Kinetic Study of the Ce(III)-, Mn(II)-, or Ferroin-Catalyzed Belousov-Zhabotinsky Reaction with Pyruvic Acid

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ABSTRACT: The Ce(III)-, Mn(II)-, or ferroin ($Fe(phen)_3{}^{2+}$)-catalyzed reaction of bromate ion and pyruvic acid (PA) or its dimer exhibits oscillatory behavior. Both the open-chain dimer (parapyruvic acid, γ-methyl-γ-hydroxyl-α-keto-glutaric acid, DPA1) and the cyclic-form dimer (α-keto-γ-valerolactone-γ-carboxylic acid, DPA2) show more sustained oscillations than PA monomer. Ferroin behaves differently from Ce(III) or Mn(II) ion in catalyzing these oscillating systems. The kinetics of reactions of PA, 3-brompyruvic acid (BrPA), DPA1, or DPA2 with Ce(IV), Mn(III), $Fe(phen)_3{}^{3+}$ ion were investigated. The order of relative reactivity of pyruvic acids toward reaction with Ce(IV), Mn(III), or $Fe(phen)_3{}^{3+}$ ion is DPA2 $>$ DPA1 $>$ BrPA $>$ PA and that of metal ions toward reaction with pyruvic acids is Mn(III) $>$ Ce(IV) $>$ $Fe(phen)_3{}^{3+}$. The rates of bromination reactions of pyruvic acids are independent of the concentration of bromine and the order of reactivity toward bromination is (DPA1, DPA2) $>$ BrPA $>$ PA. Experimental results are rationalized. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 408–418, 2000

INTRODUCTION

Theoretical and experimental studies of oscillating reactions have been of interest to biologists and chemists alike. In 1950, Belousov endeavored to model catalysis in the Krebs cycle (citric acid cycle) using cerium ion instead of the protein-bound metal ions common in the enzymes of living cells and first observed sustained, barely damped oscillations in the ratio of [Ce(IV)]/[Ce(III)] during the cerium-ion-catalyzed oxidation of citric acid or malonic acid by acidic bromate ion [1]. Zhabotinsky demonstrated that similar oscillations are observed when the malonic acid is replaced by another organic substrate with an active methylene hydrogen atom or when the cerium couple is replaced by the Mn(III)/Mn(II) couple, or by the $Fe(phen)_3^{3+/2+}$ couple [2]. Field, Körös, and Noyes (FKN) [3] proposed a detailed mechanism to rationalize successfully the cerium-ion-catalyzed bromate ion-malonic acid oscillating reaction. The FKN mechanism is strongly supported by the modeling computations of Edelson et al. [4] and of Field et al. [5].

Undoubtedly, Belousov-Zhabotinsky (BZ) reaction is one of the most thoroughly studied and understood chemical oscillating systems. In the previous work, we studied the BZ reactions with saccharides, malonic

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acid and its derivatives (methyl-, ethyl-, butyl-, phenyl-, and dibrom-malonic acids) catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion [6–10]. It is well known that pyruvate is an important metabolite in the catabolic pathways and involved in a number of enzyme-catalyzed intracellular phenomena. In stage I of catabolism, polysaccharides are degraded to hexoses or pentoses; lipids are degraded to fatty acids, glycerol, and other products; and proteins are hydrolyzed to amino acids. In stage II of catabolism, hexoses, pentoses, and glycerol from stage I are degraded to a single 3-carbon pyruvate intermediate, which is converted to acetyl-coenzyme A and CO_2 under aerobic conditions, catalyzed by pyruvate dehydrogenase. Similarly, the fatty acids and the carbon skeletons of most of the amino acids are also broken down to form acetyl-CoA. In stage III of catabolism, acetyl-CoA enters the citric acid cycle (Krebs cycle) and reacts with oxaloacetate to yield citrate, catalyzed by citrate synthase. The acetyl group of acetyl-CoA is oxidized completely to CO_2 and H_2O in the citric cycle. Furthermore, pyruvic acid is also a highly probable intermediate in the BZ reaction with methylmalonic acid [11]. Therefore, it is worthwhile to study the BZ reaction with pyruvic acid as the organic substrate.

In this work, we demonstrate that the Ce(III)-, Mn(II)-, or $Fe(phen)_3^{2+}$-catalyzed bromate-pyruvic acid reaction in aqueous H_2SO_4 exhibits oscillations in bromide ion concentration. It is observed that the dimerized pyruvic acid is more reactive than pyruvic acid monomer and also exhibits better oscillatory behavior. The kinetics of the reactions of pyruvic acid and 3-bromopyruvic acid with Ce(IV), Mn(III), and $Fe(phen)_3^{3+}$ ion is investigated. Rationalization of experimental results is also given.

EXPERIMENTAL

Materials

Ammonium cerium(IV) nitrate (99%), ammonium iron(II) sulfate (99%), cerium(III) nitrate hexahydrate (99%), and manganese(II) acetate tetrahydrate (99%) (Merck); pyruvic acid sodium salt (99%, Sigma); pyruvic acid (98%, Ferak; 98%, Aldrich); 3-bromopyruvic acid (97%, Aldrich) were used in this work. Other reagents used were of the highest-grade chemicals commercially available. Deionized water from Millipore Milli-RO 20 (reverse osmosis) was used. Solutions of Mn(III) [6], $Fe(phen)_3^{2+}$ [7], and $Fe(phen)_3^{3+}$ [7] ions, and sodium pyruvate were freshly prepared just before carrying out the kinetic run.

Procedures

Kinetic Experiment. The oscillating reaction was followed potentiometrically with a bromide-ion-selective electrode (Orion 94-35) against a double junction reference electrode (Orion 90-02) [12]. The kinetics of the oxidation reaction of pyruvic acids by 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 360 nm ($\varepsilon = 3.18 \times 10^3$ M^{-1} cm^{-1}), 480 nm (110 M^{-1} cm^{-1}), and 480 nm (1.05×10^4 M^{-1} cm^{-1}), respectively with either a stopped-flow spectrophotometer (Photol RA-401) or a conventional spectrophotometer (Hitachi U-2000). The organic substrate was in great excess stoichiometrically over the metal ion oxidant.

