the reaction, the solvents were evaporated by a vacuum line, with the flask still in the ice bath. The yellowish product was dissolved in about 10 mL of water and added to a saturated solution of 30 g potassium acetate in approximately 500 mL ethanol. This forms the dipotassium salt of BrMA. The white K₂BrMA was separated from the ethanol by filtration. The product was then further purified by dissolving it in about 100 mL of water and precipitating with approximately 500 mL of ethanol, followed by filtration. This procedure was carried out two or three times. The yield was about 60% and the residual bromide content about 0.5% for each batch.

2.3. Analysis of Bromomalonic Acid. The absorption spectrum of a solution of 10^{-3} M BrMA (produced by bromination in ether) in 1 M H₂SO₄ was found to be in good agreement with the values given in ref 10.

The BrMA produced by the ether bromination method was analyzed by ¹³C NMR spectroscopy. The ¹³C NMR spectra were taken in a 0.6 M solution of BrMA in 1 M H₂SO₄ with 20% D₂O added. As a reference, dioxane (100 μ L in 5 mL) was used. The signal of the COOH group was found at 169.6 ppm, and the signal of the central carbon at 44.6 ppm. In an additional experiment the fine splitting of the central carbon signal due to the interaction with the remaining proton was measured; a doublet was found in accordance with expectation.

To evaluate the validity of the Zhabotinskii method for brominating a large fraction of the original malonic acid, we measured the rate constant for the reaction of Br_2 with BrMA produced by the ether bromination method. The measurement was done by following the absorbance of Br_2 spectrophotometrically at 400 nm in a solution containing initially 1×10^{-3} M BrMA and 1×10^{-5} M to 6×10^{-5} M Br₂. From the slopes of the logarithmic plots of Br_2 absorbance versus time, we calculated the rate constant 70 M⁻¹ s⁻¹. This value is higher than the rate constant 28 M⁻¹ s⁻¹ found for the bromination of malonic acid by a factor of 2.5. From this result we expect that BrMA cannot be the only reaction product in the Zhabotinskii method. This will be discussed in section 3.1.

2.4. Production and Measurement of Bromide. Calibration experiments similar to those of ref 11 were performed. One milliliter of 0.1 M NaBr and 1 mL of 0.1 M AgNO₃ were added to 100 mL of 1 M H₂SO₄ with stirring. After about 2 min, the AgBr precipitate was collected on a cellulose nitrate filter (Sartorius, Göttingen and Micro Filtration Systems, Dublin, CA) with pore size 0.45 μ m. The precipitate and filter were washed with 400 mL of distilled water to remove the H₂SO₄.

2.4.1. Bromide Production in Pure BrMA. The first set of experiments was done to measure the production of bromide from pure bromomalonic acid. The experiments were done at the temperature of the laboratory, 20 ± 1 °C. First 0.025 mol (6.478 g) of K₂BrMA were dissolved in 500 mL of 1 M H₂SO₄ ([BrMA]₀ = 0.05 M). Electrodes were inserted into the solution to measure the concentration of Br⁻ or Ag⁺. The measuring electrode consisted of a silver wire coated with AgBr, prepared in the Austin laboratory by the method of Z. Noszticzius.¹² The reference electrode was a Sensorex double-junction AgCl electrode.

Then 5 mL of 0.05 M Ce(SO₄)₂ solution in 1 M H₂SO₄ was added to the K_2BrMA solution. After 15 min, the solution was titrated with 0.05 M AgNO₃ to beyond the titration endpoint. The AgBr was then filtered out using a previously-weighed cellulose nitrate membrane with pore size $0.45 \,\mu m$. This filtering method has been shown to remove AgBr quantitatively from the solution.¹¹ The H₂SO₄ was washed out of the membrane with approximately 300 mL of distilled water. The membrane and AgBr were then dried to constant weight. The procedure from addition of Ce4+ to weighing of AgBr was repeated three more times with the same BrMA solution. Then the entire procedure was repeated with a new BrMA solution. Alternatively to the titration method the residual bromide in the BrMA was removed by adding a few drops of AgNO₃ to the BrMA and filtering out the precipitated AgBr. The remaining solution of BrMA was tested for complete removal of bromide with another drop of AgNO₃. After the end of the reaction of BrMA with Ce^{4+} , a solution of AgNO₃ was added to provide at least 1 Ag⁺ for each initial Ce4+ ion.

