Kinetic Study of the Ce(III)-, Mn(II)- or $Fe(phen)_3^{2+}$-Catalyzed Belousov–Zhabotinsky Reaction with Ethyl Hydrogen Malonate

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ABSTRACT: In a stirred batch reaction, $Fe(phen)_3^{2+}$ ion behaves differently from Ce(III) or Mn(II) ion in catalyzing the bromate-driven oscillating reaction with ethyl hydrogen malonate [$CH_2COOHCOOEt$, ethyl hydrogen malonate (EHM)]. The effects of N_2 atmosphere, concentrations of bromate ion, EHM, metal ion catalyst, sulfuric acid, and additive (bromide ion or bromomalonic acid) on the pattern of oscillations were investigated. The kinetic study of the reaction of EHM with Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion indicates that under aerobic or anaerobic conditions the order of reactivity toward reacting with EHM is Mn(III) $>$ Ce(IV) $\gg$ $Fe(phen)_3^{3+}$, which follows the same trend as that of the malonic acid system. The presence of the ester group in EHM lowers the reactivity of the two methylene hydrogen atoms toward bromination or oxidation by Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion. No good oscillations were observed for the BrO_3^--$CH_2(COOEt)_2$ reaction catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion. A discussion of the effects of oxygen on the reactions of malonic acid and its derivatives (RCHCOOHCOOR') with Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion is also presented. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 52–61, 2000

INTRODUCTION

The Belousov [1]–Zhabotinsky [2] (BZ) reaction has attracted scientists for more than two decades. According to a classification by Noyes [3], the classical BZ reaction is a metal-ion-catalyzed oxidation and bromination of an organic substrate by an acidic bromate. Field et al. [4] have elucidated a detailed mechanism of the Ce(III)-catalyzed BZ reaction with malonic acid. A number of modifications of the classical BZ reaction have been reported. Körös et al. [5] identified two different kinds of metalion catalysts for the BZ reaction, namely, the labile Ce(III)/Ce(IV) and Mn(II)/Mn(III) complexes with reduction potentials of about 1.5 V and the inert $Fe(phen)_3^{2+}$/$Fe(phen)_3^{3+}$ and $Ru(phen)_3^{2+}$/$Ru(phen)_3^{3+}$ complexes with reduction potentials of about 1.0–1.3 V.

A number of other organic substrates such as citric

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acid [1,6], saccharides [7], ethyl acetoacetate [8], oxalic acid/acetone [9], and mandelic acid/ketone [10] have been shown to exhibit oscillations during Ce(III)ion catalysis, but malonic acids [$RCH(COOH)_2$, R = Me, Et, Bu, Ph, and Br] [11–17] have been studied more than any other. It is observed that the substituent R affects the reactivity of $RCH(COOH)_2$ toward bromination and toward reaction with Ce(IV), Mn(III), and $Fe(phen)_3^{3+}$ ions and modifies the pattern of oscillations. It is generally accepted that the two adjacent carboxylic groups in $RCH(COOH)_2$ activates the methylene hydrogen atom and also facilitates the complex formation during the oxidation of $RCH(COOH)_2$ by metalion oxidation like the Ce(IV) ion.

In this article, we report the study of the Ce(III)-, Mn(II)-, or $Fe(phen)_3^{2+}$-catalyzed BZ reaction with ethyl hydrogen malonate (EHM, $CH_2COOHCOOEt$). The kinetics of the reaction of EHM and Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion were investigated. Rationalization of the experimental results is also given.

EXPERIMENTAL

Materials

Ammonium ferrous sulfate (99%), manganese(II) acetate tetrahydrate (99%), and cerium(III) nitrate hexahydrate (98.5%) (Merck); ammonium cerium(IV) nitrate (guaranteed reagent, Hanawa); 1,10-phenanthroline monohydrate (guaranteed, Ishizu); and diethyl malonate (99%, Lancaster) were used in this work. Other reagents used were of the highest grade chemicals commercially available. Deionized water from reverse osmosis (Millipore Milli-RO 20) was used.

Monopotassium salt of ethyl hydrogen malonate (KEHM, $CH_2COOEtCOOK$) was prepared by modifying the literature method [18]. Next 14 g of KOH was dissolved in 160 ml of commercial absolute EtOH and then the solution was filtered to remove any residue. Under magnetic stirring, the KOH solution was added dropwise throughout 1 h to a warm (~45°C) solution that contained 40 g of diethyl malonate in 160 ml of absolute EtOH. The mixture was kept warm for 3 h and then allowed to stand for 12 h at room temperature. Bright white crystals were formed. The mixture was heated to boiling and the hot solution was filtered to remove dipotassium malonate. The KEHM crystals gradually formed on cooling the filtrate were filtered off and washed with small amounts of absolute EtOH and ether. A similar procedure was carried out to recrystallize the KEHM salt.

The analysis calculated for $C_5H_7O_4K$ was as follows: C, 35.29; H, 4.12; with C, 34.91 and H, 4.06 found. Solutions of Mn(III) [7] and $Fe(phen)_3^{3+}$ [14] were freshly prepared according to the literature methods. The solution of ethyl hydrogen malonate (EHM) was freshly prepared by neutralizing a known amount of KEHM salt in H_2SO_4 solution just before carrying out each run.

Procedures

The oscillating reactions were followed potentiometrically with a bromide-ion-selective electrode (Orion 94-35) against an Orion 90-02 double junction electrode [19]. The kinetics of the reactions of EHM with Ce(IV), Mn(III), and $Fe(phen)_3^{3+}$ ions were studied spectrophotometrically by following [Ce(IV)], [Mn(III)], and [$Fe(phen)_3^{2+}$] at 320 nm ($\epsilon = 5.52 \times 10^3\ M^{-1}\ cm^{-1}$), 310 nm ($\epsilon = 1.31 \times 10^3\ M^{-1}\ cm^{-1}$), and 480 nm ($\epsilon = 1.05 \times 10^4\ M^{-1}\ cm^{-1}$), respectively, with a conventional spectrophotometer (Hitachi U-2000).

