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Bromination Reactions Important in the Mechanism of the Belousov−Zhabotinsky System

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We investigate the kinetics of bromination of malonic acid, bromomalonic acid, tartronic acid, and ethanetetracarboxylic acid in 1 M sulfuric acid with bromine and hypobromous acid as brominating agents. In all cases the reaction occurs via the enol form of the acid, and the reaction products are brominated species. The possibility of bromide production in the reaction of malonic acid or bromomalonic acid with hypobromous acid can be ruled out. These results are important for the negative feedback loop in the Belousov−Zhabotinsky reaction.

1. Introduction

Despite much experimental and theoretical effort, there remains basic difficulty in understanding the detailed mechanism of the destabilizing, negative feedback processes in the Belousov−Zhabotinsky (BZ) reaction,[1] the metal-ion-catalyzed oxidation and bromination of malonic acid by bromate. The basic structure[2,3] of the negative feedback seems clear; it involves inhibition of an autocatalytic (positive feedback) process by a product of that autocatalysis. Bromous acid ($HBrO_2$) is the key species.[4] It may either react autocatalytically via reactions Z1 and Z2 with bromate and the reduced form of the metal-ion catalyst to lead to explosive growth in its concentration,

$$HBrO_2 + BrO_3^- + H^+ \rightarrow 2BrO_2^\bullet + H_2O \qquad (Z1)$$

$$2BrO_2^\bullet + 2\,Ce^{3+} + 2\,H^+ \rightarrow 2Ce^{4+} + 2HBrO_2 \qquad (Z2)$$

or it may be removed from the system as bromomalonic acid ($BrCH(COOH)_2$) by reaction with Br^-, reactions Z3 and Z4.

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \qquad (Z3)$$

$$CH_2(COOH)_2 + HOBr \rightarrow BrCH(COOH)_2 + H_2O \qquad (Z4)$$

A negative feedback on the autocatalytic formation of $HBrO_2$ in the BZ reaction was proposed by Field, Körös, and Noyes.[1] It results from scavenging of $HBrO_2$ in reactions Z3 and Z4 by Br^-. Br^- is generated by the interaction of Ce^{4+}, a product of the autocatalysis, with bromomalonic acid in reaction Z5.

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \rightarrow 4Ce^{3+} + HCOOH + 2CO_2 + Br^- + 5H^+ \qquad (Z5)$$

The induction period observed before the onset of oscillation in the BZ reaction is believed[5] to result from the time required for the accumulation of sufficient $BrCH(COOH)_2$, and perhaps other derivatives of $CH_2(COOH)_2$, for the Br^- generation process to become effective. Difficulties with this proposal are the following. (1) Only one Br^- is produced in reaction Z5 for each four Ce^{4+} consumed, while the theoretical analyses[6] require that fewer than four Ce^{4+} be consumed to produce one Br^- if the steady state is to be destabilized and oscillation to occur. (2) The mechanism via which Br^- is released from $BrCH(COOH)_2$ is not clear. Reactions Z6−Z9 have been suggested.[7]

$$Ce^{4+} + BrCH(COOH)_2 \rightarrow Ce^{3+} + Br\dot{C}(COOH)_2 + H^+ \qquad (Z6)$$

$$Br\dot{C}(COOH)_2 + H_2O \rightarrow HOCH(COOH)_2 + Br^\bullet \qquad (Z7)$$

$$Br^\bullet + CH_2(COOH)_2 \rightarrow \dot{C}H(COOH)_2 + Br^- + H^+ \qquad (Z8)$$

$$\dot{C}H(COOH)_2 + BrCH(COOH)_2 \rightarrow CH_2(COOH)_2 + Br\dot{C}(COOH)_2 \qquad (Z9)$$

The radical-chain nature of reactions Z7−Z9 allows for enhanced Br^- production for each occurrence of reaction Z6. However, recent experimental results[8] indicate that reaction Z7 does not occur rapidly enough to be a primary source of Br^- generation in the BZ reaction. Furthermore, simulations based on such schemes[9] have difficulty generating enough Br^- to destabilize the BZ steady state. There are at least two ways to ameliorate these mechanistic problems. (1) Identification of additional Br^- generating processes based upon $BrCH(COOH)_2$ and other derivatives of CH_2 $(COOH)_2$. (2) Identification of additional feedback processes not involving Br^-. Additional Br^- generating processes might involve HOBr and/or Br_2 which are rapidly formed from $HBrO_2$ in reactions Z10 and Z11 during the autocatalytic phase of the BZ reaction.