First, the experiments were carried out in the presence of dissolved oxygen from the air. Second, oxygen was excluded by

Ceric Oxidation of Bromomalonic Acid

bubbling nitrogen (99.99%) through the solutions. Before starting the reaction nitrogen was bubbled through the BrMA solutions for 20 min, with stirring. Nitrogen-purged $Ce(SO_4)_2$ in 1 M H₂SO₄ solution was then injected. The solution was allowed to react for 15 min. The N₂ bubbling was then stopped and AgNO₃ solution was added.

2.4.2. Bromide Production in BrMA/MA Mixtures. The second set of experiments was done to measure the effects of malonic acid on the production of bromide from Ce⁴⁺ and bromomalonic acid in nitrogen-purged solutions. In the first experiments of this set, the BrMA was produced by the Zhabotinskii method. The initial concentrations were chosen to be similar to the ones used in the ESR experiments of ref 2. The solution volume was again 100 mL, and the synthesis of BrMA was carried out as described in section 2.2 (adding bromate and bromide to MA). The reaction was allowed to continue undisturbed for 20 min after the completion of the Br- addition, and then the N₂ purging was begun. The remainder of the procedure (oxidation by Ce⁴⁺ and measurement of the AgBr precipitate) was the same as in the first set of experiments.

The MA/BrMA mixture experiments were then repeated with BrMA produced by the ether bromination method. In this case AgNO₃ solution was dropped into the MA/BrMA solution to remove the residual bromide from the synthesis process. The AgBr was filtered out, and a few more drops of AgNO₃ were added to the solution to confirm that no more bromide remained. The solution was then purged with nitrogen and injected with Ce^{4+} solution. The bromide was recovered as AgBr as in the other cases.

3. Results and Discussion

3.1. Range of Validity of the Zhabotinskii Synthesis. In the Zhabotinskii synthesis method it is assumed that the bromination of BrMA, to form Br_2MA , can be neglected in aqueous H_2SO_4 solution. The rate constant for bromination of MA is¹³ 28 M⁻¹ s⁻¹ at 20 °C. Our result for the rate constant for bromination of BrMA in 1 M H_2SO_4 solution is 70 M⁻¹ s⁻¹ at 20 °C. Thus the Zhabotinskii method will produce significant amounts of Br_2-MA if too great an extent of bromination is attempted. Figure 1 shows the simulation production of 1 M MA with initial Br concentrations (=[Br⁻]₀ + [BrO₃⁻]₀) of 0–1 M.

We see from Figure 1 that the Zhabotinskii method for synthesis of BrMA in 1 M H_2SO_4 is valid only for less than 10% bromination. These results were confirmed by measuring the ¹³C NMR spectra of BrMA solutions prepared by the Zhabotinskii method. In these spectra a signal at 35.4 ppm with a doublet fine splitting structure appears additionally to the 44.6 ppm BrMA signal. A doublet cannot be expected for Br₂MA, but for Br₂Ac (dibromoacetic acid), which results from decarboxylation of Br₂MA. In fact the ¹³C NMR signal of Br₂Ac is at 35.2 ppm. Also the ratios of the MA and BrMA peak heights are the same as expected from the kinetic data displayed in Table II.

Table II lists the calculated results for MA and BrMA for the initial conditions of the Zhabotinskii syntheses used in ref 2 and in this work. For experiments 1 through 4, the results were assumed in ref 2 to be [MA] = 0.2 M and $[BrMA] = [Br^-]_0 + [BrO_3^-]_0$. For experiments 7 and 8, the results were assumed to be [MA] = 0.4 M and $[BrMA] = [Br^-]_0 + [BrO_3^-]_0$.