Stoichiometry. It was found that Ce(IV) ion reacts rapidly with pyruvic acid (PA) to produce quantitatively acetic acid and carbon dioxide. The stoichiometry was studied by measuring the concentration of Ce(IV) ion spectrophotometrically and the amount of CO_2 gravimetrically. The CO_2 produced in the reaction was trapped in two connected flasks containing aqueous saturated solution of $Ba(OH)_2$ and precipitated as $BaCO_3$. The reliability of this gravimetric method was supported by a parallel experiment of the reaction of Ce(IV) ion and oxalic acid (OA), which gives $\Delta[CO_2]/\Delta[OA] = 1.9$, consistent with the stoichiometric equation of $2\,Ce(IV) + (COOH)_2 \rightarrow 2\,Ce(III) + 2\,H^+ + 2\,CO_2$. For (1.0, 1.5, 2.0, 2.5, and 3.0) mmol PA and keeping $[Ce(IV)]_O/[PA]_O = 4$, the values of $\Delta[CO_2]/\Delta[PA]$ and $\Delta[Ce(IV)]/\Delta[PA]$ are 1.1 ± 0.2 and 2.2 ± 0.2, respectively. This result indicates that the stoichiometric equation of the reaction of Ce(IV) ion and PA is consistent with reaction (S1).

$$2\,Ce(IV) + CH_3COCOOH \longrightarrow 2\,Ce(III) + 2\,H^+ + CH_3COOH + CO_2 \qquad (S1)$$

Similar methods were applied to study the stoichiometry of the reaction of Ce(IV) ion and 3-bromopyruvic acid (BrPA). For (1.5, 2.0, 2.5, 3.0, 3.5, and 4.0) mmol of BrPA and keeping $[Ce(IV)]_O/[BrPA]_O = 4$, the average values of $\Delta[CO_2]/\Delta[BrPA]$ and $\Delta[Ce(IV)]/\Delta[BrPA]$ are 0.7 ± 0.2 and 1.9 ± 0.2, respectively. Product analysis by NMR, MS, and potentiometric methods shows that $BrCH_2COOH$ is the main organic product and that side products include bromide ion, succinic acid ($(CH_2COOH)_2$), 2,3-dibromosuccinic acid ($(CHBrCOOH)_2$) (trace amount), and 1,4-dibromo-2,3-butanedione ($(COCH_2Br)_2$) (trace amount). The stoichiometric equation of the main reaction of Ce(IV) ion and BrPA can be expressed by reaction (S2).

$$2\ \mathrm{Ce(IV)} + \mathrm{BrCH_2COCOOH} \longrightarrow 2\ \mathrm{Ce(III)} + 2\ \mathrm{H^+} + \mathrm{BrCH_2COOH} + \mathrm{CO_2} \qquad \text{(S2)}$$

NMR Spectra

In aqueous solution, pyruvic acid is hydrated to yield the geminate diol (α,α-dihydroxypropionic acid) (reaction (R1)). Leussing et al. [13] reported that in 1.25 M PA the proportions were 46% keto-PA and 54% diol-PA and in 1.0 M NaPA about 3% of the pyruvate ion (PA^-) were hydrated.

$$\mathrm{CH_3COCOOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3C(OH)_2COOH} \qquad \text{(R1)}$$

It was reported that PA undergoes slow dimerization reaction to yield the open-chain dimer, parapyruvic acid (γ-methyl-γ-hydroxyl-α-keto-glutaric acid, DPA1) or the cyclic condensation dimer, α-keto-γ-valerolactone-γ-carboxylic acid, DPA2) (Fig. 1). The dimerization reaction is catalyzed by acid, base, or metal ion (Zn(II), Mg(II), Cu(II), or Mn(II)) [13–18]. The equilibrium constant of the dimerization reaction of PA^- ion to produce parapyruvate ion (reaction (R2)) is 6.5 [15] and that of the keto-enol tautomerization reaction (reaction (R3)) is about 1×10^{-3} [19–20].

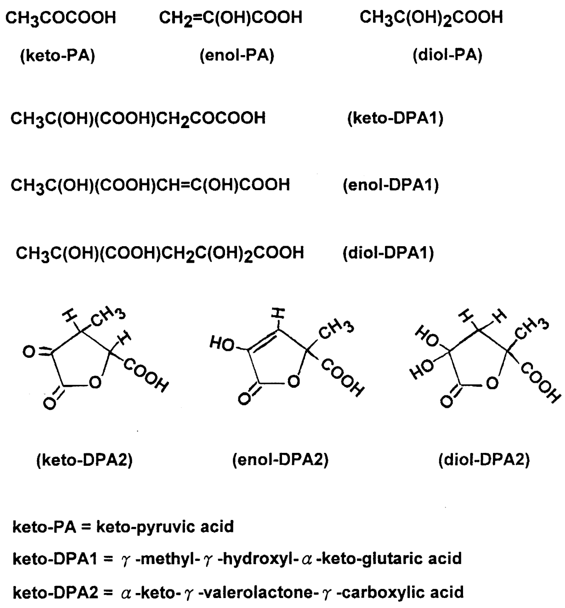

Figure 1 Structures of pyruvic acids.

$$2\ \mathrm{CH_3COCOO^-} \rightleftharpoons \mathrm{CH_3COH(COO^-)CH_2COCOO^-} \qquad \text{(R2)}$$

$$\mathrm{CH_3COCOOH} \rightleftharpoons \mathrm{CH_2{=}COHCOOH} \qquad \text{(R3)}$$

The ^1H NMR spectra of NaPA, DPA1 (Aldrich), and DPA2 (Ferak) are shown in Fig. 2. The spectrum of dimer-free NaPA in D_2O shows two peaks at δ = 1.83 and 2.71 ppm with the area ratio of about 1 : 11, which changes to 1 : 2.1 at 1.18 and 2.71 ppm, respectively, in D_2O containing 1 M D_2SO_4 (Fig. 2a). The spectrum of DPA2 (Ferak) in D_2O shows three major peaks at 1.08, 1.27, and 2.04 ppm with the area ratios of 1 : 1.1 : 3.5, which changes to 1 : 0.34 : 0.61 at 1.18, 1.31, and 2.07, respectively, in 1 M D_2SO_4 (Fig. 2b). The spectrum of DPA1 (Aldrich) in D_2O shows three major peaks at 1.31, 1.43, and 2.19 ppm with the area ratios of 1 : 0.12 : 0.98, which change to 1 : 0.08 : 0.88 at 1.23, 1.36, and 2.12 ppm, respectively, in 1 M D_2SO_4 (Fig. 2c). The results above suggest that the colorless pyruvic acid of Aldrich contains mainly the parapyruvic acid (DPA1), whereas the orange-colored pyruvic acid of Ferak contains mainly the cyclic dimer (DPA2). The ^1H NMR spectrum of BrPA in D_2O containing 1 M D_2SO_4 shows a singlet peak at 3.70 ppm, which indicates that it is dimer-free and that the amounts of the diol- and enol-BrPA are negligible.