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$$\mathrm{HBrO_2 + HBrO_2 \rightarrow HOBr + BrO_3^- + H^+} \quad \text{(Z10)}$$

$$\mathrm{Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O} \quad \text{(Z11)}$$

Reactions Z12 and Z13 are possible examples of such processes.

$$\mathrm{HOBr + BrCH(COOH)_2 \rightarrow O{=}C(COOH)_2 + 2H^+ + 2Br^-} \quad \text{(Z12)}$$

$$\mathrm{HOBr + HOCH(COOH)_2 \rightarrow O{=}C(COOH)_2 + H^+ + Br^- + H_2O} \quad \text{(Z13)}$$

We report here that reaction Z12 does not occur as written. It has been suggested[10−14] that an additional feedback route might involve scavenging of $\mathrm{Br\dot{O}^2}$ by organic radicals, e.g., $\mathrm{\dot{C}H(COOH)_2}$, rather than scavenging of $\mathrm{HBrO_2}$ by $\mathrm{Br^-}$. This process is referred to as radical-control and is illustrated by reaction Z14:

$$\mathrm{\dot{C}H(COOH)_2 + BrO_2^{\bullet} \rightarrow BrO_2CH(COOH)_2} \quad \text{(Z14)}$$

The fate of $\mathrm{BrO_2CH(COOH)_2}$ is unknown, but reaction Z15 seems reasonable:

$$\mathrm{BrO_2CH(COOH)_2 \rightarrow HOBr + O{=}C(COOH)_2} \quad \text{(Z15)}$$

Radical-control does not require the presence of $\mathrm{BrCH(COOH)_2}$ or any other derivative of $\mathrm{CH_2(COOH)_2}$ and was initially proposed to explain circumstances where the BZ reaction does not show an induction period.[15] A particularly compelling example of radical-control[16] is modeling of the $\mathrm{Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}}$-catalyzed BZ reaction, which shows no induction period. Resolution of these problems requires that careful simulations of the BZ reaction be carried out with special attention to the $\mathrm{Br^-}$ generation processes using good experimental rate parameters. The kinetics of the reactions of $\mathrm{Ce^{4+}}$ with $\mathrm{CH_2(COOH)_2}$ and $\mathrm{BrCH(COOH)_2}$ have been investigated by Försterling et al.[17−19] The products in the first case are the combination products of two forms of the malonyl radical, ethanetetracarboxylic acid (ETA),[17] and malonylmalonate (MAMA),[18] and in the second case ethenebromotricarboxylic acid,[19] the recombination product of $\mathrm{Br\dot{C}(COOH)_2}$. The kinetics of reaction Z14, the basis of radical-control, also have been directly determined.[10−14] We report here investigations of the kinetics of the reactions of $\mathrm{Br_2}$ and HOBr with $\mathrm{CH_2(COOH)_2}$, $\mathrm{BrCH(COOH)_2}$, $\mathrm{HOCH(COOH)_2}$, and $\mathrm{(HOOC)_2CHCH(COOH)_2}$.

2. Experimental Section

Malonic acid (Fluka, puriss.) was recrystallized following the procedures proposed by Noszticzius et al.,[20] because trace impurities of chloride ion can affect the experiments significantly. Tartronic acid (Heraeus, puriss.) was purified by treating the solid several times with an excess of acetic acid ethyl ester.[5] Bromomalonic acid and dibromomalonic acid were prepared following the procedure reported by Försterling and Stuk[8] (bromination of malonic acid by bromine in ether/$\mathrm{CCl_4}$ solution and isolation of the dipotassium salts). ETA (1,1,2,2-ethanetetracarboxylic acid) was prepared from its tetraethyl ester (Aldrich, 99%).[18] Sodium bromate (Fluka, puriss.) was recrystallized twice from water. $\mathrm{Br_2}$ (pa., Fluka) was dissolved in water. A solution saturated with $\mathrm{Br_2}$ ($c_{\mathrm{Br_2}} \approx 0.15$ M) was used as a stock solution. HOBr was prepared by reaction of an aqueous $\mathrm{Br_2}$ solution with $\mathrm{Ag_2SO_4}$; the precipitate of AgBr was removed by filtration, and the remaining HOBr was purified by distillation.[21] The concentration of the stock solution was $c_{\mathrm{HOBr}} \approx 0.15$ M. The solution was stored in a refrigerator at 2° C. Bromine resulting from the decomposition of HOBr was removed from the HOBr stock solution before use by purging with $\mathrm{N_2}$. The absence of significant $\mathrm{Br_2}$ contamination was checked by taking an UV spectrum. Kinetic measurements were carried out with a Hewlett−Packard 8452 diode array spectrometer and with a homemade dual wavelength spectrometer.[22] Reaction cells with an optical path length of 2 cm and of 10 cm were used. All kinetic experiments were carried out at 20° C. HPLC measurements were performed with a Shimadzu equipment (LC-10AS pump, CTO-10A column oven, SPD-10A dual wavelength UV-detector, 8 nm bandwidth, 1 cm path length, 8 μL cell volume). The sample was injected using a Rheodyne 7010 injector with a 20 μL sample loop. The eluent was 0.01 M $\mathrm{H_2SO_4}$ applied at a flow rate of 0.6 mL/min.

3. Results

Following previous investigations,[23,24] we assume that bromination occurs via the enol form of the carboxylic acid. We obtain in the case of malonic acid

$$\mathrm{(COOH){-}CH_2{-}(COOH)\ (keto\ form) \rightleftharpoons (COOH){-}CH{=}C(OH)_2\ (enol\ form)} \quad \text{(R1)}$$

$$\mathrm{(COOH){-}CH{=}C(OH)_2 + Br_2 \rightarrow (COOH){-}CHBr{-}COOH + H^+ + Br^-} \quad \text{(R2)}$$

$$\mathrm{(COOH){-}CH{=}C(OH)_2 + HOBr \rightarrow (COOH){-}CHBr{-}COOH + H_2O} \quad \text{(R3)}$$