The organic substrate was in great excess over the metal ion. The observed pseudo-first-order rate constant (k_{obs}) was calculated from the linear-least-squares (LLS) fit of the plots of $\ln(A_t - A_\infty)$ vs. time for Ce(IV) and Mn(III) ions and $\ln(A_{t+d} - A_t)$ vs. time for $Fe(phen)_3^{2+}$ ion, where the time interval d is about half of the time needed to reach the maximum absorbance [14]. Product analysis by GC/MS method showed that propanoic acid (C_2H_5COOH) is one of the main products in the reaction of Ce(IV) and EHM.

RESULTS AND DISCUSSION

Characteristics of Oscillations

In a stirred batch experiment, damped oscillations were observed in the reaction of bromate ion with ethyl hydrogen malonate (EHM) in aqueous H_2SO_4 catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion. Some oscillating responses of bromide-ion-selective electrode are shown in Figure 1 [Ce(III)catalyzed], Figure 2 [Mn(II)catalyzed], and Figure 3 [$Fe(phen)_3^{2+}$catalyzed].

The characteristics of oscillations depend on the concentrations of bromate ion, ethyl hydrogen malonate, metalion catalyst, and sulfuric acid. Generally, in the Ce(III)- or Mn(II)-catalyzed system a long induction period is required before the onset of oscillations. Under similar conditions, the Ce(III)- or Mn(II)-catalyzed BZ reaction with EHM exhibits a considerably longer induction period than that of the corresponding BZ reaction with malonic acid (MA)

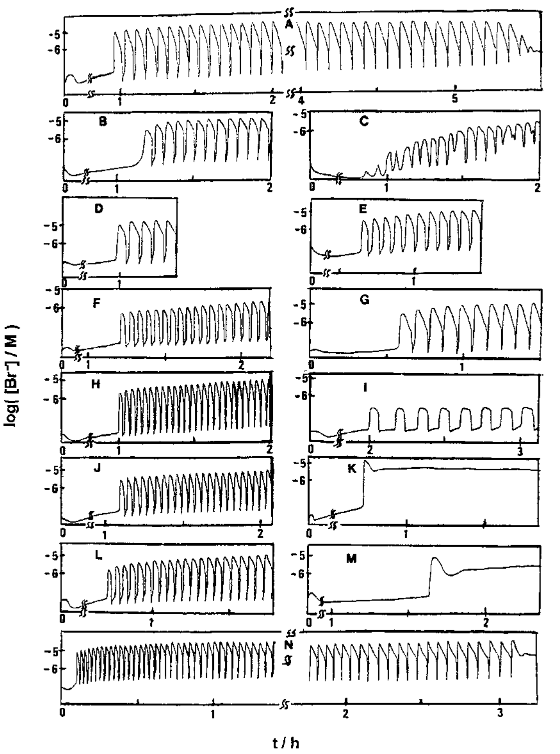

Figure 1 Potentiometric traces of log[Br^-] vs. time for the BrO_3^--EHM-Ce(III) oscillating reaction at 25°C. [BrO_3^-]$_o$ = (A–E; H–N) 0.0315 M; (F) 0.0630 M; (G) 0.0075 M; [EHM]$_o$ = (A–G; J–M) 0.0500 M; (H) 0.0890 M; (I) 0.0250 M; (N) 0 M; [Ce(III)]$_o$ = (A–I; L–N) 1.00 ×10^{-3} M; (J) 5.00 × 10^{-4} M; (k) 2.00 ×10^{-3} M; [H_2SO_4]$_o$ = (A–K; N) 1.00 M; (L) 1.50 M; (M) 0.500 M; [MA]$_o$ = (A–M) 0 M; (N) 0.0500 M;[NaBr]$_o$ = (A–C; E–N) 0 M; (D) 4.00 × 10^{-3} M; [BrMA]$_o$ = (A–D; F–N) 0 M; (E) 4.00 × 10^{-3} M; aerobic: (A; C–N); anaerobic (N_2): (B); agitation rate: (A–BB; DD–N) 150 rpm; (C) 0 rpm.

(Fig. 1, A vs. N; Fig.e 2, A vs. N). Similar to the MA system, the Fe(phen)$_3^{2+}$-catalyzed BZ reaction with EHM (Fig. 3) oscillates with an induction period considerably shorter than that of the Ce(III)- or Mn(II)-catalyzed system (Figs. 1 and 2).

Under an N_2 atmosphere, both the induction period and the period of oscillations were increased for the Ce(III) or Mn(II) system (Figs. 1B and 2B). The oscillating behavior was affected significantly by the rate of agitation, and without agitation no oscillations were observed for the Ce(III) or Mn(II) system (Figs. 1C and 2C). In contrast, the N_2 atmosphere and the rate of agitation showed relatively less effects on the oscillating pattern of the Fe(phen)$_3^{2+}$ system (Figs. 3B and 3C). In most of this work, the rate of agitation was kept constant at 150 rpm.

The initial presence of bromide ion decreased the induction period of the Ce(III) or Mn(II) system (Figs. 1D and 2D) and it showed an inhibition effect on the Fe(phen)$_3^{2+}$ system (Fig. 3D). The initial presence of bromomalonic acid (BrMA) shortened the induction period of the Ce(III) system (Fig. 1E), whereas it inhibited the reaction of the Fe(phen)$_3^{2+}$ system (Fig. 3E).