RESULTS AND DISCUSSION

The BZ Reaction with Dimer-free Pyruvic Acid

In a stirred batch experiment, oscillatory behavior was observed in the reaction of bromate ion with dimer-free sodium pyruvate (NaPA) in aqueous H_2SO_4 catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion. Typical oscillatory responses of a bromide-ion selective electrode are shown in Fig. 3a–p. The Ce(III)- or Mn(II)-catalyzed system may exhibit damped oscillations, which depend somewhat on the aging of NaPA in H_2SO_4 solution (Fig. 3a–c and d–f). The condition for the oscillations to occur is quite restricted. It was observed that the oscillation reaction took place with concomitant release of CO_2(g). In contrast, the $Fe(phen)_3^{2+}$-catalyzed $KBrO_3$-NaPA reaction may exhibit quite sustained oscillations, which take place without an induction period. The effects of N_2(g), NaPA, $KBrO_3$, $Fe(phen)_3^{2+}$ ion, and H_2SO_4 on the oscillating pattern are shown in Fig. 3 (h, i–j, k–l, m–n, and o–p).

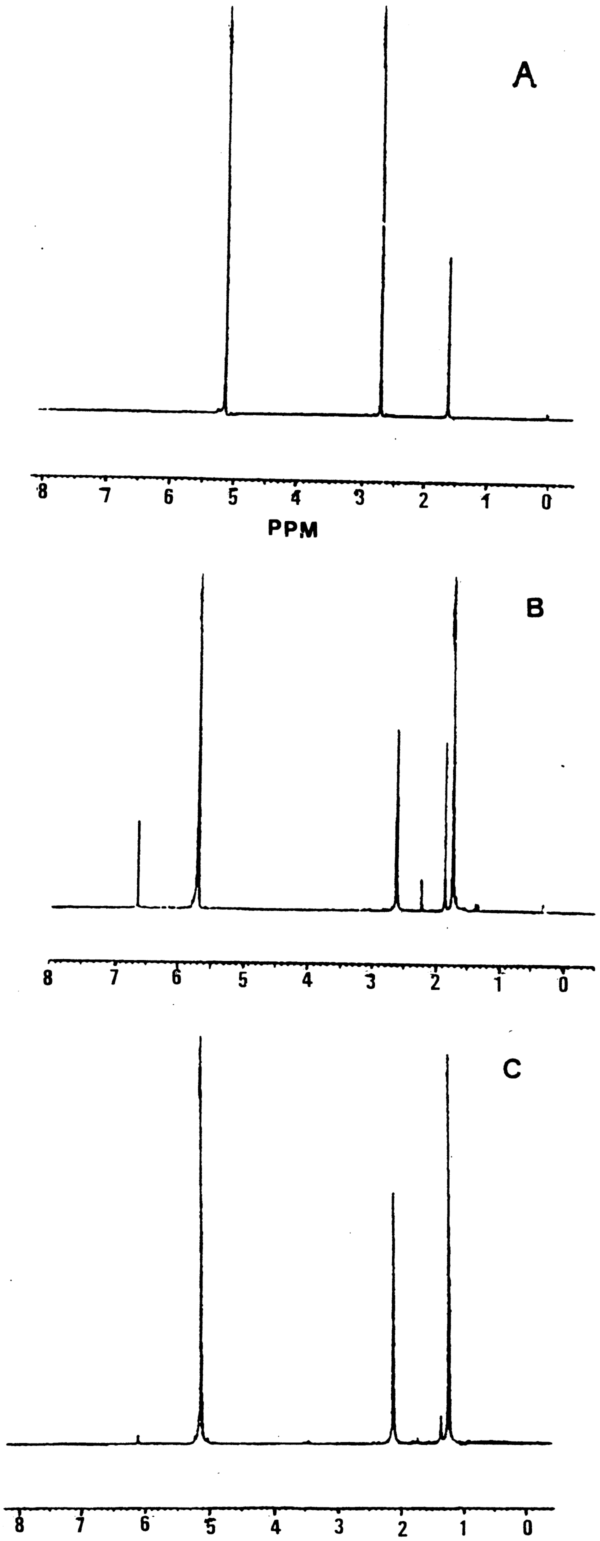

Figure 2 ^{1}H NMR spectrum of pyruvic acid in D_2O containing 1 M D_2SO_4. (a) NaPA; (b) PA (Ferak); (c) PA (Aldrich).

The BZ Reaction with Dimerized Pyruvic Acid

In contrast to the dimer-free NaPA system, the reaction of bromate ion with dimerized pyruvic acid (DPA2, Ferak) catalyzed by Ce(III) or Mn(II) ion may exhibit more sustained oscillations (Fig. 4a–i and Fig. 5a–g) and the condition for generating oscillations is less restricted. Similar to the NaPA system, the oscillation reaction occurred with concomitant release of CO_2(g) and the pattern of oscillations depends on the aging of DPA2 in H_2SO_4 solution (Fig. 4a–c and Fig. 5a–c). Interesting two-stage dual-frequency oscillations were observed (Fig. 4d–e, in the presence of BrPA or CH_3CHO, and Fig. 5d), due to the presence of different forms of pyruvic acid. The generation of HOAc during the BrO_3^--DPA2-Ce(III) or Mn(II) BZ reaction (Fig. 4a and Fig. 5a) was followed by using the ^{1}H NMR technique. The result indicates that the [HOAc]/[DPA2] ratio oscillates between 0.2 and 0.4 and between 0.04 and 0.06 for the Ce(III)- and Mn(II)-catalyzed systems, respectively. The effects of the concentrations of Ce(III) and Mn(II) ions are shown in Fig. 4a, f–i) and Fig. 5e–g). The reaction of bromate ion with dimerized pyruvic acid (DPA1, Aldrich) catalyzed by Fe(phen)$_3^{2+}$ or Ce(III) ion may also exhibit oscillations with the characteristics of the oscillation being between those of NaPA and DPA2 (Ferak) systems.