Corresponding reaction schemes are assumed for bromomalonic acid, tartronic acid, and ethanetetracarboxylic acid (ETA). The rate equations for the bromination by $\mathrm{Br_2}$ are then

$$\frac{\mathrm{d}c_{\mathrm{Br_2}}}{\mathrm{d}t} = -k_2 c_{\mathrm{enol}} c_{\mathrm{Br_2}} \quad (3.1)$$

$$\frac{\mathrm{d}c_{\mathrm{enol}}}{\mathrm{d}t} = k_1 c_{\mathrm{keto}} - k_{-1} c_{\mathrm{enol}} - k_2 c_{\mathrm{enol}} c_{\mathrm{Br_2}} \quad (3.2)$$

Following the data in the literature, only a very small fraction of the acid is in the enol form; thus the concentration of the keto form can be practically identified with the total carboxylic acid concentration. Applying the steady-state approximation for the enol form ($\mathrm{d}c_{\mathrm{enol}}/\mathrm{d}t = 0$) we obtain

$$\frac{\mathrm{d}c_{\mathrm{Br_2}}}{\mathrm{d}t} = -\left(k_1 \frac{k_2}{k_{-1}}\right) \frac{c_{\mathrm{keto}}}{1 + (k_2/k_{-1}) c_{\mathrm{Br_2}}} c_{\mathrm{Br_2}} \quad (3.3)$$

We discuss the following limiting cases: (1) High bromine concentration ($k_2 c_{\mathrm{Br_2}} \gg k_{-1}$)

$$\frac{\mathrm{d}c_{\mathrm{Br_2}}}{\mathrm{d}t} = -k_1 c_{\mathrm{keto}} \quad (3.4)$$

In this case the enolization reaction is rate determining; the decay of $\mathrm{Br_2}$ follows zero-order kinetics. We obtain k_1 from the slope of the linear $[\mathrm{Br_2}]$ vs time line. (2) Low bromine concentration ($k_2 c_{\mathrm{Br_2}} \ll k_{-1}$)

$$\frac{\mathrm{d}c_{\mathrm{Br_2}}}{\mathrm{d}t} = -\left(k_1 \frac{k_2}{k_{-1}}\right) c_{\mathrm{keto}} c_{\mathrm{Br_2}} \quad (3.5)$$

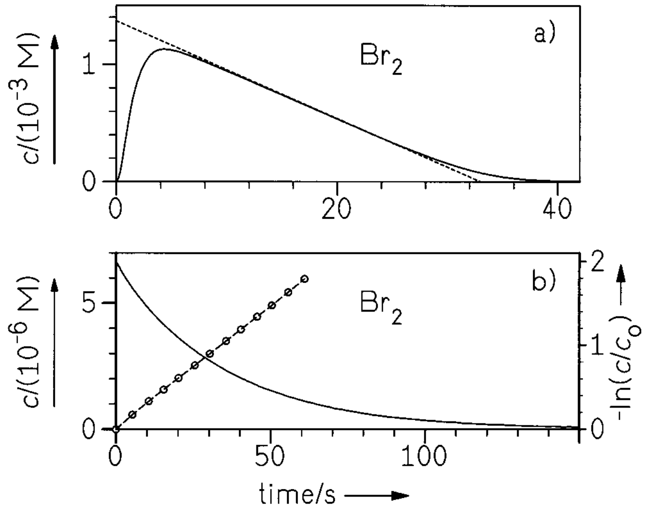

Figure 1. Decay of Br_2 concentration in the reaction with malonic acid in 1 M H_2SO_4 at 20° C (solid lines). (a) $c_{MA,0} = 0.0155$ M, $c_{Br_2,0} = 0.0014$ M; slope of the linear part $= -4.15 \times 10^{-5}$ M s^{-1} (dashed line). (b) $c_{MA,0} = 0.001$ M, $c_{Br_2,0} = 7 \times 10^{-6}$ M; circles: logarithmic plot with slope $= -0.0294$ s^{-1} (dashed line). The reaction was followed by measuring the absorbance of Br_2 at 400 nm; path length: 2 cm (a), and 10.8 cm (b), extinction coefficient see Table 1. The reaction was started by injecting bromine into the solution of malonic acid. Here and in the following figures note that a delay of some seconds is caused by slow mixing.

The bromination reaction is rate determining in this case; the decay of Br_2 follows first-order kinetics. We obtain k_1k_2/k_{-1} from the slope of the logarithmic plot.

We can evaluate k_1 and the ratio k_2/k_{-1} from these limiting cases. Although we cannot evaluate k_2 or k_{-1} separately, the overall kinetics of the bromination reaction is completely determined by k_1 and k_2/k_{-1}.

Correspondingly, for the bromination by HOBr the enolization reaction is the same, but the rate of bromination is determined by

$$\frac{dc_{HOBr}}{dt} = -k_3 c_{enol} c_{HOBr} \tag{3.6}$$

$$\frac{dc_{enol}}{dt} = k_1 c_{keto} - k_{-1} c_{enol} - k_3 c_{enol} c_{HOBr} \tag{3.7}$$

3.1. Bromination of Malonic Acid by Br_2. The decay of bromine in the reaction with malonic acid $CH_2(COOH)_2$ (MA) is followed by measuring the absorbance of bromine at 400 nm (absorption maximum of Br_2). The reaction is zero-order with a slope of -4.15×10^{-5} M s^{-1} for high bromine initial concentration (Figure 1a); with $c_{MA,0} = 0.0155$ M we obtain $k_1 = 2.6 \times 10^{-3}$ s^{-1}. For low bromine initial concentration (Figure 1b) the reaction is first-order. From the slope of the logarithmic plot -0.0294 s^{-1} and $c_{MA,0} = 0.001$ M we obtain $k_1k_2/k_{-1} = 29.4$ M^{-1} s^{-1}.

