New Experimental and Computational Results on the Radical-Controlled Oscillating Belousov-Zhabotinsky Reaction

3 AUTHORS, INCLUDING:

Randy P. Washington

Procter & Gamble

9 PUBLICATIONS **167** CITATIONS

SEE PROFILE

John Pojman

Louisiana State University

238 PUBLICATIONS **4,139** CITATIONS

SEE PROFILE

New Experimental and Computational Results on the Radical-Controlled Oscillating Belousov−Zhabotinsky Reaction

Gauri P. Misra, Randy P. Washington, and John A. Pojman*

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406

Received: September 4, 1997; In Final Form: November 5, 1997

New experimental results on the oscillatory dynamics of the radical-controlled Belousov−Zhabotinsky reaction (the Rácz system) in a batch reactor are reported. The system exhibits oscillations with no induction period, a typical feature of the radical-controlled mechanism. However, in the presence of acetylacetone ($CH_2(COCH_3)_2$), an induction period is observed before oscillations start, which increases with increasing acetylacetone concentration. There is a critical concentration of acetylacetone at which no oscillations occur. Quenching of radical-controlled oscillations is also observed at low and high malonic acid concentrations as well as at low and high sulfuric acid concentrations. An induction period is observed before the onset of radical-controlled oscillations at sulfuric acid concentrations ≥ 5.5 M. The duration of radical-controlled oscillations reaches a maximum at an intermediate sulfuric acid concentration. Numerical simulations based on the Radicalator model predict limits of malonic acid and sulfuric acid concentration within which oscillations are observed. The Radicalator model with additional reactions involving (i) $CH_2(COCH_3)_2 + Ce^{4+} \rightarrow \,^{\bullet}CH(COCH_3)_2$, (ii) $^{\bullet}CH(COCH_3)_2 + BrO_2^{\bullet} \rightarrow$ products, and (iii) $^{\bullet}CH(COCH_3)_2 + \,^{\bullet}CH(COCH_3)_2 \rightarrow$ products also predicts lengthening of induction period with the increase of acetylacetone concentration and suppression of oscillations at high acetylacetone concentration. Inclusion of the reaction between acetylacetone and HOBr had no effect.

Introduction

The oscillating Belousov−Zhabotinsky (BZ) reaction and its variants have been extensively studied from dynamical and mechanistic viewpoints.[1,2] It has been established that in most of the cases oscillations are controlled by bromide, which is produced mainly by the reaction between bromomalonic acid and cerium(IV) (Ce^{4+}).[1−3] This reaction is quite slow and is also responsible for the induction period before oscillations begin. Bromide is also produced by other reactions.[3,4] Nevertheless, the concept of bromide control has been the subject of controversy.[5−8] In their effort to find an alternative control mechanism for the BZ reaction, Noszticzius and co-workers[5−8] succeeded in overcoming the induction period by increasing both the [malonic acid]/$[BrO_3^-]$ ratio and the sulfuric acid concentration in the BZ reaction. The increase of malonic acid resulted in (i) a rapid depletion of HOBr and Br_2 and a lowering of the bromide ion concentration below the required control level and (ii) an increase in the malonyl radical concentration.

They called this modified BZ reaction the "Rácz" system.[6,7] In this case, oscillations are controlled by malonyl radical ($^{\bullet}CH(COOH)_2$) species instead of bromide,[5−8] although the occurrence of oscillations without an induction period is not a sufficient condition to the radical-controlled mechanism. They proposed an alternative model called the Radicalator.[7] This model satisfactorily explains[8] several experimental observations of the Rácz system. However, doubt arises if the Rácz system could still be bromide-controlled because bromide might be produced by the reaction of bromomalonic acid and Ce^{4+}. If this is the case, oscillations could be suppressed by the addition of a more efficient HOBr and Br_2 scavenger.

To test this hypothesis, acetylacetone, a scavenger of HOBr and Br_2, was added in the Rácz system.[6,7] The addition of acetylacetone introduced an induction period, and the suppression of oscillations was observed at relatively high acetylacetone concentration. Malonic acid also reacts with HOBr and Br_2 and thus can enhance the induction period considerably with increase of malonic acid concentration and can also suppress the oscillations at high malonic acid concentration as was observed by Rastogi and Misra in the BZ reaction.[9] To examine these effects, experiments were performed for varied malonic acid concentration. Upper and lower limits of malonic acid concentration between which oscillations without induction period occur are obtained. The sulfuric acid concentration was also varied in order to examine its effect on the radical-controlled oscillations and to check the importance of the [malonic acid]/$[BrO_3^-]$ ratio in generating the radical-controlled oscillations. We did simulate these experimental observations using the Radicalator model.[7] We report here the results of our experiments and simulations.

Experimental Section

Experiments were performed in a double-walled glass reactor (100 mL) maintained at 25 ± 0.1 °C using a circulating water bath. A bright platinum electrode (Orion) in conjunction with a saturated calomel electrode (Radiometer) was used to record the redox potential. The data were collected at the rate of 10 Hz using a data acquisition board (Strawberry Tree 12 bit A/D board) in a Macintosh IIvx computer. The platinum electrode was connected to the computer through a pH meter (Corning). Sodium bromate (Aldrich), ceric ammonium nitrate (Aldrich), malonic acid (Aldrich), acetylacetone (Fisher Scientific, reagent grade), and sulfuric acid (Fisher Scientific, certified grade) were