Interesting two-stage dual-frequency oscillations were observed for the Mn(II) system with the initial addition of BrMA (Fig. 2E). For the Ce(III) system, increasing [BrO_3^-] increased the induction period and the frequency of oscillations (Figs. 1A, 1G, and 1F). For the Mn(II) system, increasing [BrO_3^-] increased the induction period and the period of oscillations (Figs. 2A, 2G, and 2F). For the Fe(phen)$_3^{2+}$ system,

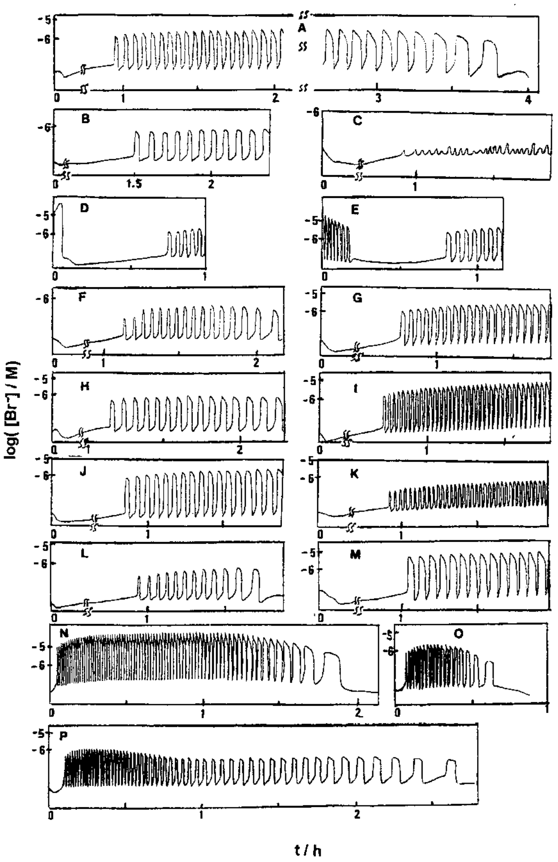

Figure 2 Potentiometric traces of log[Br^-] vs. time for the BrO_3^-–EHM–Mn(II) oscillating reaction at 25°C. [BrO_3^-]$_o$ = (A–E; H–P) 0.0630 M; (F) 0.0940 M; (G) 0.0390 M; [EHM]$_o$ = (A–G; J–M) 0.0300 M; (H) 0.0230 M; (I) 0.0450 M;(N–O) 0 M; (P) 0.0210 M; [Mn(II)]$_o$ = (A–I; L–P) 3.00 × 10^{-3} M; (J) 5.00 × 10^{-3} M; (K) 1.00 × 10^{-3} M; [H_2SO_4]$_o$ = (A–K; N–P) 1.00 M; (L) 1.50 M; (M) 0.500 M; [MA]$_o$ = (A–M) 0 M; (N) 0.0300 M; (O–P) 0.0090 M; [NaBr]$_o$ = (A–C; E–P) 0 M; (D) 4.00 × 10^{-3} M; [BrMA]$_o$ = (A–D; F–P) 0 M; (E) 4.00 × 10^{-3} M; aerobic: (A; C–P); anaerobic (N_2): (B); agitation rate : (A–B; D–P) 150 rpm; (C) 0 rpm.

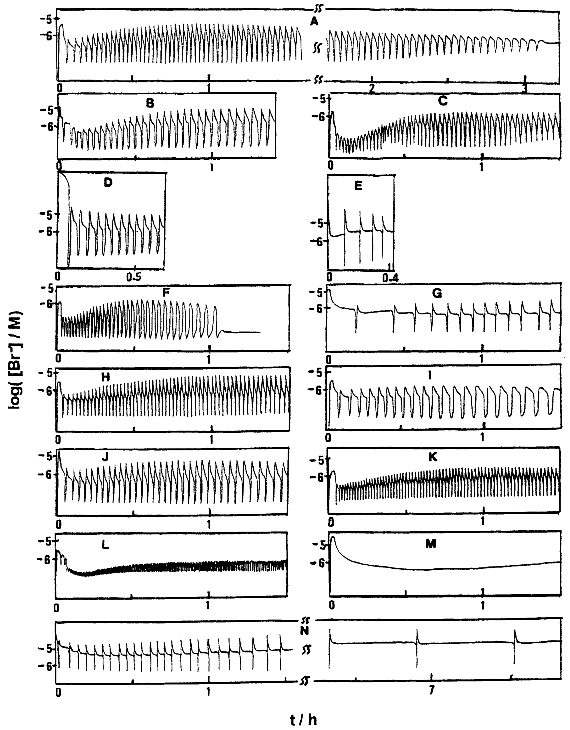

Figure 3 Potentiometric traces of log[Br$^-$] vs. time for the BrO_3^-–EHM–$Fe(phen)_3^{2+}$ oscillating reaction at 25°C. $[BrO_3^-]_o$ = (A–E; H–N) 0.0260 M; (F) 0.0470 M; (G) 0.0140 M; $[EHM]_o$ = (A–G; J–M) 0.0212 M; (H) 0.0313 M; (I) 0.0108 M; (N) 0 M; $[Fe(phen)_3^{2+}]_o$ = (A–I; L–N) 2.00×10^{-3} M; (J) 3.00×10^{-3} M; (K) 1.00×10^{-3} M; $[H_2SO_4]_o$ = (A–K; N) 1.00 M; (L) 1.50 M; (M) 0.500 M; $[MA]_o$ = (A–M) 0 M; (N) 0.0212 M; $[NaBr]_o$ = (A–C; E–N) 0 M; (D) 4.00×10^{-3} M; $[BrMA]_o$ = (A–D; F–N) 0 M; (E) 4.00×10^{-3} M; aerobic: (A; C–N); anaerobic (N_2): (B); agitation rate: (A–B; D–N) 150 rpm; (C) 0 rpm.

increasing $[BrO_3^-]$ increased the frequency of oscillations (Figs. 3A, 3G, and 3F).

For these three systems, increasing [EHM] decreased the induction period and the period of oscillations (Figs. 1A, 1H, and 1I; Figs. 2A, 2H, and 2I; Figs. 3A, 2H, and 2I). For the Ce(III) system, increasing [Ce(III)] decreased the induction period and the frequency of oscillations (Figs. 1A and 1J) and no good oscillations were observed for [Ce(III)] = 2.0×10^{-3} M (Fig. 1K). For the Mn(II) or $Fe(phen)_3^{2+}$ system, increasing the concentration of metalion catalyst decreased the frequency of oscillations and increased significantly the amplitude of oscillations (Figs. 2A, 2J, and 2K; Figs. 3A, 3J, and 3K). The concentration of Mn(II) ion showed less effect on the induction period of the Mn(II) system (Figs. 2A, 2J, and 2K). For the Ce(III) system, increasing $[H_2SO_4]$ decreased the induction period and the period of oscillations (Figs. 1A and 1L) and no good oscillations were observed for $[H_2SO_4]$ = 0.5 M (Fig. 1M). For the Mn(II) system, increasing $[H_2SO_4]$ decreased the induction period and the amplitude of oscillations (Figs. 2A, 2L, and 2M). For the $Fe(phen)_3^{2+}$ system, increasing $[H_2SO_4]$ decreased significantly the period and the amplitude of oscillations (Figs. 3A, 3L, and 3M).