Although it is not necessary to evaluate k_2 explicitly to describe the overall bromination kinetics, it is convenient to include an estimated value for the equilibrium constant[9] $K_1 = k_1/k_{-1} = 1.5 \times 10^{-5}$ in the presentation of the results. Then we obtain $k_{-1} = 180$ s^{-1} and $k_2 = 2.0 \times 10^6$ M^{-1} s^{-1}.

Using these data we checked if the conditions for the two limiting cases are fulfilled. For high bromine initial concentration ($c_{Br_2,0} = 0.0014$ M): $k_2c_{Br_2,0} = 2800$ s^{-1}; this is large enough compared with $k_{-1} = 180$ s^{-1}. For low bromine initial concentration (7×10^{-6} M): $k_2c_{Br_2,0} = 14$ s^{-1}; this is small compared with k_{-1}.

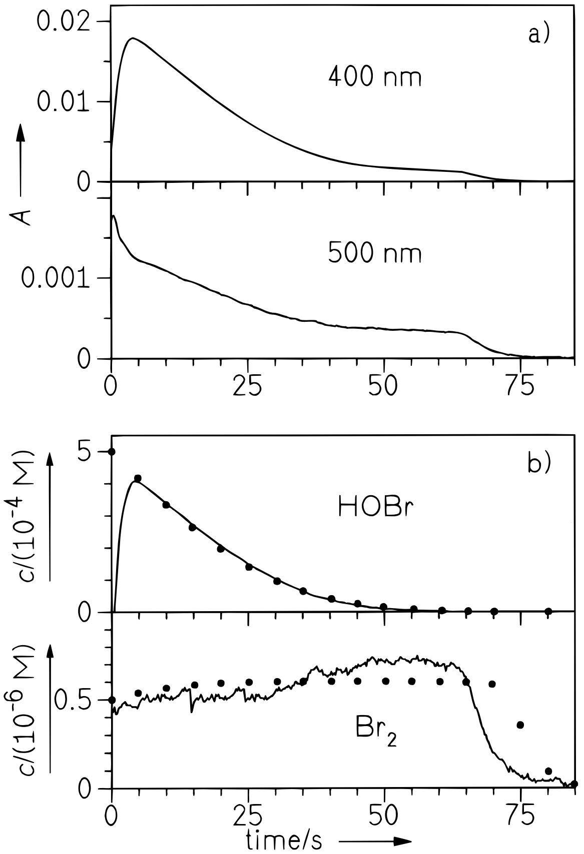

Figure 2. Reaction of HOBr ($c_{HOBr,0} = 5 \times 10^{-4}$ M) with malonic acid ($c_{MA,0} = 0.002$ M) in 1 M H_2SO_4 at 20° C. (a) Absorbance A followed at 400 and 500 nm (dual wavelength spectrometer, path length 10.8 cm). (b) Concentrations c_{HOBr} and c_{Br_2} calculated from the absorbances (using the extinctions coefficients listed in Table 1). Solid lines: experimental data. Dots: concentrations calculated by numerical solution of the differential equations corresponding to reactions R1–R4 with the rate constants k_1–k_3 in Table 2, $k_4 = 8 \times 10^9$ M^{-2} s^{-1}, $k_{-4} = 80$ s^{-1}, and $c_{Br_2,0} = 5 \times 10^{-7}$ M. The reaction was started by injecting HOBr into the solution of malonic acid.

TABLE 1: Extinction Coefficients ϵ of Br_2 and HOBr at Different Wavelengths

λ (nm)	$\epsilon(Br_2)$ (M^{-1} cm^{-1})	ϵ(HOBr) (M^{-1} cm^{-1})
300	9.0	43.4
400	172	4.0
500	37.3	0.27

3.2. Bromination of Malonic Acid by HOBr. It cannot be avoided in this experiment that the hypobromous acid contains traces of bromine. Therefore the reaction initially was followed by measuring the absorbances at 300 nm (strong absorption of HOBr, weak absorption of Br_2) and at 400 nm (weak absorption of HOBr, strong absorption of Br_2) simultaneously. However, it turned out that measuring at 400 nm and 500 nm simultaneously using a dual-wavelength spectrometer leads to a better signal-to-noise ratio. First we used a high concentration of HOBr (Figure 2a). The kinetics at both wavelengths is different, indicating that bromine is absorbing as well as HOBr. An evaluation of c_{HOBr} and c_{Br_2} from the measured absorbances reveals (Figure 2b) that during the decay of HOBr bromine is present at a nearly constant concentration (≈0.1% of the initial HOBr concentration).