Kinetics and Mechanism

The kinetics of the Ce(IV)-NaPA, Mn(III)-NaPA, and Mn(III)-BrPA reactions in aqueous H_2SO_4 were studied by using a stopped-flow technique. A conventional spectrophotometric method was applied to study the kinetics of Fe(phen)$_3^{3+}$-NaPA, Ce(IV)-BrPA, and Fe(phen)$_3^{3+}$-BrPA reactions. For the Ce(IV)-NaPA, Mn(III)-NaPA, or Ce(IV)-BrPA reaction, the observed pseudo-first-order rate constant (k_{obs}) was calculated from the linear-least-square (LLS) fit of the plot of $\ln(A_t - A_\infty)$ vs time. For the Fe(phen)$_3^{3+}$-NaPA reaction, k_{obs} was obtained from the LLS fit of the plot of $\ln(A_{t+d} - A_t)$ vs time, where the time interval d is about half of the time needed to reach the maximum absorbance. Typical plots are shown in Fig. 6A. For the Mn(III)-NaPA reaction, the plot of k_{obs}^{-1} vs $[\text{NaPA}]_O^{-1}$ is linear (Fig. 6B), which suggests that k_{obs} can be expressed by $k_{\text{obs}} = k\,[\text{PA}]/(1 + K_m\,[\text{PA}])$ (Eq. (1), shown below). The values of k and K_m obtained at various temperatures for the Mn(III)-NaPA reaction are shown in Table I. For the Ce(IV)-NaPA, Ce(IV)-BrPA, Fe(phen)$_3^{3+}$-NaPA, and Fe(phen)$_3^{3+}$= BrPA