The initial presence of MA caused a substantial effect on the characteristics of oscillations of the BZ reaction with EHM. For example, traces of oscillations of the Mn(II)–EHM–MA BZ system (Fig. 2P) exhibited both the characteristics of oscillations of the Mn(II)–EHM (Fig. 2A) and the Mn(II)–MA (Fig. 2O) BZ systems. No good oscillations were observed for the BrO_3^-–$CH_2(COOEt)_2$ reaction catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{3+}$ ion.

Kinetics

A conventional spectrophotometric method was used to investigate the kinetics of reactions of EHM with Ce(IV), Mn(III), and $Fe(phen)_3^{3+}$ ions. It was observed that the presence of O_2 did not show significant effect on the rate of the Ce(IV)- or $Fe(phen)_3^{3+}$–EHM reaction. In contrast, the presence of O_2 accelerated the rate of the Mn(III)–EHM reaction (Fig. 4). Therefore, the reactant solutions were deaerated with N_2 before starting the kinetic runs. The observed pseudo-first-order rate constant (k_{obs}) was calculated from the LLS

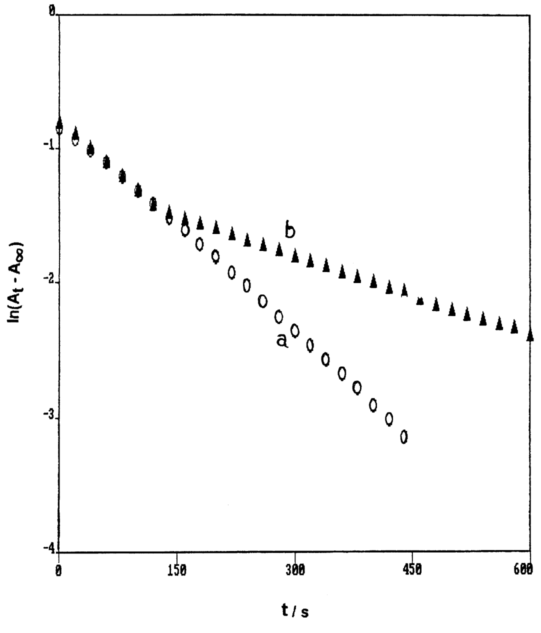

Figure 4 Plots of $\ln(A_t - A_\infty)$ vs. time for the Mn(III)–EHM reaction. $[Mn(III)]_o = 4.00 \times 10^{-4}$ M, $[EHM]_o = 6.00 \times 10^{-3}$ M, $[H_2SO_4]_o$ = 1.00 M, 25°C, 310 nm. (a) aerobic; (b) deaerated with N_2.

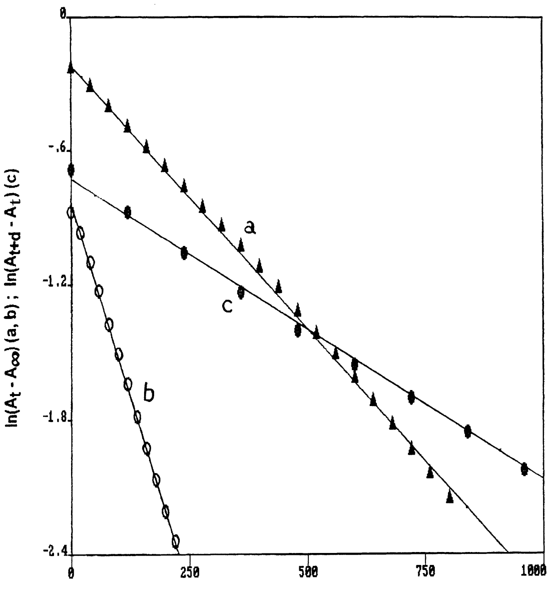

Figure 5 Plots of $\ln(A_t - A_\infty)$ (a, b) or $\ln(A_{t+d} - A_t)$ (c) vs. time for (a) Ce(IV)–EHM, (b) Mn(III)–EHM, and (c) $Fe(phen)_3^{3+}$–EHM reactions in 1.00 M H_2SO_4 and at 25°C. (a) $[Ce(IV)]_o = 1.50 \times 10^{-4}$ M, $[EHM]_o = 0.0166$ M, 320 nm; (b) $[Mn(III)] = 4.00 \times 10^{-4}$ M, $[EHM]_o = 6.00 \times 10^{-3}$ M, 310 nm, deaerated with N_2; (c) $[Fe(phen)_3^{3+}]_o = 1.00 \times 10^{-4}$ M, $[EHM]_o = 0.200$ M, 480 nm.

fit of the linear plot of $\ln(A_t - A_\infty)$ vs. time for the Ce(IV)–EHM or Mn(III)–EHM reaction or the plot of $\ln(A_{t+d} - A_t)$ vs. time for the $Fe(phen)_3^{3+}$–EHM reaction (Fig. 5). As shown in Figures 6 and 7, the plots of k_{obs}^{-1} vs. $[EHM]^{-1}$ are linear for the Ce(IV)- and Mn(III)–EHM reactions. These results are consistent with a Michaelis–Menten mechanism (M1) as suggested by Kasperek and Bruice [6].

$$M^{(n+1)+} + EHM \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M(EHM)]^{(n+1)+}$$
$$\xrightarrow{k_2} M^{n+} + \text{other products} \qquad (M1)$$

The derived rate law is shown in Eq. (1), where $M^{(n+1)+}$ = Ce(IV) or Mn(III), and $K_m = (k_{-1} + k_2)/k_1$.

$$-d[M^{(n+1)+}]/dt = k_2\,[EHM][M^{(n+1)+}]/(K_m + [EHM]) = k_{obs}\,[M^{(n+1)+}] \qquad (1)$$

The values of k_2 and K_m obtained from the plots of k_{obs}^{-1} vs. $[EHM]^{-1}$ at various temperatures are shown in Table I. The apparent activation energies calculated