The measured bromine concentration is the remaining bromine impurity of the HOBr stock solution, even after a very careful purification. If traces of Br_2 react with malonic acid, then bromide appears as a product reacting with excess HOBr

TABLE 2: Rate Constants k_1, k_{-1}, k_2, and k_3 for Bromomalonic Acid (BrMA), Ethanetetracarboxylic Acid (ETA), Malonic Acid (MA), and Tartronic Acid (TA)[a]

	enolization			
acid	k_1 (10^{-3} s^{-1})	k_{-1} (s^{-1})	reaction with Br_2 k_2 (10^6 M^{-1} s^{-1})	reaction with HOBr k_3 (10^6 M^{-1} s^{-1})
BrMA	12	800	3.5	1.1
ETA	6.2	413	10.0	
MA	2.6	180	2.0	0.67
TA	0.023	1.5	0.3	0.2

[a] Measured at 20° C. k_{-1} is calculated from k_1 and the equilibrium constant[9] K_1=1.5 × 10^{-5}. The rate constants are averages of the values obtained in Figures 1−7 and of additional data.

to yield bromine according to R4:

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (R4)$$

with the rate constants[16] $k_4 = 8 \times 10^9$ M^{-2} s^{-1} and $k_{-4} = 80$ s^{-1}. Thus the bromine concentration remains constant at its initial value until all HOBr has disappeared.

We confirmed by HPLC analysis after completion of the reaction that bromomalonic acid is the only detectable product of the reaction. No tartronic acid is detected. Thus the possibility that malonic acid reacts with HOBr to form tartronic acid and bromide in a side reaction can be ruled out.

The decay of HOBr at low HOBr initial concentration ($c_{HOBr,0}$ = 8 × 10^{-5} M) follows first-order kinetics. From the slope −0.016 s^{-1} of the logarithmic plot and the initial concentration $c_{MA,0}$ = 2 × 10^{-3} M we calculate k_1k_3/k_{-1} = 8 M^{-1} s^{-1}. Then, including the same value for the equilibrium constant K_1 as used before, we obtain k_3 = 0.53 × 10^6 M^{-1} s^{-1}.

In this case we find $k_3c_{HOBr,0}$ = 42 s^{-1}; this is on the same order as k_{-1} = 180 s^{-1}. Therefore we improved the evaluation of the experimental data by regarding reactions R1−R4 and solving the corresponding differential equations numerically. Good agreement with the experimental data was achieved (dots in Figure 2) by using the value k_3 = 0.67 × 10^6 M^{-1} s^{-1} instead of k_3 = 0.53 × 10^6 M^{-1} s^{-1}.

3.3. Bromination of Bromomalonic Acid by Br_2. The decay of bromine by its reaction with bromomalonic acid BrCH(COOH)$_2$ (BrMA) was followed by measuring the absorbance at 400 nm (Figure 3a for high bromine initial concentration, Figure 3b for low bromine initial concentration). From the slope −2.3 × 10^{-4} M s^{-1} in Figure 3a ($c_{MA,0}$ = 0.02 M) we obtain k_1 = 0.012 s^{-1}; then $k_{-1} = k_1/K_1$ = 800 s^{-1}. From the slope −0.053 s^{-1} of the logarithmic plot in Figure 3b and $c_{MA,0}$ = 0.001 M we obtain k_1k_2/k_{-1} = 53 M^{-1} s^{-1}; then k_2 = 3.5 × 10^6 M^{-1} s^{-1}.

In the case of high bromine initial concentration ($c_{Br_2,0}$ = 0.0028 M) we obtain $k_2c_{Br_2,0}$ = 9800 s^{-1}; this is large enough compared with k_{-1} = 800 s^{-1}. In the case of low bromine initial concentration (1.3 × 10^{-5} M) we obtain $k_2c_{Br_2,0}$ = 46 s^{-1}; this is small enough compared with k_{-1} = 800 s^{-1}. Thus no refinement in the evaluation of the kinetic data was necessary.

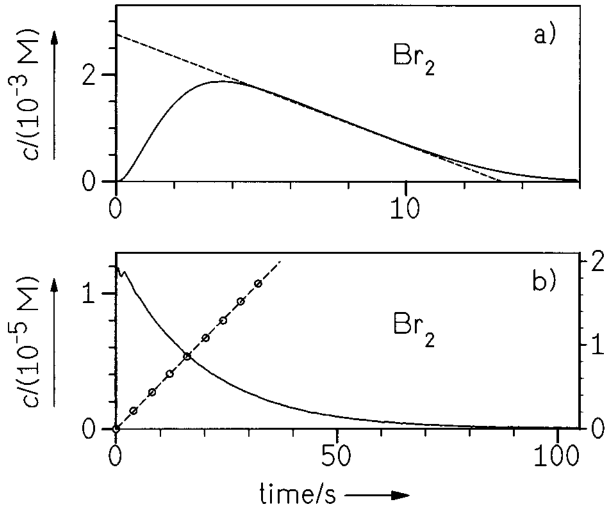

Figure 3. Decay of Br_2 in the reaction with bromomalonic acid in 1 M H_2SO_4 at 20° C (solid lines). (a) $c_{BrMA,0}$ = 0.02 M, $c_{Br_2,0}$ = 0.0028 M; slope = −2.3 × 10^{-4} M s^{-1} (dashed line). (b) $c_{BrMA,0}$ = 0.001 M, $c_{Br_2,0}$ = 1.2 × 10^{-5} M; circles: logarithmic plot with slope −0.053 s^{-1} (dashed line). The reaction was followed by measuring the absorbance of Br_2 at 400 nm (path length 10.8 cm, extinction coefficient see Table 1).