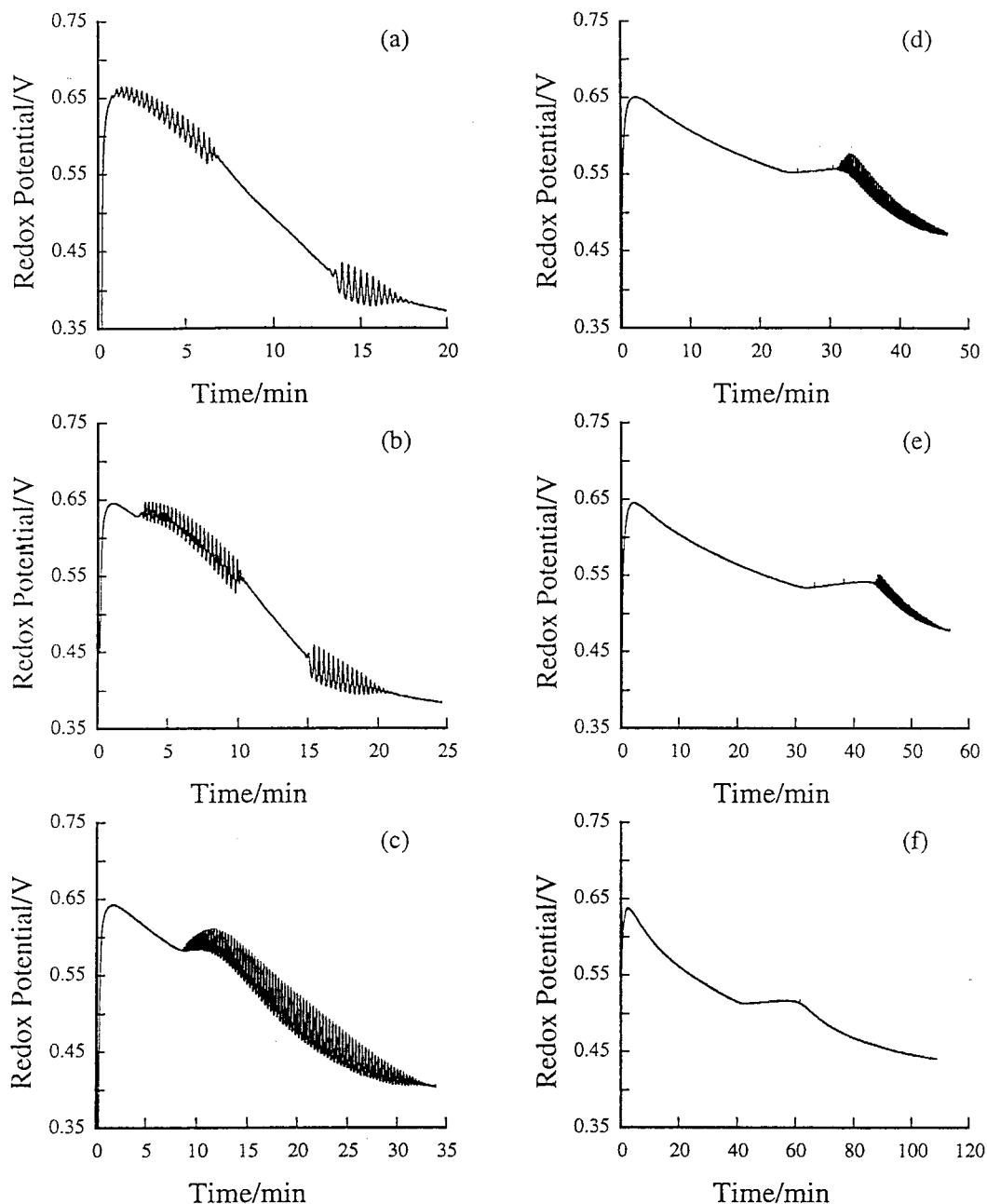* Address for correspondence. Phone: 601-266-5035. FAX: 601-266-5075. E-mail: john.pojman@usm.edu.

Radical-Controlled Oscillating BZ Reaction

J. Phys. Chem. A, Vol. 102, No. 3, 1998 **613**

Figure 1. Dependence of oscillatory characteristics on acetylacetone concentrations. System: [malonic acid]$_0$ = 0.60 M, [BrO$_3^-$]$_0$ = 0.015 M, [Ce^{4+}]$_0$ = 0.001 M, [H$_2$SO$_4$]$_0$ = 3.0 M with and without acetylacetone. [Acetylacetone]$_0$ = (a) without acetylacetone, (b) 7.2 × 10^{-4} M, (c) 1.7 × 10^{-3} M, (d) 6.0 × 10^{-3} M, (e) 8.5 × 10^{-3} M, and (f) 1.0 × 10^{-2} M.

used as received. All the solutions were prepared in deionized water. The sulfuric acid solution was bubbled with argon for 2 h to remove dissolved oxygen. All the reactants except bromate and cerium were placed in the reactor in desired proportions. Argon was bubbled for 15 min, and then bromate and cerium were added. The removal of dissolved oxygen, particularly from the sulfuric acid solution, was necessary in order to achieve oscillations. A total volume of 40 mL reaction mixture was used in all the experiments. A Perkin-Elmer Lambda 6 spectrophotometer was used to determine the rate constant of the acetylacetone and Ce^{4+} reaction.

Results and Discussion

Typical experimental results on the radical-controlled BZ reaction (the Rácz system) with and without acetylacetone (CH$_2$-(COCH$_3$)$_2$) are plotted in Figure 1. Oscillations start im-

mediately without any induction period after mixing the reactants in the absence of acetylacetone as shown in Figure 1a. These oscillations have been described as malonyl radical-controlled oscillations.[6,7] The second type of oscillations observed with an induction period of about 12 min corresponds to the bromide-controlled oscillations.[7]