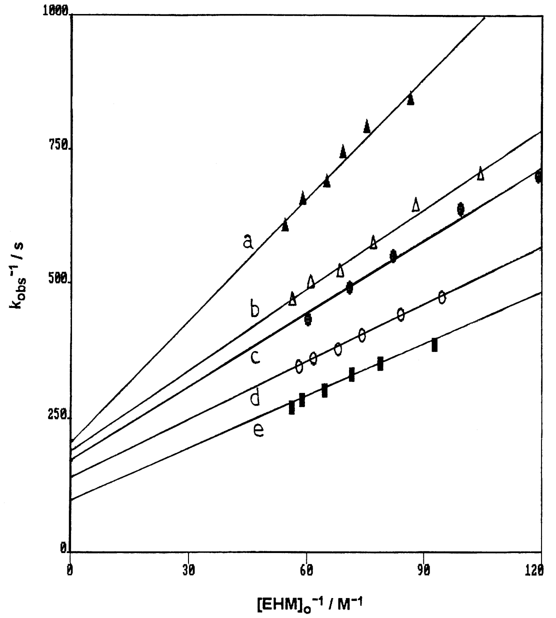

Figure 6 Plots of k_{obs}^{-1} vs. $[EHM]_o^{-1}$ for the Ce(IV)–EHM reaction at various temperatures. $[Ce(IV)]_o = 1.50 \times 10^{-4}$ M, $[H_2SO_4]_o = 1.00$ M, 320 nm. (a) 21.3°C, (b) 23.0°C, (c) 25.1°C, (d) 27.3°C, (e)30.8°C.

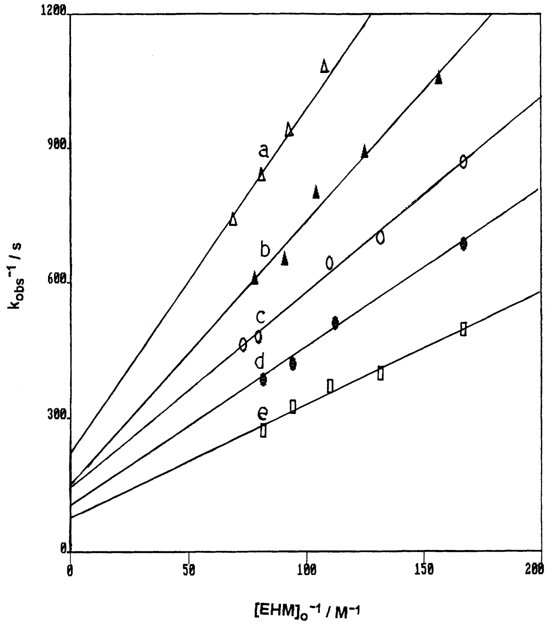

Figure 7 Plots of k_{obs}^{-1} vs. $[EHM]_o^{-1}$ for the Mn(III)–EHM reaction at various temperatures. $[Mn(III)]_o = 4.00 \times 10^{-4}$ M, $[H_2SO_4]_o = 1.00$ M, 310 nm. (a) 17.2°C, (b)19.7°C, (c) 22.0°C, (d) 25.6°C (e) 28.2°C.

Table I The Rate Coefficients of the Reactions of Ethyl Hydrogen Malonate (EHM) with Ce(IV), Mn(III), and $Fe(phen)_3^{3+}$ Ions at Various Temperatures

T (°C)	k_2 (10^{-2} s^{-1})	K_m (10^{-2} M)	T (°C)	k_2 (10^{-2} s^{-1})	K_m (10^{-2} M)	T (°C)	k_2' (10^{-2} M^{-1} s^{-1})
Ce(IV)–EHM Reaction			Mn(III)–EHM Reaction			$Fe(phen)_3^{3+}$–EHM Reaction	
21.3	0.491	3.71	17.2	0.460	3.54	19.0	0.477
23.0	0.528	2.63	19.7	0.691	4.06	22.1	0.552
25.1	0.589	2.68	22.0	0.709	3.09	25.2	0.688
27.3	0.723	2.59	25.6	1.07	3.81	28.3	0.968
30.8	1.05	3.41	28.2	1.29	3.24	31.6	1.39

from the LLS fits of the plots of $\ln(k_2/K_m)$ vs. T^{-1} are (61.7 ± 13.8 and 70.1 ± 5.1) kJ mol^{-1} for Ce(IV)–EHM and Mn(III)–EHM reactions, respectively. The dissociation reaction of $Fe(phen)_3^{3+}$ or $Fe(phen)_3^{2+}$ ion is negligible because the values of the first-order rate constants of both reactions are about twoorders of magnitude smaller than that of k_{obs} of the $Fe(phen)_3^{3+}$–EHM reaction. For the $Fe(phen)_3^{3+}$–EHM reaction, the plot of k_{obs} vs. [EHM] is linear (Fig. 8), which implies that this reaction follows a second-order kinetics. The values of the second-order rate constant (k_2') calculated from the LLS fits of the plots of k_{obs} vs. [EHM] at various temperatures are also shown in Table I. The apparent activation energy obtained from the LLS fit of the plot of $\ln k_2'$ vs. T^{-1} is 63.6 ± 6.6 kJ mol^{-1}.

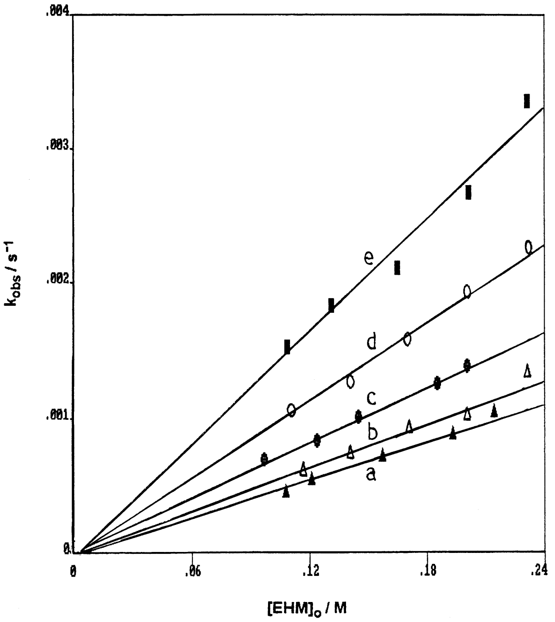

Figure 8 Plots of k_{obs} vs. $[EHM]_o$ for the $Fe(phen)_3^{3+}$–EHM reaction at various temperatures. $[Fe(phen)_3^{3+}]_o$ = 1.00 × 10^{-4} M, $[H_2SO_4]_o$ = 1.00 M, 480 nm. (a) 19.0°C, (b) 22.1°C, (c): 25.2°C, (d) 28.3°C (e): 31.6°C.