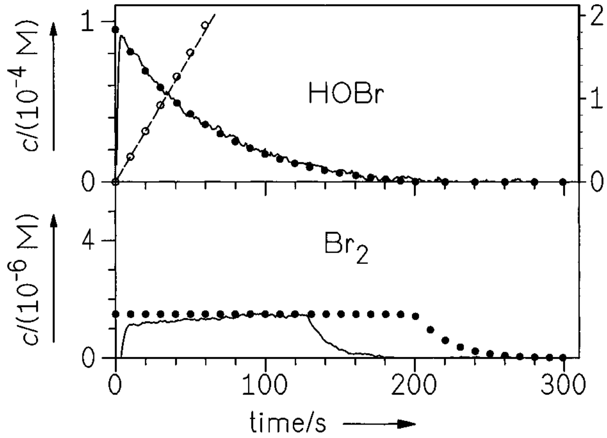

Figure 4. Reaction of HOBr with bromomalonic acid ($c_{BrMA,0}$ = 0.001 M, $c_{HOBr,0}$ = 9.5 × 10^{-5} M) in 1 M H_2SO_4 at 20° C. Concentration c_{HOBr} calculated from the absorbances at 400 and 500 nm (solid line). Circles: logarithmic plot with slope = −3 × 10^{-2} s^{-1} (dashed line). Dots: concentration calculated by numerical solution of the differential equations corresponding to reactions R1−R4 with the rate constants k_1−k_3 in Table 2, k_4 = 8 × 10^9 M^{-2} s^{-1}, k_{-4} = 80 s^{-1}, and $c_{Br_2,0}$ = 3 × 10^{-6} M.

3.4. Bromination of Bromomalonic Acid by HOBr. It is crucial for this experiment that the bromide ion impurity of bromomalonic acid (originating from the synthesis) be sufficiently low. This is achieved by very careful recrystallization resulting in a final bromide ion content of less than 0.1%. The decay of HOBr was followed by measuring the absorbances at 400 and 500 nm simultaneously (dual wavelength spectrometer). The decay of HOBr at low HOBr initial concentration (Figure 4, $c_{HOBr,0}$ = 9.5 × 10^{-5} M) follows first-order kinetics. We calculate k_1k_3/k_{-1} = 29 M^{-1} s^{-1} from the slope −0.029 s^{-1} of the logarithmic plot and the initial concentration $c_{BrMA,0}$ = 0.001 M. Then, including the same value for the equilibrium constant K_1, we obtain k_3 = 1.9 × 10^6 M^{-1} s^{-1}. Thus $k_3c_{HOBr,0}$ = 180 s^{-1}; this is not small enough compared with k_{-1} = 800 s^{-1}.

We therefore improved the evaluation of the experimental data by regarding reactions R1−R4 and solving the corresponding differential equations numerically. Using the rate constant k_3 = 1.1 × 10^6 M^{-1} s^{-1} instead of k_3 = 1.9 × 10^6 M^{-1} s^{-1} the result (dots in Figure 4) is in good agreement with the experimental data.

We confirmed by HPLC analysis after completion of the reaction that dibromomalonic acid is the product of the reaction. No bromotartronic acid or decomposition products of this acid could be detected. Thus the possibility that bromomalonic acid reacts with HOBr to form bromotartronic acid and bromide in a side reaction can be ruled out.

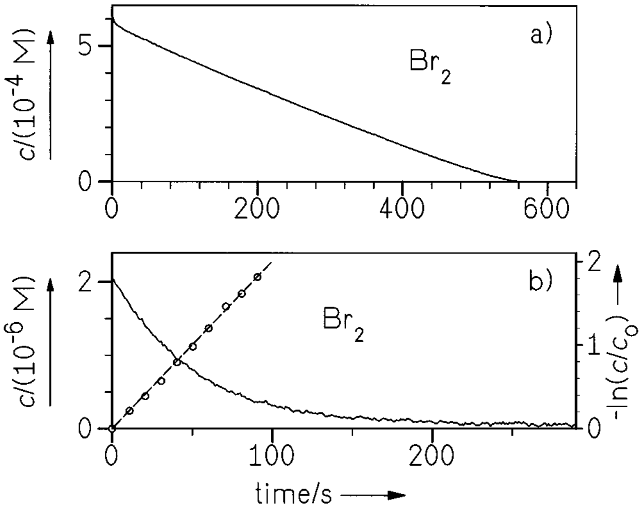

Figure 5. Decay of Br_2 in the reaction with tartronic acid in 1 M H_2SO_4 at 20° C. The concentration of Br_2 is calculated from the absorbance at 400 nm. (a) $c_{TA,0} = 0.05$ M, $c_{Br_{2,0}} = 6 \times 10^{-4}$ M; slope $= -1.15 \times 10^{-6}$ M s^{-1}. (b) $c_{TA,0} = 0.005$ M, $c_{Br_{2,0}} = 2 \times 10^{-6}$ M; circles: logarithmic plot with slope $= -0.02$ s^{-1} (dashed line).