Forsterling et al. distinguished between the malonyl radical-controlled and bromide-controlled oscillations by following the potential behavior of the AgBr electrode in the Rácz system and comparing it with the bromide-controlled BZ system.[7] It has been pointed out that the bromide level is below the detection limit of the AgBr electrode during the first type of oscillations, and oscillations in the AgBr electrode potential are due to the corrosion by HOBr not due to bromide.[7] The second type of oscillations appearing after a transition period has been described as bromide-controlled because the AgBr electrode
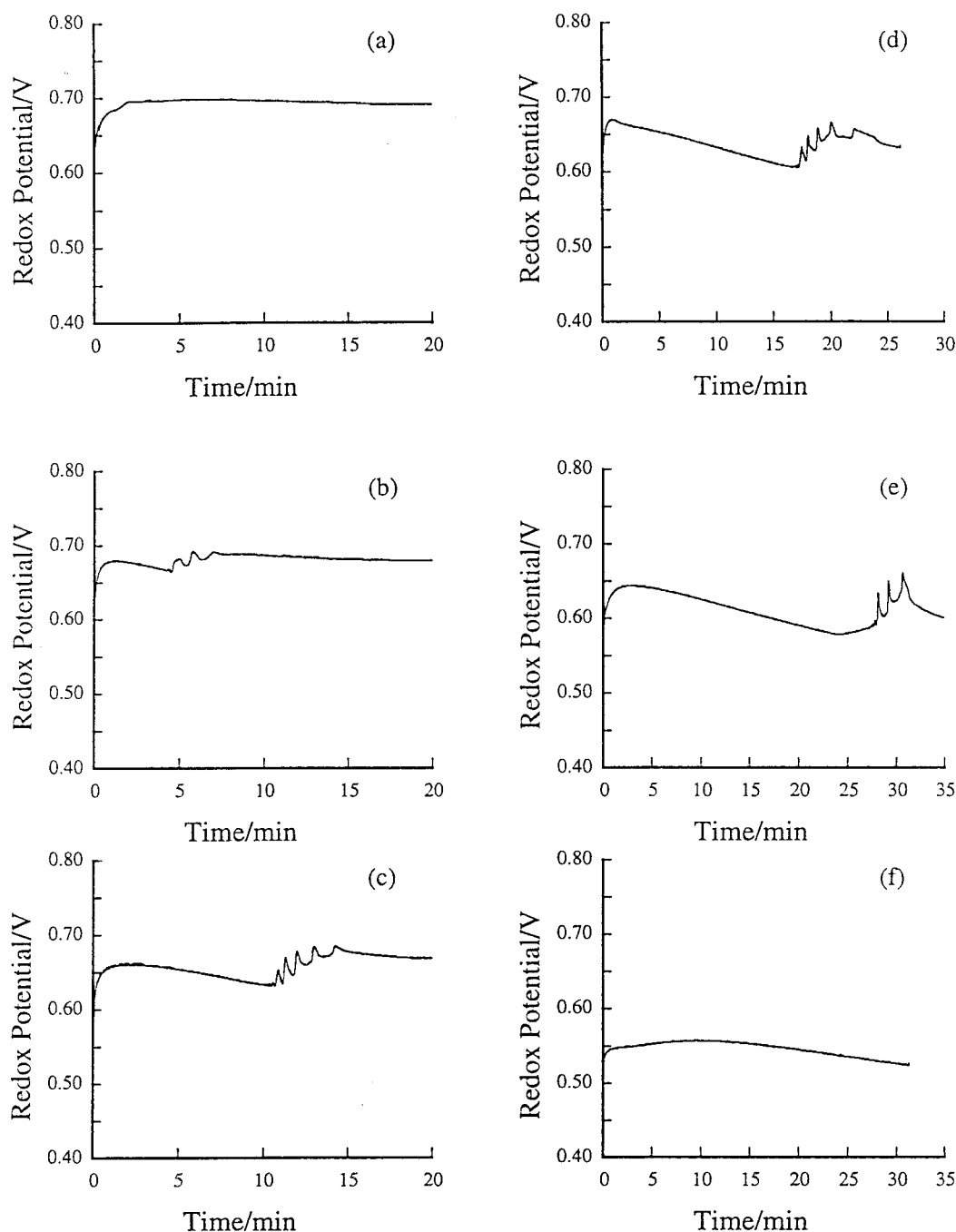
Figure 2. Dependence of oscillatory characteristics in acetylacetone $+ BrO_3^-$ (0.015 M) $+ Ce^{4+}$ (0.001 M) $+ H_2SO_4$ (3.0 M) system. $[\text{Acetylacetone}]_0$ = (a) 1.2×10^{-3} M, (b) 2.4×10^{-3} M, (c) 4,8 $\times 10^{-3}$ M, (d) 7.2×10^{-3} M, (e) 1.1×10^{-2} M, and (f) 1.0×10^{-1} M.

potential was well within the detection limit.[7] We used this classification in the present work to distinguish between the radical-controlled and bromide-controlled oscillations.

In the presence of acetylaceteone, an induction period is introduced before the start of radical-controlled oscillations (Figure 1b) that increases with the increase of acetylaceteone concentration (Figure 1b−e). These oscillations are still radical-controlled.
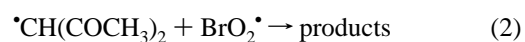
Bromide-controlled oscillations diminish with the increase of acetylacetone concentration, and only radical-controlled oscillations remain at high acetylacetone concentration (Figure 1c−e). The suppression of bromide-controlled oscillations by the addition of a ketone has earlier been reported and explained as the scavenging of bromine.[9] When the critical concentration of acetylaceteone is reached, no oscillations are observed, as

shown in Figure 1f. The quenching of oscillations by the addition of acetylaceteone could be achieved via the following two routes.

1. Acetylacetone free radical can be produced via the following reaction

$$CH_2(COCH_3)_2 + Ce^{4+} \rightarrow {}^{\bullet}CH(COCH_3)_2 + Ce^{3+} + H^+ \quad (1)$$

and could inhibit the production of either $BrO_2^{\bullet}$ or ${}^{\bullet}CH(COOH)_2$ via the following reactions:

$$^{\bullet}CH(COCH_3)_2 + BrO_2^{\bullet} \rightarrow \text{products} \quad (2)$$

$$^{\bullet}CH(COCH_3)_2 + {}^{\bullet}CH(COOH)_2 \rightarrow \text{products} \quad (3)$$