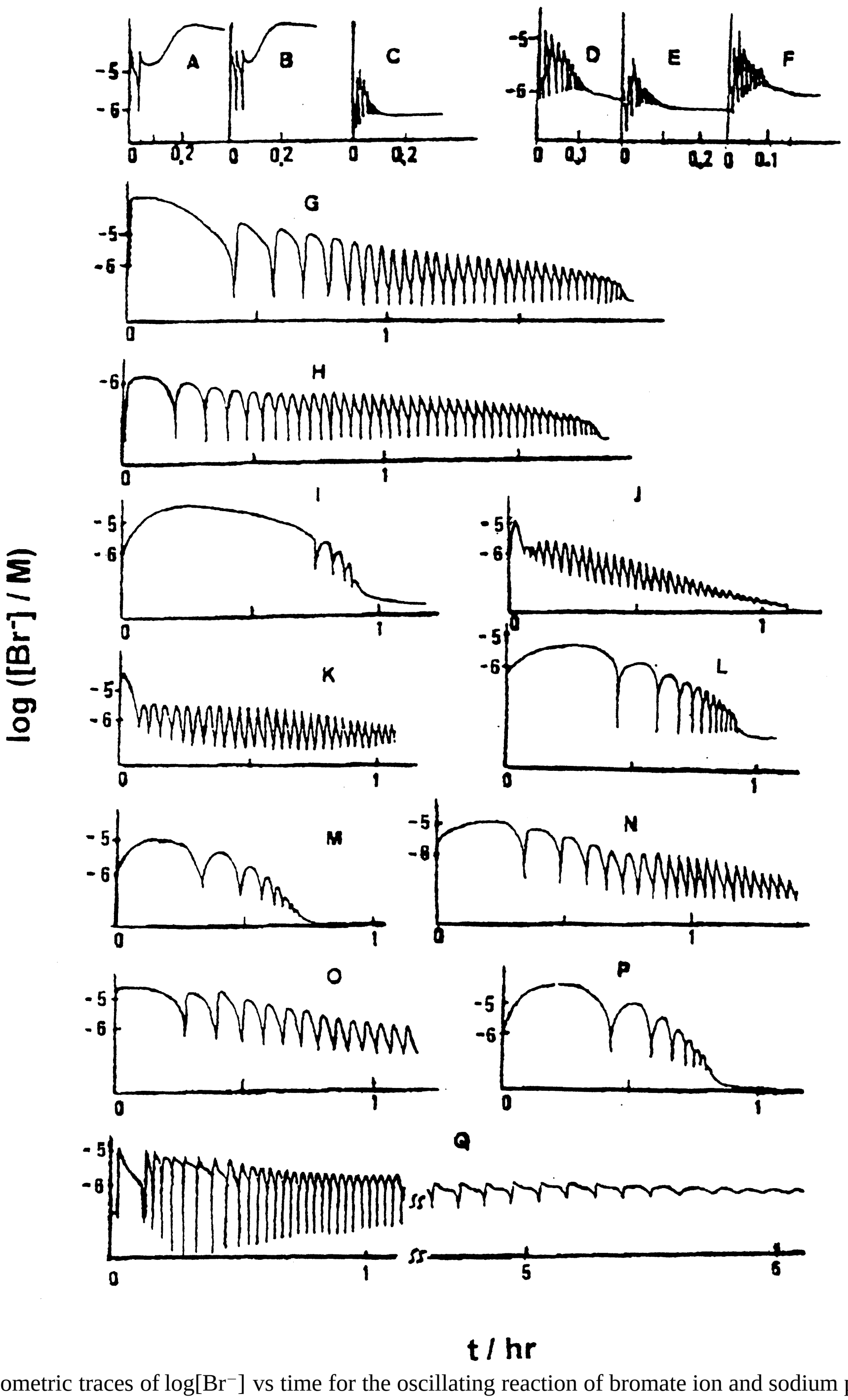

Figure 3 Potentiometric traces of log[Br⁻] vs time for the oscillating reaction of bromate ion and sodium pyruvate catalyzed by Ce(III), Mn(II), or $Fe(phen)_3^{2+}$ ion at 25°C under aerobic conditions except (h). (a, b, c): $[Ce(III)]_O = 1.00 \times 10^{-3}$ M, $[NaPA]_O = 0.300$ M, $[BrO_3^-]_O = 0.0300$ M, $[H_2SO_4]_O = 0.850$ M; (d, e, f): $[Mn(II)]_O = 1.00 \times 10^{-3}$ M, $[NaPA]_O = 0.300$ M, $[BrO_3^-]_O = 0.0300$ M, $[H_2SO_4]_O = 0.850$ M; (g, h): $[Fe(phen)_3^{2+}]_O = 2.00 \times 10^{-3}$ M, $[NaPA]_O = 0.300$ M, $[BrO_3^-]_O = 0.0500$ M, $[H_2SO_4]_O = 0.525$ M; (i, j): $[Fe(phen)_3^{2+}]_O = 2.00 \times 10^{-3}$ M, $[BrO_3^-]_O = 0.0500$ M, $[H_2SO_4]_O = 0.525$ M, $[NaPA]_O$ = (i) 0.200 M, (j) 0.350 M; (k, l): $[Fe(phen)_3^{2+}]_O = 2.00 \times 10^{-3}$ M, $[NaPA]_O = 0.300$ M, $[H_2SO_4]_O = 0.525$ M, $[BrO_3^+]_O$ = (k) 0.0400 M, (l) 0.0600 M; (m, n): $[NaPA]_O = 0.300$ M, $[BrO_3^-]_O = 0.0500$ M, $[H_2SO_4]_O = 0.525$ M, $Fe(phen)_3^{2+}]_O$ = (m) 1.00×10^{-3} M, (n) 3.00×10^{-3} M; (o, p) $[Fe(phen)_3^{2+}]_O = 2.00 \times 10^{-3}$ M, $[NaPA]_O = 0.300$ M, $[BrO_3^-]_O = 0.0500$ M, $[H_2SO_4]_O$ = (o) 0.500 M, (p) 0.600 M; (q): $[Fe(phen)_3^{2+}]_O = 2.00 \times 10^{-3}$ M, [PA (Aldrich)]$_O$ = 0.300 M, $[BrO_3^-]_O = 0.0800$ M, $[H_2SO_4]_O = 0.550$ M. (h): de-areated with N_2. The time (t_{mix}) for the aging of pyruvic acid solution before mixing the reactant solutions: (a, d) 2 min; (c, f) 30 min; (b, e, g–q) 15 min.