3.5. Bromination of Tartronic Acid by Bromine. The decay of bromine in the reaction with tartronic acid, $HOCH(COOH)_2$ (TA), is followed by measuring the absorbance at 400 nm (Figure 5a for high bromine concentration, Figure 5b for low bromine initial concentration). We obtain $k_1 = 0.023 \times 10^{-3}$ s^{-1}; then $k_{-1} = k_1/K_3 = 1.5$ s^{-1} from the slope -1.15×10^{-6} M s^{-1} in Figure 5a ($c_{TA,0} = 0.05$ M). We obtain $k_2 = 0.26 \times 10^6$ M^{-1} s^{-1} in the low bromine concentration case from the slope of the logarithmic plot (Figure 5b, $c_{Br_{2,0}} = 2 \times 10^{-6}$ M).

In the case of high bromine initial concentration ($c_{Br_{2,0}} = 6 \times 10^{-4}$ M) we find $k_2c_{Br_{2,0}} = 156$ s^{-1}; this is large enough compared to $k_{-1} = 1.5$ s^{-1} . For low bromine initial concentration ($c_{Br_{2,0}} = 2 \times 10^{-6}$ M) we obtain $k_2c_{Br_{2,0}} = 0.5$ s^{-1}; this is not small enough compared with $k_{-1} = 1.5$ s^{-1}. Therefore we improved the evaluation of the experimental data by solving the differential equations (3.1) and (3.2) numerically. By using the rate constant $k_2 = 0.30 \times 10^6$ M^{-1} s^{-1} instead of 0.26×10^6 M^{-1} s^{-1} a good agreement with the experimental data was achieved.

3.6. Bromination of Tartronic Acid by HOBr. According to the results of Gao et al.[16] bromotartronic acid, the reaction product in the bromination of tartronic acid (TA), is not stable, but decomposes into mesoxalic acid and bromide. The formation of bromide during the bromination by bromine does not affect the evaluation of the kinetics. However, with HOBr as brominating agent reaction R4 leads to a simultaneous formation of bromine. Then it cannot be avoided that part of the initially present HOBr reacts with bromide to form bromine.

For this reason the reaction was followed by measuring the absorbances at 300 and 400 nm simultaneously. The concentrations of HOBr and Br_2 evaluated from this measurement are displayed in Figure 6. From the linear decay of the HOBr concentration we conclude that the rate-determining step is the enolization, as for the bromination by bromine. From the slope of the straight line -8×10^{-7} M s^{-1} and $c_{TA,0} = 0.02$ M we obtain $k_1 = 4 \times 10^{-5}$ s^{-1}. This value is too large by a factor of two, because of the additional consumption of HOBr by bromide according to R1. As expected, the concentration of Br_2 increases linearly corresponding to the decay of HOBr. After the consumption of HOBr, the bromine disappears by reaction with TA. After the maximum of the bromine concentration there is a small contribution of Br_3^- to the overall absorbance (due to an equilibrium between bromide and excess bromine), which must be taken into account in the evaluation of the concentrations of HOBr and Br_2.

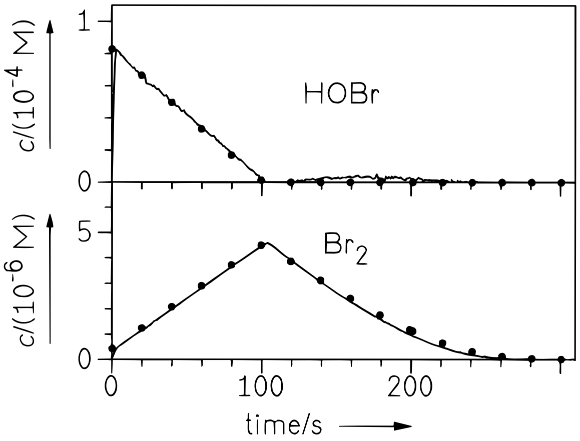

Figure 6. Reaction of HOBr with tartronic acid in 1 M H_2SO_4 at 20° C. The concentrations of HOBr and of Br_2 are calculated from the absorbances (path length 10.8 cm, extinction coefficients see Table 1). $c_{TA,0} = 0.02$ M, $c_{HOBr,O} = 8.3 \times 10^{-5}$ M, $c_{Br_2,o} = 5.0 \times 10^{-6}$ M; slope $= -8 \times 10^{-7}$ M s^{-1}. Dots: concentration calculated by numerical solution of the differential equations corresponding to reactions R1−R4 with the rate constants k_1−k_3 in Table 2, $k_4 = 8 \times 10^9$ M^{-2} s^{-1}, $k_{-4} = 80$ s^{-1}, and $c_{Br_{2,0}} = 5 \times 10^{-6}$ M.