Discussion

Basically, the characteristics of the Ce(III)-, Mn(II)-, or $Fe(phen)_3^{2+}$-catalyzed BZ reaction with EHM are similar to those of the corresponding classical BZ reaction with MA. The FKN (Field, Körös, and Noyes) mechanism [4] and the more detailed GTF (Györgyi, Turányi, and Field) mechanism [20] are applicable to rationalize the main features of these systems. It may be considered that the FKN mechanism contains an inorganic subset mainly involving reactions of oxybromine species among themselves and with the metalion catalyst, and an organic subset involving the reactions of organic substrate like malonic acid and its derivatives with oxybromine species and the oxidized form of the metalion catalyst like Ce(IV).

Based on the results of the Ce(IV)–MA reaction [20–23], mechanistic steps (s1–s10) are proposed to rationalize the reaction of EHM with $M^{(n+1)+}$ ion ($M^{(n+1)+}$ = Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$).

$$\text{s1: } M^{(n+1)+} + CH_2COOHCOOEt \longrightarrow M^{n+} + \dot{C}HCOOHCOOEt + H^+$$

$$\text{s2: } 2\dot{C}HCOOHCOOEt + H_2O \longrightarrow CH_2COOHCOOEt + HOCHCOOHCOOEt$$

$$\text{s3: } M^{(n+1)+} + HOCHCOOHCOOEt \longrightarrow M^{n+} + HO\dot{C}COOHCOOEt + H^+$$

$$\text{s4: } 2HO\dot{C}COOHCOOEt \longrightarrow HOCHCOOHCOOEt + O{=}CCOOHCOOEt$$

$$\text{s5: } M^{(n+1)+} + O{=}CCOOHCOOEt \longrightarrow M^{n+} + O{=}\dot{C}COOEt + CO_2 + H^+$$

$$\text{s6: } O{=}\dot{C}COOEt \rightleftharpoons O{=}CEtCOO\cdot$$

$$\text{s7: } M^{(n+1)+} + O{=}CEtCOO\cdot + H_2O \longrightarrow M^{n+} + EtCOOH + CO_2 + H^+$$

$$\text{s8: } 2O{=}CEtCOO\cdot + H_2O \longrightarrow O{=}CEtCOOH + EtCOOH + CO_2$$

$$\text{s9: } M^{(n+1)+} + O{=}CEtCOOH \longrightarrow M^{n+} + O{=}\dot{C}Et + CO_2 + H^+$$

$$\text{s10: } M^{(n+1)+} + O{=}\dot{C}Et + H_2O \longrightarrow Mn^+ + EtCOOH + H^+$$

When the amount of EHM is in excess over that of $M^{(n+1)+}$ ion, the EHM· radical (·CHCOOHCOOEt) produced in reaction (s1) undergoes the disproportionation reaction (s2) to yield HOCHCOOHCOOEt. When a sufficient amount of $M^{(n+1)+}$ ion is present, HOCHCOOHCOOEt can be oxidized further via reaction (s3) to produce $HO\dot{C}COOHCOOEt$ radical, which undergoes the disproportionation reaction (s4) to yield ethyl hydrogen mesoxalate ($O{=}CCOOH$-$COOEt$). The oxidative decarboxylation reaction of $O{=}CCOOHCOOEt$ by $M^{(n+1)+}$ ion (s5) generates the ethyl glyoxylate radical ($O{=}\dot{C}COOEt$). Subsequent reactions (s6–s10) of $O{=}\dot{C}COOEt$ radical rationalize the production of propanoic acid (EtCOOH). The generation of carboxylate radical ($O{=}CEtCOO\cdot$) via a rearrangement reaction (s6) of $O{=}\dot{C}OOEt$ radical is similar to the hypothesis of the carboxylate malonyl radical ($CH_2COOHCOO\cdot$) in the Ce(IV)–MA reaction [23].

The characterization of the preceding mechanistic steps was carried out according to the method developed by Happel et al. [24–26]. The eight intermediate species are $\dot{C}HCOOHCOOEt$, HOCHCOOHCOOEt, $HO\dot{C}COOHCOOEt$, $O{=}CCOOHCOOEt$, $O{=}\dot{C}COOEt$, $O{=}CEtCOO\cdot$, $O{=}CEtCOOH$, and $O{=}\dot{C}Et$. The seven terminal species are $M^{(n+1)+}$, M^{n+}, $CH_2COOHCOOEt$, EtCOOH, H_2O, H^+, and CO_2. The diagonalization of the step-by-species matrix of (s1–s10) generates one direct overall reaction (R1) (2s1 + s2 + 2s3 + s4 + s5 + s6 + s7) and one cycle (2s7 − s8 − s9 − s10). Reaction (R1) was supported by the spectrophotometric study of the stoichiometry of the Ce(IV)–EHM reaction.

$$\text{(R1): } 6M^{(n+1)+} + CH_2COOHCOOEt + 2H_2O \longrightarrow 6M^{n+} + EtCOOH + 2CO_2 + 6H^+$$

Under aerobic or anaerobic conditions, the order of reactivity toward reacting with EHM is Mn(III) > Ce(IV) $\gg$ $Fe(phen)_3^{3+}$, which follows exactly the same trend as that of the malonic acid system. For MA, methylmalonic acid (MeMA), ethylmalonic acid (EtMA), *n*-butylmalonic acid (BuMA), phenylmalonic acid (PhMA), and EHM, the order of reactivity under aerobic or anaerobic conditions is (PhMA, MA) > EHM > MeMA > EtMA > BuMA toward reacting with Ce(IV) ion [16,17] and is MA > PhMA > MeMA > (EtMA, BuMA) > EHM toward reacting with Mn(III) ion [15,16]. Under aerobic conditions, the order of reactivity toward reacting with $Fe(phen)_3^{3+}$ ion is PhMA > MeMA > (BuMA, EtMA) > MA > EHM [14,16,17].