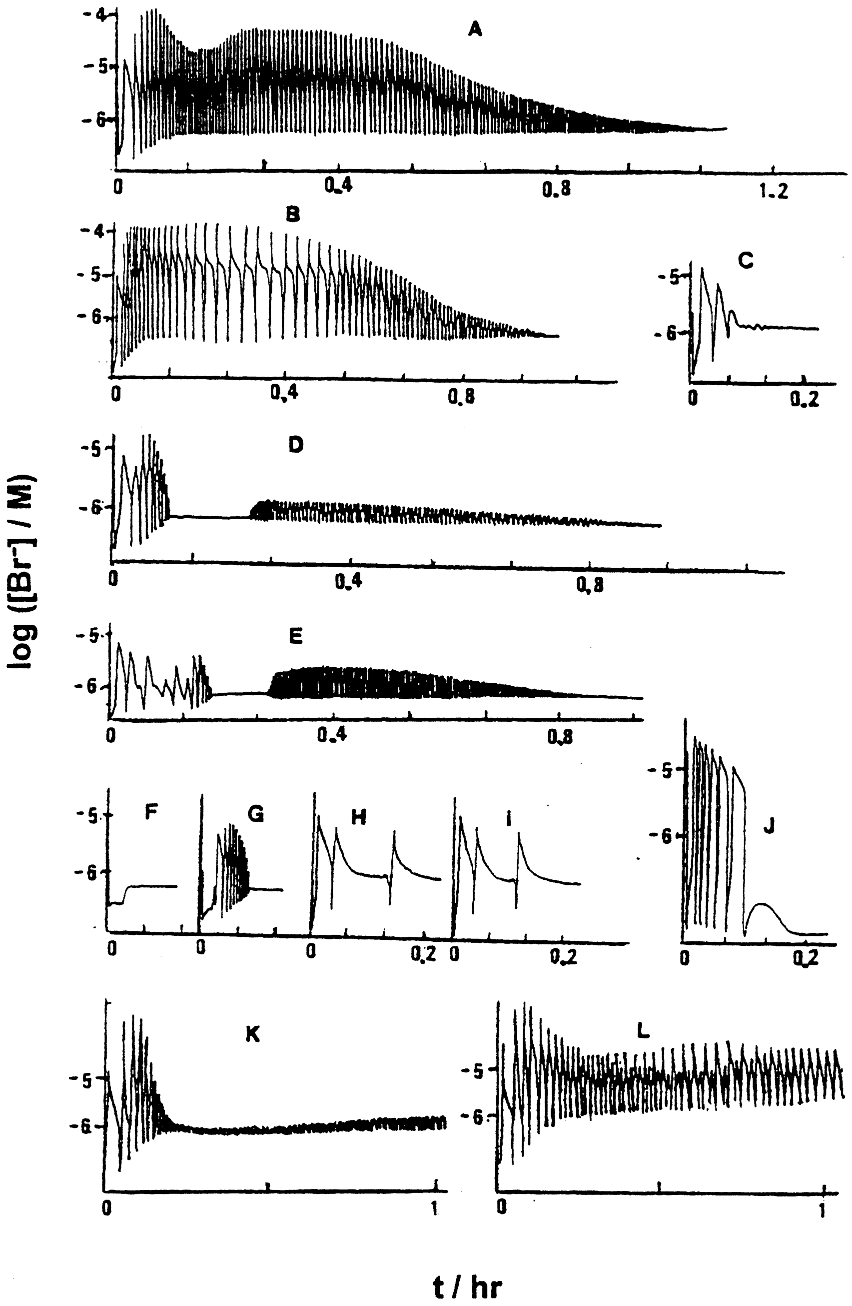

Figure 4 Potentiometric traces of log[Br$^-$] vs time for the oscillating reaction of bromate ion and dimerized pyruvic acid catalyzed by Ce(III) ion in 1 M H_2SO_4 at 25°C. $[Ce(III)]_O$ = (a–e, j, k, l) 3.00×10^{-3} M, (f) 1.20×10^{-3} M, (g) 1.90×10^{-3} M, (h) 0.0250 M, (i) 0.0813 M; $[BrO_3^-]_O$ = (a–i) 0.0670 M, (j) 0.100 M, (k, l) 0.0720 M; $[PA\ (Ferak)]_O$ = (a–i) 0.300 M, (j, k–l) 0 M; $[BrPA]_O$ = (d) 0.0150 M, (j) 0.100 M, (a–c, e–i, k–l) 0 M; $[PA\ (Aldrich)]_O$ = (k, l) 0.300 M, (a–j) 0 M; $[CH_3CHO]_O$ = (e) 0.0100 M, (a–d, f–l) 0 M; t_{mix} = (a, d–l) 15 min, (b) 75 min, (c) 2 min.

reactions, the plots of k_{obs} vs $[PA]_O$ or $[BrPA]_O$ are linear (Fig. 6C–F), which indicates that these reactions follow a second-order kinetics. The values of the second-order rate constant (k) obtained at various temperatures for these reactions are given in Table I. The following mechanistic steps (M0–M6) are proposed to rationalize the kinetic results of the oxidation reactions of PA:

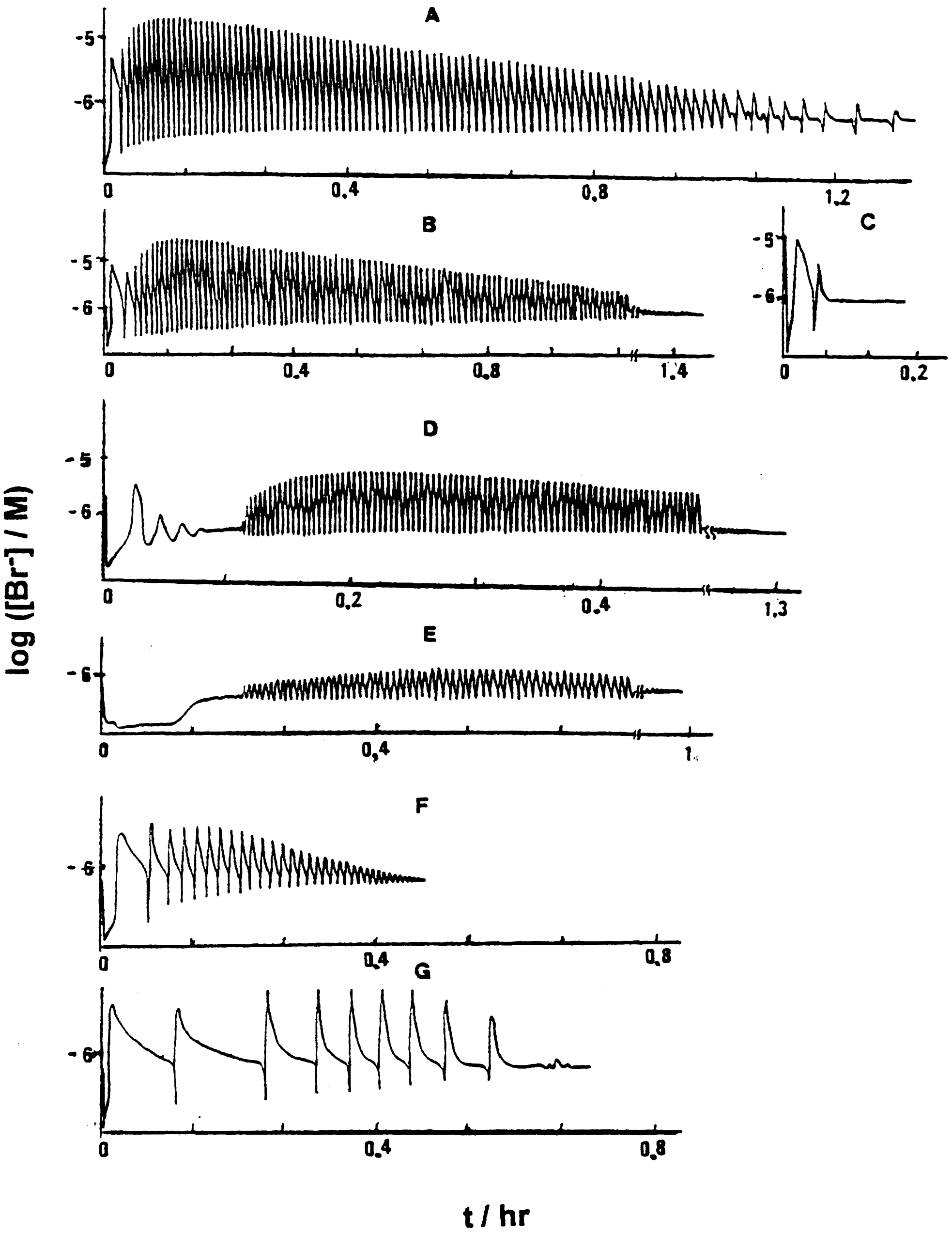

Figure 5 Potentiometric traces of log[Br$^-$] vs. time for the oscillating reaction of bromate ion and dimerized pyruvic acid catalyzed by Mn(II) ion in 1 M H_2SO_4 at 25°C. $[Mn(II)]_O$ = (a–c) 5.00 × 10^{-3} M, (d, f) 1.20 × 10^{-3} M, (e) 1.20 × 10^{-4} M, (g) 0.101 M; $[BrO_3^-]_O$ = (a–c) 0.0670 M, (d) 0.0820 M, (e–g) 0.0300 M; $[PA\ (Ferak)]_O$ = (a–c) 0.300 M, (d) 0.450 M, (e–g) 0.0600 M; t_{mix} = (a, d–g) 15 min, (b) 75 min, (c) 2 min.