Radical-Controlled Oscillating BZ Reaction

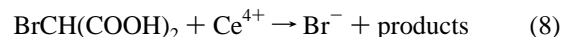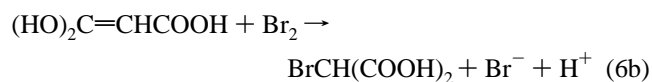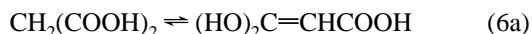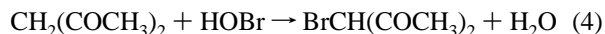*J. Phys. Chem. A, Vol. 102, No. 3, 1998* **615**
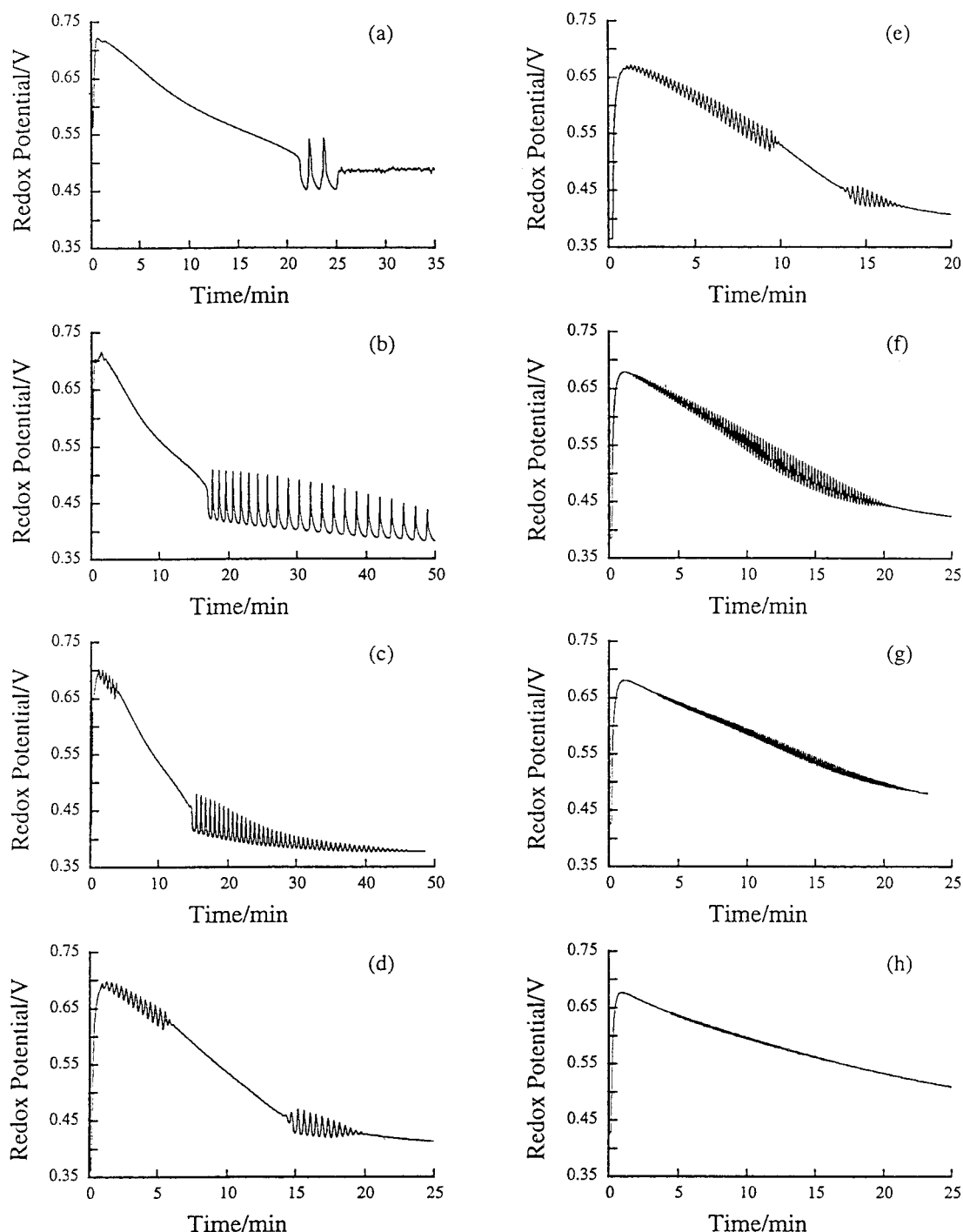
Figure 3. Dependence of oscillatory characteristics on malonic acid concentrations. System: $[BrO_3^-]_0 = 0.015$ M, $[Ce^{4+}]_0 = 0.001$ M, $[H_2SO_4]_0 = 3.0$ M, and [malonic acid]$_0$ = (a) 0.05 M, (b) 0.15 M, (c) 0.30 M, (d) 0.45 M, (e) 0.75 M, (f) 0.90 M, (g) 1.50 M, and (h) 2.00 M.

2. Acetylacetone can also suppress the production of Br^- by consuming HOBr and Br_2 and thus depleting bromomalonic acid $(BrCH(COOH)_2)$ via the following reactions.

$$CH_2(COCH_3)_2 + HOBr \rightarrow BrCH(COCH_3)_2 + H_2O \quad (4)$$

$$CH_2(COCH_3)_2 + Br_2 \rightarrow BrCH(COCH_3)_2 + Br^- + H^+ \quad (5)$$

$$CH_2(COOH)_2 \rightleftharpoons (HO)_2C=CHCOOH \quad (6a)$$

$$(HO)_2C=CHCOOH + Br_2 \rightarrow$$
$$BrCH(COOH)_2 + Br^- + H^+ \quad (6b)$$

$$CH_2(COOH)_2 + HOBr \rightarrow BrCH(COOH)_2 + H_2O \quad (7)$$

$$BrCH(COOH)_2 + Ce^{4+} \rightarrow Br^- + \text{products} \quad (8)$$

where $CH_2(COOH)_2$, $(HO)_2C=CHCOOH$, and $BrCH(COCH_3)_2$ refer to malonic acid, its enol form, and bromoacetylacetone, respectively.

It has already been pointed out[5−7] that in the Rácz system the bromide concentration is much below the detection limit of the AgBr electrode, and oscillations are controlled by malonyl radical. Thus, any depletion of Br^- would not affect the dynamics. Route 1 is the most probable path in inhibiting oscillations in the presence of acetylacetone. Experimental
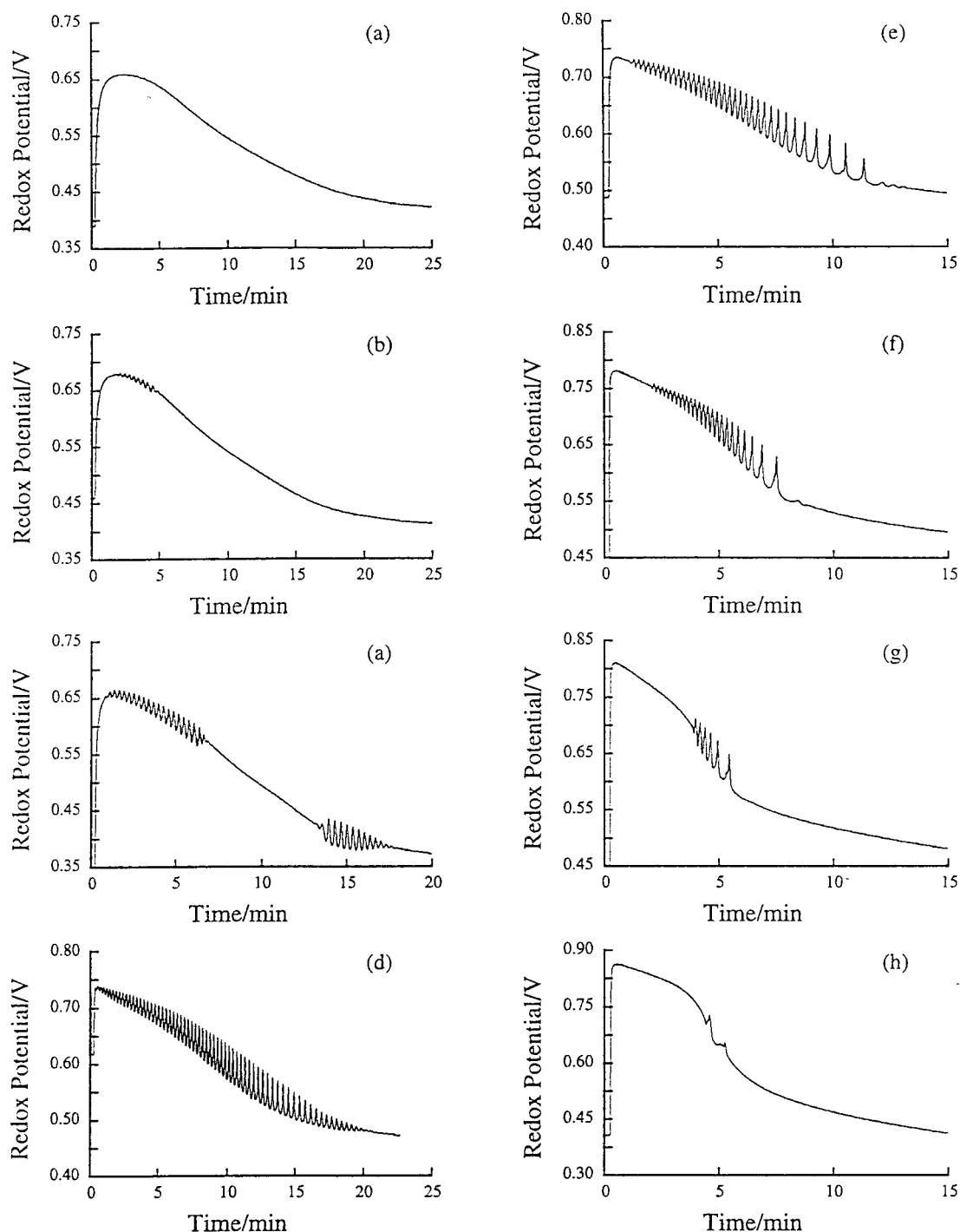
Figure 4. Dependence of oscillatory characteristics on sulfuric acid concentrations. System: [malonic acid]$_0$ = 0.60 M, [BrO$_3^-$]$_0$ = 0.015 M, [Ce^{4+}]$_0$ = 0.001 M, and [H$_2$SO$_4$]. [H$_2$SO$_4$]$_0$ = (a) 1.5 M, (b) 2.0 M, (c) 3.0 M, (d) 4.0 M, (e) 5.5 M, (f) 6.5 M, (g) 7.5 M, and (h) 9.5 M.