In the classical BZ reaction with MA, the bromination of MA to produce bromomalonic acid (BrMA) is one of the paths to generate bromide ion. Decreasing the rate of bromination of organic substrate is expected to increase the length of the induction period. The rate of the isotope exchange reaction of EHM in D_2O measured by using ^1H NMR spectroscopy is about one order of magnitude slower than that of MA. As expected, the induction period of the Ce(III)- or Mn(II)-catalyzed BZ reaction with EHM is considerably longer than that of the corresponding MA system (Fig. 1, A vs. N; Fig. 2, A vs. N). As suggested by Györgyi et al. [20], the ethyl hydrogen bromomalonate (BrEHM, BrCHCOOHCOOEt) can be produced by reactions (R2–R4). An attempt to synthesize BrEHM was unsuccessful. However, the initial presence of BrMA shows different effects on the Ce(III)-, Mn(II)-, and $Fe(phen)_3^{2+}$-catalyzed EHM–BZ systems (Figs. 1E, 2E, and 3E).

$$\text{(R2): } CH_2COOHCOOEt + Br_2 \longrightarrow BrCHCOOHCOOEt + Br^- + H^+$$

$$\text{(R3): } CH_2COOHCOOEt + HOBr \longrightarrow BrCHCOOHCOOEt + H_2O$$

$$\text{(R4): } \dot{C}HCOOHCOOEt + Br_2 \longrightarrow BrCHCOOHCOOEt + Br\cdot$$

Oxygen effects on the BZ reaction and the oxidation of the organic substrate by the oxidized form of the metalion catalyst have been studied extensively [11,14–17,21,23,27–33]. The presence of O_2 may shorten or lengthen the induction period or the frequency of oscillations. Barkin et al. [21] and Ganapathisubramanian and Noyes [29] reported the acceleration effects of O_2 on the rate of the Ce(IV)–MA reaction and the rate of generating Br^- ion in the Ce(IV)–MA–BrMA reaction. Tkac and Treindl [31]

Table II The Effect of Oxygen on the Reaction of RCHCOOHCOOR′ and Ce(IV), Mn(III), or Fe(phen)_3^{3+} Ion

RCHCOOHCOOR′	Ce(IV)	Ref.	Mn(III)	Ref.	Fe(phen)_3^{3+}	Ref.
$\text{CH}_2\text{(COOH)}_2$	A	21	A	31	A	14
$\text{CH}_2\text{COOHCOOEt}$	NS	*	A	*	NS	*
MeCH(COOH)_2	I	17	I	15	A	14
EtCH(COOH)_2	NS	17	I	15	A	17
BuCH(COOH)_2	NS	17	I	15	A	17
PhCH(COOH)_2	I	16	I	16	NS	16
BrCH(COOH)_2	I	29,34	I	15	NS	14

A, acceleration; I, inhibition; NS, not significant; *, this work.

also found that O_2 accelerated the release of Br^- ion in the Mn(III)–MA–BrMA reaction. The RCH(COOH)_2-assisted liberation of Br^- ion from the reactions of Ce(IV), Mn(III), or Fe(phen)_3^{3+} ion and BrCR(COOH)_2 (R = Me, Et, Bu, or Ph) under aerobic conditions was also observed by Sun et al. [15], Lin and Jwo [16], and Chen et al.[17]. Treindll et al. [33] reported the detailed study of the influence of O_2 and RCH(COOH)_2 (R = H, Me, Et, Bu, Ph, and Bz) on oscillations and the autocatalytic oxidation of the metalion catalyst by bromate in the BZ reaction. Their results indicate that in both the presence and absence of RCH(COOH)_2, oxygen always increases the inflection time of the autocatalysis when compared with anaerobic conditions and that the scavenging of $\dot{\text{B}}\text{rO}_2$ radicals, probably by $\dot{\text{C}}\text{R(COOH)}_2$ and $\cdot\text{OOCR(COOH)}_2$ radicals, affects the inflection time. It is expected that reactions involving $\cdot$CHCOOHCOOEt and $\cdot$OOCHCOOHCOOEt radicals are similar to those of $\dot{\text{C}}\text{R(COOH)}_2$ and $\cdot\text{OOCR(COOH)}_2$ radicals.

The effects of oxygen on the kinetics of the reactions of $\text{M}^{(n+1)+}$ ion and MA derivatives (RCHCOOHCOOR′) are summarized in Table II. The following conclusions can be deduced:

1. An oxygen-acceleration effect is generally observed in the reactions of $\text{CH}_2\text{(COOH)}_2$ or $\text{CH}_2\text{COOHCOOEt}$ and Ce(IV), Mn(III), or Fe(phen)_3^{3+} ion.
2. An oxygen-inhibition effect is generally observed in the reaction of monosubstituted malonic acid (RCH(COOH)_2) and Ce(IV) or Mn(III) ion.
3. The reaction of Fe(phen)_3^{3+} ion and RCHCOOHCOOR′ generally requires the assistance of oxygen.