$$CH_3COCO_2H + H_2O \rightleftharpoons CH_3C(OH)_2CO_2H \qquad K \qquad (M0)$$

$$M^{(n+1)+} + CH_3COCO_2H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M^{(n+1)+}\ CH_3COCO_2H] \qquad (M1)$$

$$M^{(n+1)+} + CH_3C(OH)_2CO_2H \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [M^{(n+1)+}\ CH_3C(OH)_2CO_2H] \qquad (M2)$$

$$[M^{(n+1)+} + CH_3COCO_2H] \xrightarrow{k_1'} M^{n+} + CH_3\dot{C}O + CO_2 + H^+ \qquad (M3)$$

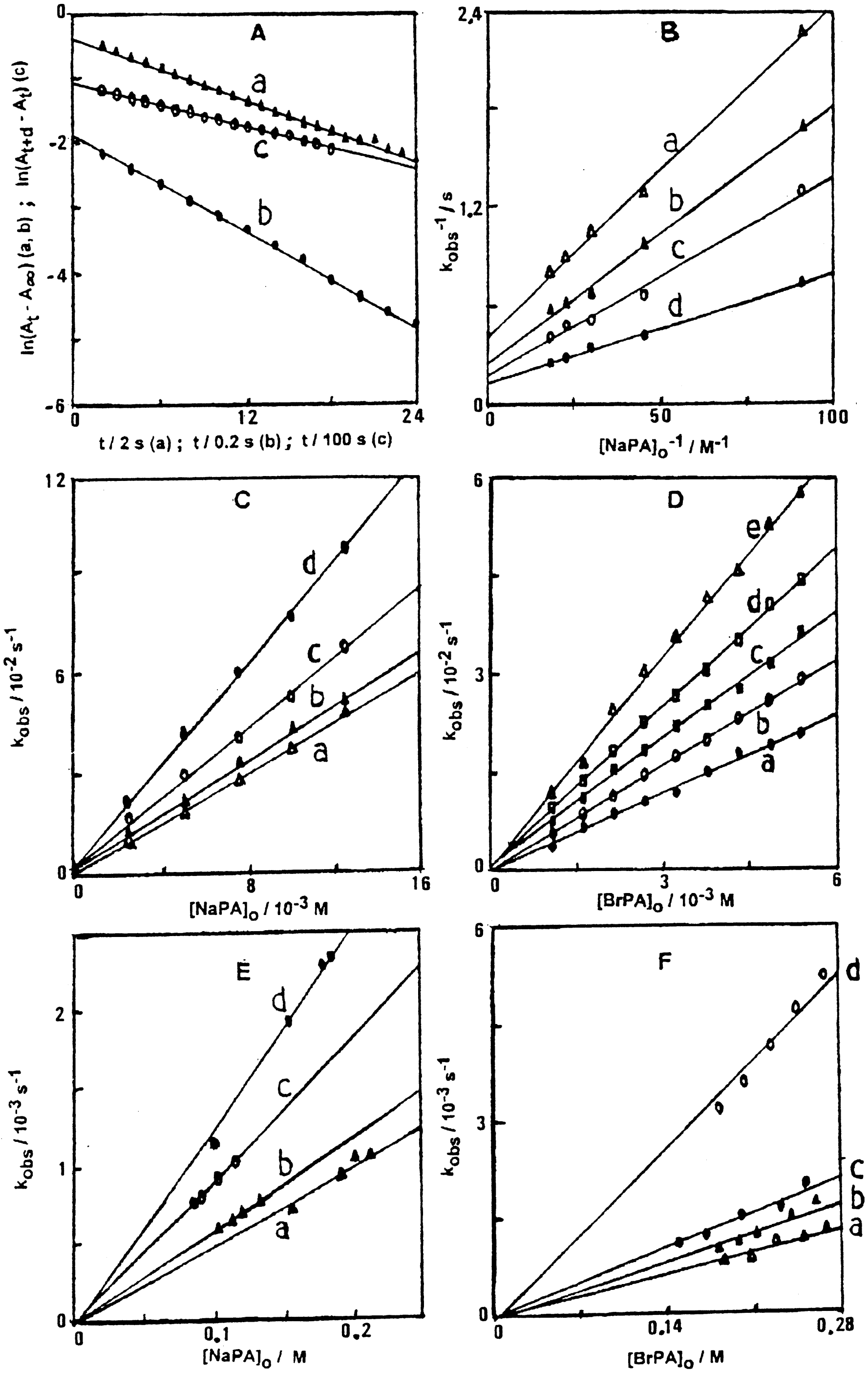

Figure 6 (A) Plots of $\ln(A_t - A_\infty)$ (a, b) or $\ln(A_{t+d} - A_t)$ (c) vs time for Ce(IV)-NaPA (a), Mn(III)-NaPA (b), and $\mathrm{Fe(phen)_3^{3+}}$-NaPA (c) reactions in 1 M H_2SO_4 and at 25°C. (a) $[\mathrm{Ce(IV)}]_O = 2.5 \times 10^{-4}$ M, $[\mathrm{NaPA}]_O = 0.0100$ M, 360 nm; (b) $[\mathrm{Mn(III)}]_O = 1.10 \times 10^{-3}$ M, $[\mathrm{NaPA}]_O = 0.0110$ M, 480 nm; (c) $[\mathrm{Fe(phen)_3^{3+}}]_O = 1.00 \times 10^{-4}$ M, $[\mathrm{NaPA}]_O = 0.101$ M, 480 nm, de-aerated with N_2. (B) Plots of k_{obs}^{-1} vs $[\mathrm{NaPA}]_O^{-1}$ for the Mn(III)-NaPA reaction. (C–F) Plots of k_{obs} vs $[\mathrm{NaPA}]_O$ for the Ce(IV)-NaPA reaction (C), the Ce(IV)-BrPA reaction (D), the $\mathrm{Fe(phen)_3^{3+}}$-NaPA reaction (E), and $\mathrm{Fe(phen)_3^{3+}}$-BrPA reaction (F).