3.2. Another Look at the ESR Results in Ref 2. Considering the results reported in section 3.1, the results for the ESR experiments of ref 2 must be re-evaluated. Table III lists the calculated initial concentrations of MA and BrMA for the ESR experiments of ref 2, along with the malonyl radical concentrations predicted from the GTF model,¹ by the simple model of reactions R1-R5, and calculated from the observed ESR signal. We see that neither theory is a good fit, but the simple model is closer



Figure 1. Calculated final concentrations $[MA]_f$, $[BrMA]_f$, and $[Br_2-MA]_f$ after the addition of BrO_3^- and Br^- (with a total initial Br concentration of [total $Br]_0$) to malonic acid ($[MA]_0 = 1 M$) in 1 M H_2SO_4 . The results are calculated from numerical simulation of reactions Z1b and Z2. Reaction Z1a is assumed to be fast. Solid lines: $k_{Z1b} = 28 M^{-1} s^{-1}$, $k_{Z2} = 70 M^{-1} s^{-1}$. Dashed lines: $k_{Z1b} = 28 M^{-1} s^{-1}$, $k_{Z2} = 0$.

TABLE II: Calculated Results of Zhabotinskii Synthesis in 1 M H₂SO₄ for Initial Concentrations Used in This Work and in Ref 2

expt	[MA] ₀ (M)	[Br ⁻] ₀ + [BrO ₃ ⁻] ₀ (M)	[MA] _f (M)	[BrMA] _f (M)	[Br ₂ MA] _f (M)
1	0.25	0.05	0.21	0.033	0.008
2	0.30	0.10	0.22	0.053	0.023
3	0.40	0.20	0.26	0.083	0.059
4	0.65	0.45	0.35	0.141	0.154
5	0.45	0.05	0.41	0.039	0.005
6	0.50	0.10	0.42	0.066	0.017
7	0.60	0.20	0.45	0.107	0.047
8	0.80	0.40	0.52	0.166	0.117
9	0.65	0.05	0.60	0.042	0.004
10	0.85	0.05	0.80	0.044	0.003

TABLE III: Corrected Initial Concentrations for ESR Experiments of Ref 2 (Reaction of Mixtures of MA and BrMA with 0.02 M Ce⁴⁺ in 1 M H₂SO₄), Experimental and Calculated Malonyl Radical Steady-Flow Concentrations

			10 ⁷ [MA•] _{ss} (M)		
expt	$[MA]_0(M)$	$[BrMA]_0(M)$	calc, GTF	calc, simple	expt
1	0.20	0	3.8	3.8	3.8
2	0.21	0.033	2.0	3.9	3.8
3	0.22	0.053	1.6	4.0	3.8
4	0.26	0.083	1.3	4.3	3.8
5	0.35	0.141	1.1	5.0	3.8
6	0.40	0	5.3	5.3	5.3
7	0.45	0.107	1.7	5.7	5.3
8	0.52	0.166	1.3	6.1	5.3

to the data. The GTF model provides the right type of corrections, lowering the predicted malonyl radical concentration because of the effects of BrMA, but the model overestimates the effects of BrMA on the MA[•] concentrations: $[MA[•]] = 1.1 \times 10^{-7}$ M is calculated instead of 3.8×10^{-7} M in experiment 4, and [MA[•]]= 1.3×10^{-7} M instead of 5.3×10^{-7} M in experiment 8.