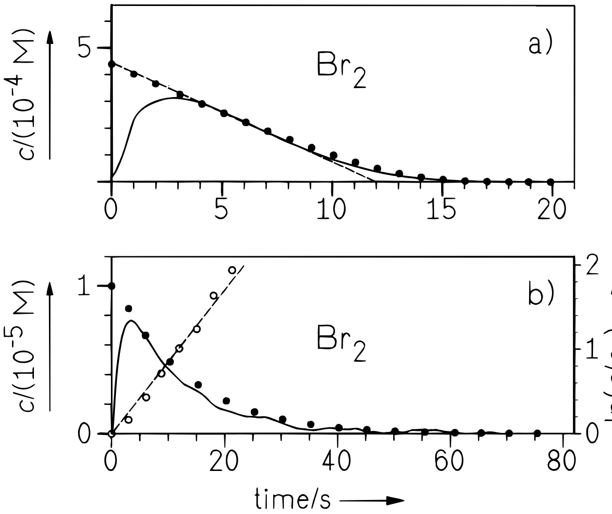

Figure 7. Reaction of Br_2 with ETA in 1 M H_2SO_4 at 20° C. (a) $c_{ETA,0} = 0.0063$ M, $c_{Br_{2,0}} = 4.4 \times 10^{-4}$ M; slope $= -3.7 \times 10^{-5}$ M s^{-1}. (b) $c_{ETA,0} = 6 \times 10^{-4}$ M, $c_{Br_2O} = 1 \times 10^{-5}$ M; slope of the logarithmic plot $= -0.089$ s^{-1}. The reaction was followed by measuring the absorbance of Br_2 at 400 nm (path length 10.8 cm, extinction coefficient see Table 1). Dots: concentration calculated by numerical solution of eq 3.1 and eq 3.2, using the rate constants shown in Table 2.

As for the bromination by bromine we were not able to decrease the HOBr concentration sufficiently to match the condition for the low HOBr limiting case. Therefore the experimental curves are compared with the result of a numerical solution of the differential equations corresponding to reactions R1−R4. The best fit of the experiments was achieved by choosing $k_3 = 2.0 \times 10^6$ M^{-1} s^{-1} (dots in Figure 6).

3.7. Bromination of ETA by Bromine. The decay of bromine in the reaction with ethanetetracarboxylic acid, $(COOH)_2CHCH(COOH)_2$ (ETA), is followed by measuring the absorbance at 400 nm (Figure 7a for high bromine initial concentration, Figure 7b for low bromine initial concentration). From the slope -3.7×10^{-5} M s^{-1} in Figure 7a ($c_{ETA,0} = 0.0063$ M) we obtain $k_1 = 6.2 \times 10^{-3}$ s^{-1}; then $k_{-1} = k_1/K_1 = 413$

TABLE 3: Final Concentrations $[BrMA]_f$ and $[Br_2MA]_f$ of the Products Bromomalonic Acid and Dibromomalonic Acid in the Bromination of Malonic Acid (initial concentration 1 M) with Bromine (initial concentration $[Br_2]_0$) in 1 M Sulfuric Acid

$[Br_2]_0$/M	$[BrMA]_f$/M	$[Br_2MA]_f$/M
0.1	0.07	0.015
0.2	0.11	0.046
0.5	0.15	0.18
1.0	0.12	0.44

s^{-1}. From the slope of the logarithmic plot in Figure 7b we obtain $k_1k_2/k_{-1} = 147\ M^{-1}\ s^{-1}$; then $k_2 = 1.0 \times 10^7\ M^{-1}\ s^{-1}$.

We checked using these data if the conditions for the two limiting cases are fulfilled. High bromine initial concentration ($c_{Br_{2,0}} = 4.4 \times 10^{-4}$ M): $k_2c_{Br_{2,0}} = 4400\ s^{-1}$; this is large enough compared to $k_{-1} = 413\ s^{-1}$. Low bromine initial concentration ($c_{Br_{2,0}} = 1 \times 10^{-5}$ M): $k_2c_{Br_{2,0}} = 100\ s^{-1}$; this is small enough compared with $k_{-1} = 413\ s^{-1}$.

4. Discussion

Our results confirm that the bromination reactions considered occur via the enol forms of the organic acids. The enolization rate constant k_1 decreases by a factor of 500 when proceeding from BrMA to TA. Under the usual conditions of the BZ system the concentrations of bromine and hypobromous acid are small compared with the concentration of the organic acids, thus the rate constants k_2 and k_3 are decisive for the rate of bromination. In all cases the bromination by HOBr is slower than the bromination by bromine. From our experiments it is clear that the reaction of malonic acid with HOBr leads exclusively to bromomalonic acid; this means that the possibility of a reaction to tartronic acid and bromide (which would provide an additional bromide source in the BZ) can be ruled out. This is important for the negative feedback loop involving bromide ions in the BZ reaction. Correspondingly, the reaction of bromomalonic acid with HOBr leads to dibromomalonic acid, and the possibility of reaction Z12 (formation of mesoxalic acid and bromide) can be ruled out. Another important conclusion can be drawn about the products in the reaction of malonic acid with bromine in acidic solution. At low bromine initial concentration the main product will be bromomalonic acid, but at higher bromine initial concentration bromomalonic acid will be further brominated to dibromomalonic acid. Table 3 shows the calculated product concentrations for different initial bromine concentrations. Starting with an initial Br_2/MA ratio of 0.1 we expect 10% BrMA in the reaction mixture if the bromination of BrMA is neglected; actually we find 7% BrMA and 1.5% Br_2 MA. For an initial Br_2/MA ratio of 1.0 we find 12% BrMA and 44% Br_2MA instead of 100% BrMA. This theoretical prediction was confirmed by HPLC and by polarographic studies, where it turned out that Br_2MA is not stable and decomposes rapidly to dibromoacetic acid and CO_2.[25] This means that in the so-called “Zhabotinsky synthesis” of bromomalonic acid a mixture of BrMA and of dibromoacetic acid is obtained, as has been already pointed out earlier.[26]

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