observation of Forsterling et al.[6] did indicate oscillations in the AgBr electrode potential which, they claimed, were exclusively due to the oscillations in HOBr concentration and not due to Br$^-$. There could be another possibility that bromomalonic acid free radical (BrC$^•$(COOH)$_2$) produced from the reaction between BrCH(COOH)$_2$ and Ce^{4+} might be a controlling intermediate instead of malonyl radical. However, the concentrations of BrCH(COOH)$_2$ and BrC$^•$(COOH)$_2$ will always be lower than the malonic acid concentration as these are the products of malonic acid itself. Therefore, the role of BrC$^•$(COOH)$_2$ in the inhibition of the autocatalytic production of BrO$_2^•$ will always be less important than the corresponding role of malonyl radical, assuming equal rate constants.

We studied the reaction of acetylacetone with Ce^{4+} in 3.0 M sulfuric acid spectrophotometrically by following the absorbance of Ce^{4+}, to compare the acetylacetone free radical and malonyl free radical production and to estimate the corresponding rate constants. In the case of acetylacetone and Ce^{4+} reaction, the second-order rate constant was estimated to be 294 ± 5 M^{-1} s^{-1} from the initial rate. The corresponding rate constant of the malonic acid and Ce^{4+} reaction has been reported to be 0.23 M^{-1} s^{-1}.[5,6] This clearly indicates that the generation of the acetylacetone free radical is faster than the malonyl radical formation.

Furthermore, it may be argued that the acetylacetone/BrO$_3^-$/ Ce^{4+}/H$_2$SO$_4$ system without malonic acid could generate

Radical-Controlled Oscillating BZ Reaction
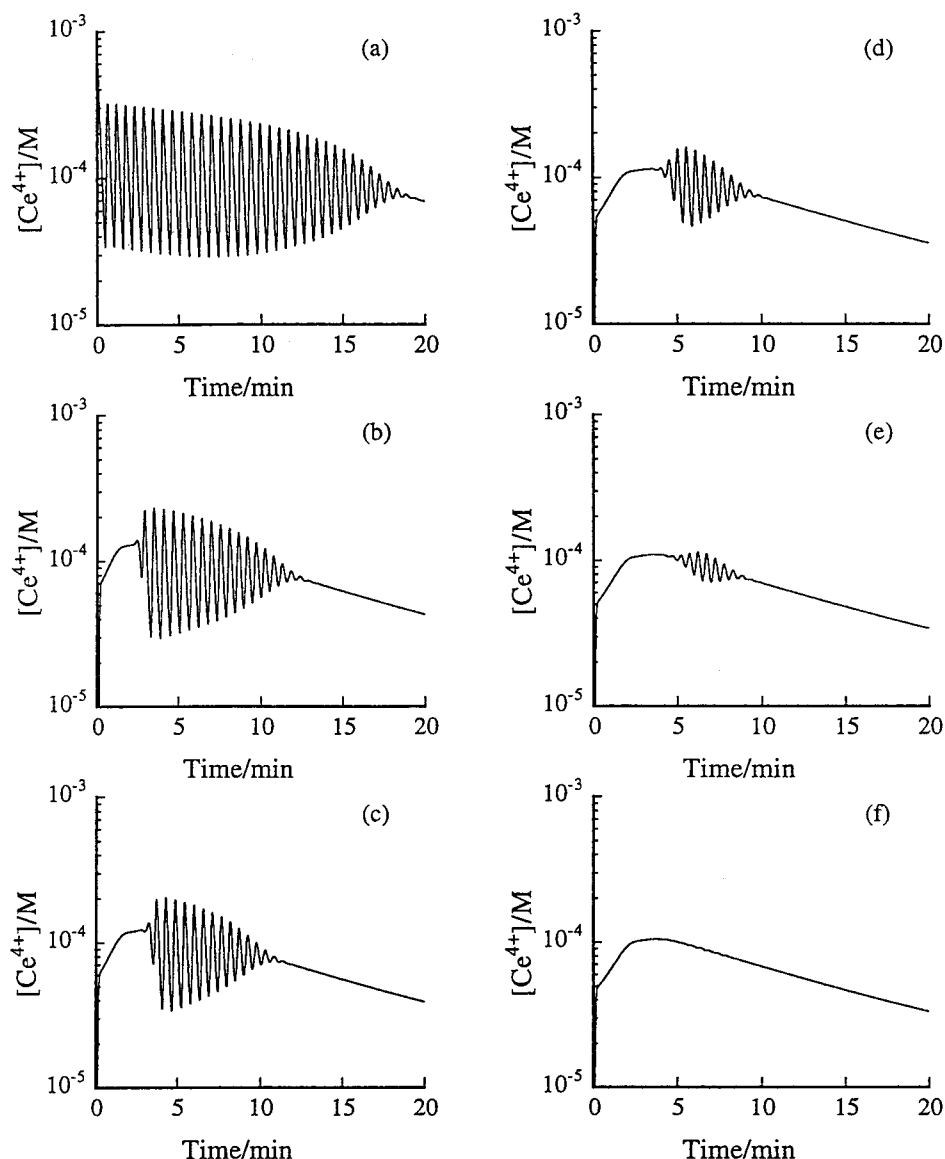
J. Phys. Chem. A, Vol. 102, No. 3, 1998 **617**