The calculations for Table III were done with the old value for malonyl radical disproportionation,⁸ 3.2×10^9 M⁻¹ s⁻¹. Using the new value⁷ of 4.2×10^8 M⁻¹ s⁻¹ would change the values in the table as follows. With no BrMA present, both theories agree with the experimental values by definition. The steady-state

TABLE IV: Experimental Stoichiometry of Bromide Production in Air and in Nitrogen-Purged Solutions for Various Initial Ratios of [Ce⁴⁺] to [BrMA]^a

	[Ce ⁴⁺] ₀ /[BrMA] ₀	$[Ce^{4+}]_0/[Br^-]_f$	
[Ce4+]/M		in N ₂	in air
5 × 10-4	0.010	1.8	1.0
1 × 10 ⁻³	0.020	2.1	1.4
1.4×10^{-3}	0.028	1.9	
2.5×10^{-3}	0.050	2.3	
5 × 10-3	0.100	2.7	2.6

^a The initial concentration of BrMA was 0.05 M.

malonyl radical concentration for these cases is

$$[\mathbf{MA}^*]_{\rm ss} = \left(\frac{[\mathbf{Ce}^{4+}]_0[\mathbf{MA}]_0}{2k_3}\right)^{1/2} \tag{1}$$

Thus for experiments 1 and 6 of Table III, use of the new k_3 value would require us to multiply all the [MA[•]]_{ss} values by $(3.2 \times 10^9/4.2 \times 10^8)^{1/2} = 2.76$.

For the other runs, eq 1 still applies to the simple theory calculations. Thus all the $[MA^*]_{ss}$ values calculated from the simple theory must be multiplied by 2.76. The experimentally observed ESR signals provide only relative concentrations, so multiplying the experimental values for experiments 1 and 6 by the factor 2.76 requires that we multiply all the experimental values by 2.76. The new rate constant provides a simple scale factor in the comparison of the simple theory with the experimental data.

The adjustment for the new value of k_3 is more problematic for the GTF model calculations. A number of rate constants, including those for the reactions labeled (R4)–(R8) of this paper, were adjusted to fit the data presented in ref 1. If only k_3 is changed in the GTF model, then the model will not fit the data of ref 1 unless the other rate constants for malonyl radical reactions are also updated. In this paper we do not want to examine a dramatically altered version of the GTF theory, so we present all the calculations in Table III with the old value of k_3 .

For experiments 1 through 4 of Table II, we originally assumed that the concentration of MA was 0.2 M in each case. Thus the observed independence of malonyl radical concentration from BrMA was interpreted to mean that the BrMA had no effect. The present analysis indicates that there are two competing effects on the malonyl radical concentration: (a) the concentration of MA is increasing, because some of the Br_2 used in the Zhabotinskii synthesis was consumed by BrMA instead of by MA; and (b) the malonyl radicals may be consumed by bromomalonyl radicals in reaction R6, or by BrMA in reaction R7, or both.

Of course, the concentration of malonyl radicals alone does not provide enough information to show what part of the GTF model should be revised. Thus we turn now to the Brstoichiometry results.

3.3. Confirmation of Jwo/Noyes Results in the Absence of MA. For the first set of experiments in the presence of oxygen, the ratio of Ce⁴⁺ consumed to Br⁻ produced was calculated from the weight of AgBr and the initial quantity of Ce⁴⁺. The results for the individual runs were: Ce⁴⁺/Br⁻ = 1.0, 1.1, 1.2, 0.9, 0.98, 1.0, 0.95, and 1.0. So the average value is 1.0 ± 0.1 for a ratio $[Ce^{4+}]_0/[BrMA_0] = 0.01$ (Table IV, column 4). In each case, approximately 5 mL of AgNO₃ solution were required to reach the titration endpoint. Thus the electrode results agree with the weighing because of the small amounts of AgNO₃ solution used. The volume of added AgNO₃ solution was kept small in order to make repeated runs on the same K₂BrMA solution.

Our results are in agreement with the results of Jwo and Noyes⁴ for $[BrMA]_0/[Ce^{4+}]_0 = 100$. Thus, we have confirmed by another



Figure 2. Observed and predicted Br^- production from ceric oxidation of mixtures of MA and BrMA. $[Br^-]_f$ is the final bromide concentration at the end of the reaction. Initial concentrations: $[Ce^{4+}]_0 = 0.02$ M, $[MA]_0 = 0.2 to 0.8$ M, $[BrMA]_0 = 0.03 to 0.08$ M. Circles: experiments with BrMA synthesized by the Zhabotinskii method. Triangles: experiments with BrMA synthesized by bromination of MA in ether solution. Lower solid line: simple theory, reactions R1-R5, $[Br^-]_f$ calculated from eq 2. Upper solid line: the 80-equation GTF theory from ref 1, $[Br^-]_f$ calculated from numerical integration of the rate equations. Results from the GTF theory are essentially the same as those calculated using only reactions R1 to R8.

method that the stoichiometry used by Györgyi et al.^{5,6} for systems in the presence of oxygen is correct.