In the presence of oxygen, the following reactions (R5–R9) are assumed to occur for the reaction of $\text{M}^{(n+1)+}$ ion and RCHCOOHCOOR′.

$$\text{(R5): } \text{M}^{(n+1)+} + \text{RCHCOOHCOOR}' \xrightarrow{} \text{M}^{n+} + \dot{\text{C}}\text{RCOOHCOOR}' + \text{H}^+$$

$$\text{(R6): } \dot{\text{C}}\text{RCOOHCOOR}' + \text{O}_2 \xrightarrow{} \dot{\text{O}}\text{OCRCOOHCOOR}'$$

$$\text{(R7): } \text{RCHCOOHCOOR}' + \dot{\text{O}}\text{OCRCOOHCOOR}' \xrightarrow{} \text{HOOCRCOOHCOOR}' + \dot{\text{C}}\text{RCOOHCOOR}'$$

$$\text{(R8): } \text{M}^{(n+1)+} + \text{HOOCRCOOHCOOR}' \xrightarrow{} \text{M}^{n+} + \dot{\text{O}}\text{OCRCOOHCOOR}' + \text{H}^+$$

$$\text{(R9): } \text{M}^{n+} + \dot{\text{O}}\text{OCRCOOHCOOR}' + \text{H}^+ \xrightarrow{} \text{M}^{(n+1)+} + \text{HOOCRCOOHCOOR}'$$

$$\text{(R10): } 2\dot{\text{C}}\text{RCOOHCOOR}' + \text{H}_2\text{O} \xrightarrow{} \text{RCHCOOHCOOR}' + \text{HOCRCOOHCOOR}'$$

$$\text{(R11): } 2\ \dot{\text{C}}\text{RCOOHCOOR}' \xrightarrow{} (\text{CRCOOHCOOR}')_2$$

$$\text{(R12): } \text{HOOCRCOOHCOOR}' \xrightarrow{} \text{O}{=}\text{CRCOOR}' + \text{CO}_2 + \text{H}_2\text{O}$$

Reactions (R6–R8) explain the acceleration effect of oxygen on the rate of disappearance of $\text{M}^{(n+1)+}$ ion. The inhibition effect of oxygen can be rationalized by invoking reactions R6 and R9 as suggested by Drummond and Waters [35]. The participation of reactions R10 and R11 leads to the production of HOCRCOOHCOOR′, although Gao et al. [36] have shown that there is no tartronic acid (HOCH(COOH)_2) among the first molecular intermediates of the Ce(IV)–MA reaction.

As shown in Table II, the presence of oxygen exhibits opposite effects on the reactions of Ce(IV) or Mn(III) and $\text{CH}_2\text{(COOH)}_2$ and RCH(COOH)_2 ($\text{R} \neq \text{H}$), probably due to the presence of two reactive methylene hydrogen atoms in $\text{CH}_2\text{(COOH)}_2$. These observations may be explained by invoking reactions (R10–R12). The presence of the substituent R in

$RCH(COOH)_2$ affects the reactivity of $\dot{C}RCOOHCOOR'$ radicals in the disproportionation and recombination reactions (R10 and R11) and the reactivity of HOOCRCOOHCOOR′ in its decarboxylation reaction (R12). It is expected that the presence of the substituent R decreases the reactivities of HOCRCOOHCOOR′, $(CRCOOHCOOR')_2$, and O═CRCOOR′ toward further reaction with Ce(IV) or Mn(III) ion, due to the absence of reactive methylene hydrogen atom.

The results of this work also strongly support the observations by Ruoff et al. [33] that the period lengths of the $RCH(COOH)_2$–BZ systems in aerobic conditions show the same trend when the substituent R of $RCH(COOH)_2$ is varied as in anaerobic conditions. However, the exception is with $CH_2(COOH)_2$.

Both Körös et al. [5] and Smoes [37] have reported that the BZ reaction with MA catalyzed by $Fe(phen)_3^{2+}$ ion oscillates without an induction period in contrast to its Ce(III)-catalyzed system. Noyes [3] has first pointed out that both thermodynamic and kinetic arguments indicate that $Fe(phen)_3^{3+}$ ion should not oxidize MA by the same mechanism appropriate for the Ce(IV) ion. This argument is strongly supported by the results of the kinetic study of the $Fe(phen)_3^{3+}$—$RCH(COOH)_2$ (R═H, Me, Et, Bu, Ph, or Br) reactions [14,16,17]. The result of this work indicates that the $Fe(phen)_3^{3+}$–EHM reaction follows the same trend. Furthermore, unlike Ce(III) or Mn(II) ions, the oxidation of $Fe(phen)_3^{2+}$ ion by bromine species (BrO_3^-, $HBrO_2$, HOBr, and Br_2) besides $BrO_2\cdot$ radicals as suggested by Kéki et al. [38] also needs to be considered to characterize more closely the $Fe(phen)_3^{2+}$-catalyzed BZ reaction with EHM.

Similar to the MA system, the $Fe(phen)_3^{2+}$-catalyzed BZ reaction with EHM oscillates with an induction period considerably shorter than that of the Ce(III)- or Mn(II)-catalyzed system. Under aerobic or anaerobic conditions, the order of reactivity toward reacting with EHM is Mn(III) $>$ Ce(IV) $\gg$ $Fe(phen)_3^{3+}$, which follows the same trend as that of the MA system. The presence of the ester group in EHM lowers the reactivity of the two methylene hydrogen atoms toward bromination or oxidation by Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion.

An oxygen-acceleration effect is generally observed in the reactions of $CH_2(COOH)_2$ or $CH_2COOHCOOEt$ and Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion. An oxygen-inhibition effect is generally observed in the reaction of monosubstituted malonic acid ($RCH(COOH)_2$) and Ce(IV) or Mn(III) ion. The reaction of $Fe(phen)_3^{3+}$ ion and RCHCOOHCOOR′ generally requires the assistance of oxygen. No good oscillations were observed for the bromate-diethyl malonate ($CH_2(COOEt)_2$) reaction catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion.

SUMMARY

In a stirred batch experiment, the reaction of bromate ion with ethyl hydrogen malonate ($CH_2COOHCOOEt$, EHM) in aqueous H_2SO_4 catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion exhibits damped oscillations. Basically, the characteristics of the Ce(III)-, Mn(II)-, or $Fe(phen)_3^{2+}$-catalyzed BZ reaction with EHM are similar to those of the corresponding classical BZ reaction with malonic acid (MA).

The characteristics of the oscillations depend on the concentrations of bromate ion, EHM, metalion catalyst, sulfuric acid, and oxygen. Under similar conditions, the Ce(III)- or Mn(II)-catalyzed BZ reaction with EHM exhibits a considerably longer induction period than that of the corresponding BZ reaction with MA. $Fe(phen)_3^{2+}$ ion behaves differently from Ce(III) and Mn(II) ions in catalyzing this oscillating reaction.

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