Figure 5. Plot of $[Ce^{4+}]$ versus time obtained from the modified Radicalator model (reactions 7, 9−19, 1, 2, and 20) in the presence of acetylacetone. $[Acetylacetone]_0$ = (a) without acetylacetone, (b) 5.0×10^{-3} M, (c) 6.0×10^{-3} M, (d) 7.0×10^{-3} M, (e) 7.5×10^{-3} M, and (f) 8.0×10^{-3} M. $[Malonic\ acid]_0$ = 0.60 M, $[BrO_3^-]_0$ = 0.015 M, $[Ce^{4+}]_0$ = 0.001 M, $[H^+]_0$ = 4.0 M (4.0 M H^+ corresponds to 3.0 M H_2SO_4), $[HBrO_2]_0$ = 7.0 × 10^{-7} M, $[Br_2O_4]_0$ = 1.0×10^{-20} M, $[Br^-]_0$ = 1.0×10^{-20} M, $[HOBr]_0$ = 1.0×10^{-20} M, $[Br_2]_0$ = 1.0×10^{-20} M, $[BrO_2^{\bullet}]_0$ = 2.0×10^{-7} M, $[MA^{\bullet}]_0$ = 1.0×10^{-20} M, and $[aetylacetone^{\bullet}]_0$ = 1.0×10^{-20} M.

oscillations because acetylacetone can act as a reducing agent as well as a Br_2/HOBr scavenger similar to the malonic acid. Therefore, experiments were performed for various concentrations of acetylacetone. The results are shown in Figure 2. No radical-controlled oscillations are observed in this system; the bromide-controlled oscillations only occur for a short duration after an induction period. These results indicate that the oscillations in the Rácz system in the presence of acetylacetone, as shown in Figure 1b−f, are not due to acetylacetone.

Figure 3 shows the effect of the variation of malonic acid concentration in the radical-controlled BZ reaction. These radical-controlled oscillations are observed in a range (0.3−1.5 M) of malonic acid concentration as shown in Figure 3c−g. Decreasing the malonic acid concentration results in the disappearance of radical-controlled oscillations, and only bromide-controlled oscillations exist (Figure 3a,b). At low malonic acid concentration, radical-controlled oscillations appear only for a short duration (Figure 3c). The duration of bromide-controlled oscillations decreases with the increase of the malonic acid

concentration (Figure 3b−e). Bromide-controlled oscillations of only a few cycles are observed when the malonic acid concentration reaches the lower limit (Figure 3a). This observation is in agreement with the experimental and computational results reported earlier by Rastogi and Misra.[9] As malonic acid concentration increases, the duration of radical-controlled oscillations increases (Figure 3c−g) while the duration of bromide-controlled oscillations decreases (Figure 3b−e). At relatively high concentration of malonic acid, bromide-controlled oscillations disappear, and only radical-controlled oscillations for about 20 min duration along with diminution of amplitude are observed (Figure 3f,g). Further increase in malonic acid concentration results in the suppression of radical-controlled oscillations (Figure 3h). These two limits for the occurrence of radical-controlled oscillations could be related to the low and high concentration of malonyl radical whose production is directly related to the malonic acid concentration.[5−8]

Figure 4 illustrates the effect of sulfuric acid concentration on the radical-controlled oscillations. Upper and lower limits

TABLE 1

3.0 M sulfuric acid		1.5 M sulfuric acid	
$[MA]/[BrO_3^-]$	oscillatory feature	$[MA]/[BrO_3^-]$	oscillatory feature
3.3	bromide-controlled		
10.0	bromide-controlled		
20.0	both radical- and bromide-controlled		
30.0	both radical- and bromide-controlled	30.0	bromide-controlled
		36.6	bromide-controlled
40.0	both radical- and bromide-controlled	40.0	no oscillation
50.0	both radical- and bromide-controlled		
60.0	radical-controlled	60.0	no oscillation
100.0	radical-controlled		
133.0	no oscillations	133.0	no oscillation

TABLE 2: Values of Rate Constants Used in Computation

	rate constant		
reaction	forward	reverse	reference
1	$294\ M^{-1}\,s^{-1}$		present work
2	$1.0 \times 10^9\ M^{-1}\,s^{-1}$		assigned by us
3	$1.0 \times 10^9\ M^{-1}\,s^{-1}$		assigned by us
6a	$3.0 \times 10^{-3}\,s^{-1}$	$200.0\,s^{-1}$	Gyorgyi et al.[3]
6b	$1.91 \times 10^6\ M^{-1}\,s^{-1}$		Gyorgyi et al.[3]
7	$1.0\ M^{-1}\,s^{-1}$		Försterling et al.[7]
8	$0.09\ M^{-1}\,s^{-1}$		Gyorgyi et al.[7]
9	$8 \times 10^9\ M^{-2}\,s^{-1}$	$80\,s^{-1}$	Försterling et al.[7]
10	$2.5 \times 10^6\ M^{-2}\,s^{-1}$	$2 \times 10^5\ M^{-1}\,s^{-1}$	Försterling et al.[7]
11	$1.6\ M^{-3}\,s^{-1}$	$3.2\ M^{-1}\,s^{-1}$	Försterling et al.[7]
12	$3 \times 10^3\ M^{-2}\,s^{-1}$	$1 \times 10^{-8}\ M^{-2}\,s^{-1}$	Försterling et al.[7]
13	$33\ M^{-1}\,s^{-1}$	$2.2 \times 10^3\,s^{-1}$	Försterling et al.[7]
14	$7.5 \times 10^4\,s^{-1}$	$1.4 \times 10^9\ M^{-1}\,s^{-1}$	Försterling et al.[7]
15	$6.2 \times 10^4\ M^{-2}\,s^{-1}$	$8.4 \times 10^3\ M^{-1}\,s^{-1}$	Försterling et al.[7]
16	$0.23\ M^{-1}\,s^{-1}$	$2.2 \times 10^4\ M^{-2}\,s^{-1}$	Försterling et al.[7]
17	$3.2 \times 10^9\ M^{-1}\,s^{-1}$		Försterling et al.[7]
18	$5 \times 10^9\ M^{-1}\,s^{-1}$		Försterling et al.[7]
19	$7 \times 10^{-7}\ M^{-3}\,s^{-1}$		Försterling et al.[7]
20	$1.0 \times 10^9\ M^{-1}\,s^{-1}$		assigned by us