3.4. Production of Bromide from Pure Bromomalonic Acid in Nitrogen-Purged Solutions. The ratio of Ce⁴⁺ consumed to Brproduced was calculated as in the previous case. The results are shown in Table IV (column 3).

Surprisingly, we see that in the absence of oxygen, two Ce⁴⁺ are consumed to produce one bromide when the initial BrMA concentration is sufficiently in excess of the Ce⁴⁺ concentration. The observed stoichiometry changes to even higher values as the fraction of Ce4+ is increased above 5%. This phenomenon was also noted by Jwo and Noyes⁴ and was attributed to consumption of some of the Ce⁴⁺ by the products of the initial oxidation reaction. It is interesting to see that at the highest $[Ce^{4+}]_0/[BrMA]_0$ ratio the result for bromide production is the same whether oxygen is excluded or not. In this case the initial Ce4+ concentration is 5 \times 10⁻³ M, which is much more than the concentration of oxygen which can be dissolved by an aqueous solution in contact with air¹⁴ (3 \times 10⁻⁴ M); the oxygen is consumed by forming peroxy compounds with bromomalonyl radicals.¹⁵ Hence most of the Ce4+ is reacting in an oxygen-free medium. In part, this effect can already be seen at $[Ce^{4+}]_0 = 1 \times 10^{-3} \text{ M}$ (line 2 in Table IV). The 1:1 stoichiometry for air-saturated solutions at $[Ce^{4+}]_0 = 5$ $\times 10^{-4}$ M probably results from the decomposition of the peroxy compounds. It should be noted that in BrMA solutions saturated with pure oxygen the $[Ce^{4+}]_0/[Br^-]_f$ ratio is even smaller than 1 (approximately 0.25).

The results from the nitrogen-purged solutions support the assumption of the bromomalonyl radical disproportionation reaction used by Györgyi, Turányi, and Field¹ to model systems from which oxygen was excluded. This reaction is (R4) of our simple model.

The difference between the results in the presence and in the absence of oxygen implies that the oxygen consumes the bromomalonyl radicals faster than they can react with each other, when the experiments are done in air-saturated solution. The 1:1 stoichiometry found in the presence of air probably results from the decomposition of the peroxide formed from the reaction of oxygen with bromomalonyl radicals.

3.5. Effects of Malonic Acid. Figure 2 shows the production of bromide predicted by the GTF theory and by the simple model of reactions R1-R5 for a set of experiments. All experiments were done in 1 M H₂SO₄, and all GTF simulations were done with $[H^+] = 1.29$ M. The initial concentration of Ce⁴⁺ was always 0.02 M for theory and experiment. The initial concentration of BrMA was always 0.05 M for the simulations of the GTF theory.

For the simple theory of reactions R1-R5 the Br⁻ production was calculated according to the following, with (R5) assumed as a fast reaction:

$$[Br^{-}]_{f} = \frac{[Ce^{4+}]_{0}}{2} \frac{k_{2}[BrMA]_{0}}{k_{1}[MA]_{0} + k_{2}[BrMA]_{0}}$$
(2)

The experimental results are displayed as circles and triangles in the figure. The circles represent experiments done with BrMA synthesized by the Zhabotinskii method, and the triangles represent experiments done with BrMA synthesized by bromination of MA in ether solution.

We see that the GTF theory seriously overestimates the Brproduction from the experiments. The simple theory slightly underestimates the Br- production, but is a reasonable fit to the data.