of sulfuric acid concentration between which radical-controlled oscillations occur are observed. At 2.0 M sulfuric acid concentration, oscillations during a short interval appear while bromide-controlled oscillations disappear. The radical-controlled oscillations disappear completely with a further decrease in sulfuric acid concentration. The period of radical-controlled oscillations increases with an increase in sulfuric acid concentration and reaches a maximum value (4.0 M sulfuric acid). An induction period before the start of radical-controlled oscillations is also introduced at higher sulfuric acid (≥ 5.5 M) concentration. With further increase in sulfuric acid concentration, the period of radical-controlled oscillations decreases, and oscillations cease at 9.5 M sulfuric acid concentration.
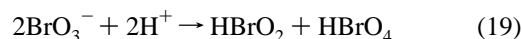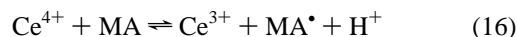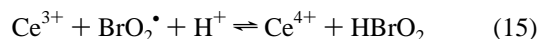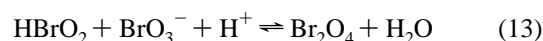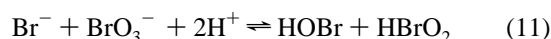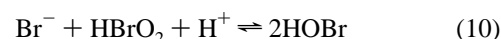
We examined the role of the [malonic acid]/$[BrO_3^-]$ ratio in the generation of radical-controlled oscillations. Table 1 demonstrates the radical- and bromide-controlled oscillatory features at 3.0 and 1.5 M sulfuric acid concentrations. Under the Rácz condition the [malonic acid]/$[BrO_3^-]$ ratio was 40 at which both radical-controlled and bromide-controlled oscillations were observed. However, at the same [malonic acid]/$[BrO_3^-]$ ratio, no radical-controlled oscillations were observed at 1.5 M sulfuric acid. An increase or a decrease in the [malonic acid]/$[BrO_3^-]$ ratio does not exhibit radical-controlled oscillations at 1.5 M sulfuric acid. Below a certain value of this ratio, bromide-controlled oscillations were observed at both low and high sulfuric acid concentrations. This suggests that not only

the [malonic acid]/$[BrO_3^-]$ ratio but also the concentration of H^+ is important in generating the radical-controlled oscillations. The observed radical-controlled oscillations at relatively high sulfuric acid concentration are due to the high tendency of $BrO_2^\bullet$ formation under this condition as pointed out by Försterling et al.[7] We expected the radical-controlled oscillations at low sulfuric acid concentration by lowering the malonic acid concentration. But this was not observed experimentally probably due to the significant effect of the sulfuric acid on other reactions.

Försterling et al.[7] proposed a 12-step model called the "Radicalator" to simulate the oscillatory features of the radical-controlled BZ reaction. The model consists of reactions 7 and 9−19:
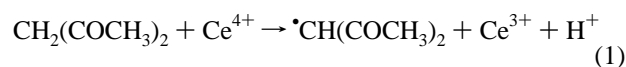
$$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O \tag{9}$$
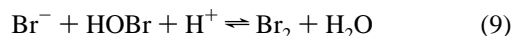
where MA and $MA^\bullet$ refer to the malonic acid and malonyl

$$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr \tag{10}$$

$$Br^- + BrO_3^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \tag{11}$$

$$2HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+ \tag{12}$$

$$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O \tag{13}$$

$$Br_2O_4 \rightleftharpoons 2BrO_2^\bullet \tag{14}$$

$$Ce^{3+} + BrO_2^\bullet + H^+ \rightleftharpoons Ce^{4+} + HBrO_2 \tag{15}$$

$$Ce^{4+} + MA \rightleftharpoons Ce^{3+} + MA^\bullet + H^+ \tag{16}$$

$$HOBr + MA \rightarrow BrMA + H_2O \tag{7}$$

$$2MA^\bullet \rightarrow products \tag{17}$$

$$MA^\bullet + BrO_2^\bullet \rightarrow products \tag{18}$$
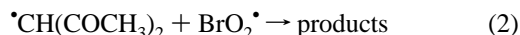
$$2BrO_3^- + 2H^+ \rightarrow HBrO_2 + HBrO_4 \tag{19}$$

radical, respectively. In reaction 17, products are 1,1,2,2-ethanetetracarboxylic acid (ETA) and malonyl malonate (MAMA), respectively.[10,11] Br^-, HOBr, Br_2, $HBrO_2$, BrO_3^-, Br_2O_4, $BrO_2^\bullet$, Ce^{4+}, MA, and $MA^\bullet$ have been considered as dynamic variables. It may be noted that the concentrations of malonic acid, H^+, and BrO_3^- were regarded as constants in previous calculations[7,8] using the Radicalator model.

The STIFF3 subroutine[12] was used to solve the differential equations obtained from the model. The rate constants used in the computation are listed in Table 2. The Radicalator model predicts the limits of malonic acid and sulfuric acid concentrations between which oscillations occur. No significant difference is observed when H^+ is treated as a dynamic variable.

We attempted to simulate the introduction of an induction period and suppression of oscillations in the presence of acetylacetone. The following additional reactions were added to the Radicalator model.

$$CH_2(COCH_3)_2 + Ce^{4+} \rightarrow {}^\bullet CH(COCH_3)_2 + Ce^{3+} + H^+ \tag{1}$$

The Radicalator model (reactions 7 and 9−19) with these

Radical-Controlled Oscillating BZ Reaction

J. Phys. Chem. A, Vol. 102, No. 3, 1998 **619**

$$\text{}^{\bullet}CH(COCH_3)_2 + BrO_2^{\bullet} \rightarrow products \qquad (2)$$

$$\text{}^{\bullet}CH(COCH_3)_2 + \text{}^{\bullet}CH(COCH_3)_2 \rightarrow products \qquad (20)$$

three additional reactions (1, 2, and 20) simulate the oscillatory characteristics including the lengthening of the induction period in the presence of acetylacetone quite well, as shown in Figure 5.