The simple theory can be corrected by adjusting the rate constants for reactions R4, R6, R7, and R8 to allow for a small effect of BrMA[•] and BrMA. At this point all four rate constants are speculative, since bromomalonyl radicals have not been observed in solution.

Use of the new value for k_3 would have no effect on the predictions of the simple model. It would change the predictions of the GTF model, but as noted before, it would also disturb the fit of the GTF model to the data from oscillating BZ systems presented in ref 1. The rate constants finally accepted for reactions R4 and R6–R8 should be consistent with the new value of k_3 , the data from oscillating BZ systems, and the stoichiometry presented in this work.

4. Conclusion

Our experiments on the stoichiometry of Br⁻ production from ceric oxidation of BrMA in the presence of MA support our earlier conclusion² that the 80-equation model of Györgyi, Turányi, and Field¹ predicts too much Br- formation in subsets of the Belousov-Zhabotinskii reaction in which no oxybromine

species are present. Our data are not sufficient to provide a complete model, but we have shown that the simple model of reactions R1 through R5 predicts a reasonable approximation to the Br-production and needs only small corrections, not the severe corrections of the GTF model. Further experiments are necessary to provide a full understanding of Br-production in the BZ system.

Acknowledgment. We thank Prof. Z. Noszticzius (visiting the Center for Nonlinear Dynamics, The University of Texas at Austin) for assistance with the electrochemistry measurements, Dr. L. Györgyi for stimulating discussions, and Prof. S. Berger (Fachbereich Chemie, Phillipps-Universität Marburg) for the measurement of the ¹³C NMR spectra. This work was supported by the Stiftung Volkswagenwerk, the Fonds der Chemischen Industrie, the Robert A. Welch Foundation (Grant F-805), and the Department of Energy, Office of Basic Energy Sciences.

References and Notes

Györgyi, L.; Turányi, T.; Field, R. J. J. Phys. Chem. 1990, 94, 7162.
 Försterling, H. D.; Stuk, L. J. Phys. Chem. 1991, 95, 7320.
 Turányi, T.; Györgyi, L.; Field, R. J. J. Phys. Chem., in press.
 Jwo, J. J.; Noyes, R. M. J. Am. Chem. Soc. 1975, 97, 5422.

- (5) Györgyi, L.; Rempe, S.; Field, R. J. J. Phys. Chem. 1991, 95, 3159.
 (6) Györgyi, L.; Field, R. J. J. Phys. Chem. 1991, 95, 6594.
 (7) Försterling, H. D.; Stuk, L. J. Phys. Chem. 1992, 96, 3067.
 (8) Dense M.A. Delivitation of the chemical statement of the chemical s

(8) Brusa, M. A.; Perissinotti, L. J.; Colussi, A. J. J. Phys. Chem. 1985, 89. 1572.

- (9) Zaikin, A. N.; Zhabotinskii, A. M. Nature 1970, 225, 535.
- (10) Försterling, H. D.; Idstein, H.; Pachl, R.; Schreiber, H. Z. Naturforsch. 1984. 39A. 993.

(11) Roberts, J.; Stuk, L.; McCormick, W. D. J. Phys. Chem. 1991, 95, 3165.

(12) Noszticzius, Z.; Wittmann, M.; Stirling, P. In 4th Symposium on Ion-Selective Electrodes, Punger, E., Ed.; Elsevier: Amsterdam, 1985; p 579. (13) Pachl, R. Ph.D. Thesis, Philipps-Universität Marburg, 1989

 (14) CRC Handbook of Physics and Chemistry; Weast, R. C., Ed.; CRC
 Press: Boca Raton, FL, 1977. The solubility of O₂ in water is given as 3.2 mL/100 mL at room temperature. This corresponds to a concentration of 1.4 \times 10⁻³ M. Regarding a 20% content of O₂ in air, we find 2.9 \times 10⁻⁴ M oxygen in water saturated with air.

(15) Barkin, S.; Bixon, M.; Noyes, R. M.; Bar-Eli, K. Int. J. Chem. Kin. 1978, 10, 619.