As mentioned in the preceding section, $\text{}^{\bullet}CH(COCH_3)_2$ could also react with the $MA^{\bullet}$ (reaction 2), and this reaction might be responsible for an induction period in the presence of acetylacetone. Therefore, we tried to replace reaction 2 with reaction 3.

$$\text{}^{\bullet}CH(COCH_3)_2 + MA^{\bullet} \rightarrow products \qquad (3)$$
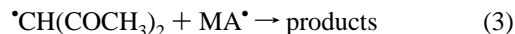
Under this condition, no induction period was predicted, and only shortening of the duration of oscillations was obtained. Thus, it is quite evident that the reaction between $MA^{\bullet}$ and $\text{}^{\bullet}CH(COCH_3)_2$ is not responsible for the introduction of an
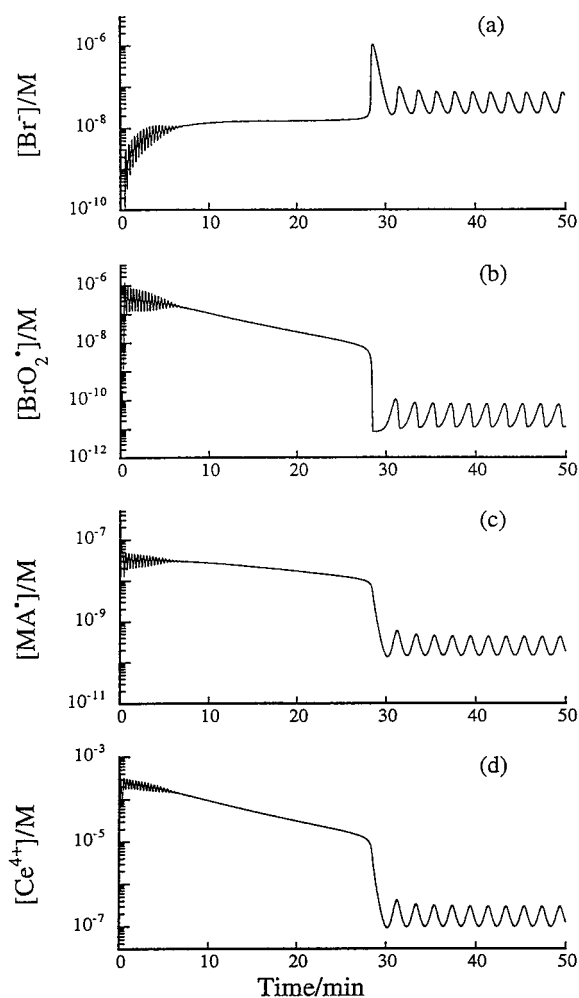
induction period and cessation of radical-controlled oscillations in the presence of acetylacetone in the BZ reaction.

Reactions 4–8 can also be operative, and the induction period as well as the suppression of oscillations in the presence of acetylacetone might be due to these reactions instead of reactions 1, 2, and 20. Computations were performed by including the reactions 4–8 and reaction 1 in the Radicalator model. No effect on the oscillatory characteristics was found. This is in agreement with an earlier report of Noszticzius et al.[8] that the Br^--related reactions 9–11 in the Radicalator model have no effect on oscillations. This clearly supports the view that these oscillations are not bromide-controlled.

It may be noted that the Radicalator model as such does not predict the bromide-controlled oscillations as it does not include the bromide regeneration reactions. We did attempt to simulate the bromide-controlled oscillations using this model by adding reactions 6 and 8 to the Radicalator model. The computed results are plotted in Figure 6. Both the bromide-controlled oscillations with an induction period of about 30 min as well as the radical-controlled oscillations are predicted.

Conclusions

The radical-controlled oscillations in the Rácz system are found to occur in a range of malonic acid and sulfuric acid concentration. Observation of an induction period may not necessarily be used as a criterion in distinguishing between radical-controlled and bromide ion-controlled oscillations in the BZ reaction. Radical-controlled oscillations with an induction period can also be observed in the Rácz system at higher sulfuric acid concentration and also in the presence of acetylacetone. Bromide-controlled, radical-controlled, or a combination of both oscillations can be obtained by varying the malonic acid or the sulfuric acid concentration in the Rácz system. The performance of the Radicalator model is found to be quite satisfactory. A modification of the Radicalator model also predicts both radical- and bromide-controlled oscillations.

Figure 6. Plot of computed (a) $[Br^-]$, (b) $[BrO_2^{\bullet}]$, (c) $[MA^{\bullet}]$, and $[Ce^{4+}]$ versus time obtained from the modified Radicalator model (reactions 7, 9–19, 6, and 8) showing both radical-controlled and bromide-controlled oscillations. The bromide-controlled oscillations start after 30 min. $k_8 = 13.5\ M^{-1}\ s^{-1}$, and $k_{18} = 2.0 \times 10^9\ M^{-1}\ s^{-1}$. Other conditions were the same as used in Figure 5.

References and Notes

(1) Field, R. J.; Burger, M. *Oscillations and Traveling Waves in Chemical Systems*; Wiley: New York, 1985.

(2) Gray, P.; Scott, S. K. *Chemical Oscillations and Instabilities*; Clarendon: Oxford, 1990.

(3) Györgyi, L.; Turányi, T.; Field, R. J. *J. Phys. Chem.* **1990**, *94*, 7162–7170.

(4) Varga, M.; Györgyi, L.; Körös, E. *J. Am. Chem. Soc.* **1985**, *107*, 4780–4781.

(5) Försterling, H.-D.; Noszticzius, Z. *J. Phys. Chem.* **1989**, *93*, 2740–2748.

(6) Försterling, H.-D.; Murányi, S.; Noszticzius, Z. *React. Kinet. Catal. Lett.* **1990**, *42*, 217–226.

(7) Försterling, H.-D.; Murányi, S.; Noszticzius, Z. *J. Phys. Chem.* **1990**, *94*, 2915–2921.

(8) Noszticzius, Z.; Bodnár, Z.; Garamszegi, L.; Wittmann, M. *J. Phys. Chem.* **1991**, *9*, 6575–6580.

(9) Rastogi, R. P.; Misra, G. P. *J. Phys. Chem.* **1992**, *96*, 4426–4431.

(10) Sirimungkala, A.; Försterling, H.-D.; Noszticzius, Z. *J. Phys. Chem.* **1996**, *100*, 3051–3055.

(11) Gao, Y.; Forsterling, H. D.; Noszticzius, Z.; Meyer, B. *J. Phys. Chem.* **1994**, *98*, 8377–8380.

(12) Villadsen, J.; Michelsen, M. L. *Solution of Differential Equation Models by Polynomial Approximation*; Prentice Hall: Englewood Cliffs, NJ, 1978.