(B, C): (a) 22°C, (b) 25°C, (c) 28°C, (d) 32°C;

(D): (a) 15°C, (b) 18°C, (c) 20°C, (d) 22°C, (e) 25°C;

(E): (a) 22°C, (b) 25°C, (c) 28°C, (d) 30°C;

(F): (a) 19°C, (b) 22°C, (c) 25°C, (d) 30°C.

Table I Rate Constants and Apparent Activation Energies of the Reactions of Pyruvic Acid and 3-Bromopyruvic acid with Ce(IV), Mn(III), and $Fe(phen)_3^{3+}$ Ions

Ce(IV)-PA reaction		Ce(IV)-BrPA reaction	
T/°C	k/M^{-1} s^{-1}	T/°C	k/M^{-1} s^{-1}
22	3.79	15	3.88
25	4.11	18	5.28
28	5.29	20	6.39
32	7.75	22	8.08
		25	10.7
E_a/kJ mol^{-1}	55.1 ± 8.7		72.1 ± 1.3

$Fe(phen)_3^{3+}$-PA reaction		$Fe(phen)_3^{3+}$-BrPA reaction	
T/°C	k/M^{-1} s^{-1}	T/°C	k/M^{-1} s^{-1}
22	4.99	19	4.62
25	5.85	22	6.22
28	9.10	25	7.55
30	12.8	30	19.1
E_a/kJ mol^{-1}	88.5 ± 14		72.3 ± 0.8

Mn(III)-PA reaction			Mn(III)-BrPA reaction	
T/°C	k/M^{-1} s^{-1}	K_m/M^{-1}	T/°C	k_1'/s^{-1}
22	49.4	20.1	22	0.478
25	63.4	15.6	25	0.683
28	83.2	14.4	27	0.818
32	150	19.6	30	1.08
E_a/kJ mol^{-1}	82.7 ± 9.3			75.1 ± 3.3

$$[M^{(n+1)+} + CH_3C(OH)_2CO_2H] \xrightarrow{k_2'} M^{n+} + CH_3\dot{C}(OH)_2 + CO_2 + H^+ \quad (M4)$$

$$M^{(n+1)+} + CH_3\dot{C}O + H_2O \longrightarrow M^{n+} + CH_3CO_2H + H^+ \quad (M5)$$

$$M^{(n+1)+} + CH_3\dot{C}(OH)_2 \longrightarrow M^{n+} + CH_3CO_2H + H^+ \quad (M6)$$

$$(M^{(n+1)+} = \text{Ce(IV), Mn(III), or } Fe(phen)_3^{3+})$$

This mechanism is consistent with the stoichiometric equation (S1) for the Ce(IV)-PA reaction. If initially $[PA]_O \gg [M^{(n+1)+}]_O$, the rate law (Eq. (1)) can be derived by applying the steady-state approximation to two metal-substrate complexes.

$$\begin{aligned} -d[M^{(n+1)+}]/dt &= \frac{((k_1' K_{m1} + k_2' K K_{m2})/(1+K))\,[PA]_t}{1 + ((K_{m1} + K K_{m2})/(1+K))\,[PA]_t}[M^{(n+1)+}]_t \\ &= (k\,[PA]_t/(1 + K_m\,[PA]_t))\,[M^{(n+1)+}]_t \\ &= k_{obs}\,[M^{(n+1)+}]_t \qquad (1) \end{aligned}$$

In Eq. (1), $[M^{(n+1)+}]_t$ is the total concentration of $M^{(n+1)+}$ species, $[PA]_t = [CH_3COCO_2H] + [CH_3C(OH)_2CO_2H]$, $K_{m1} = k_1/(k_{-1} + k_1')$, $K_{m2} = k_2/(k_{-2} + k_2')$, $k = (k_1'K_{m1} + k_2'K\,K_{m2})/(1 + K)$, $K_m = (K_{m1} + K\,K_{m2})/(1 + K)$, $K = [CH_3C(OH)_2CO_2H]/[CH_3COCO_2H]$, and $k_{obs} = k\,[PA]_t/(1 + K_m\,[PA]_t)$. This rate equation is similar to the Michaelis-Menten-like kinetics as suggested by Kasperek and Bruice [21]. The kinetics of the Mn(III)-NaPA reaction is consistent with rate equation of Eq. (1). At sufficiently low [PA] ($K_m\,[PA]_t \ll 1$), k_{obs} reduces to $k_{obs} = k\,[PA]_t$ and a second-order kinetics is obtained as observed in the Ce(IV)-NaPA and $Fe(phen)_3^{3+}$-NaPA reactions. As reported by Zuman et al. [22], the pH-independent rate constants of the solvent-catalyzed hydration and dehydration at 25°C are 0.27 s^{-1} and 0.092 s^{-1}, respectively. The equilibrium of step (M0) can be maintained under the present reaction conditions, since $[PA]_O \gg [M^{(n+1)+}]_O$.

Since the diol form of BrPA is negligible, the mechanism of the oxidation reactions of BrPA consists of steps similar to (M1), (M3), and (M5), which is consistent with the stoichiometric equation (S2) for the Ce(IV)-BrPA reaction. The derived rate law is shown in Eq. (2), where $k_{obs} = k_1'\ K_{m1}\ [BrPA]/(1 + K_{m1}\ [BrPA])$.

$$\begin{aligned} -d[M^{(n+1)+}]/dt &= (k_1'\ K_{m1}\ [BrPA]/(1 + K_{m1}\ [BrPA]))\ [M^{(n+1)+}]_t \\ &= k_{obs}\ [M^{(n+1)+}]_t \qquad (2) \end{aligned}$$

At sufficiently low [BrPA] (K_{m1} [BrPA] $\ll 1$), k_{obs} reduces to $k_{obs} = k$[BrPA] ($k = k_1'\ K_{m1}$) and a second-order kinetics is obtained, as observed in the Ce(IV)-BrPA and $Fe(phen)_3^{3+}$-BrPA reactions. However, the values of (k_{obs}/s^{-1}) of the Mn(III)-BrPA reaction are (0.474, 0.476, 0.478, 0.478, and 0.485) at 22°C; (0.689, 0.685, 0.681, 0.682, and 0.679) at 25°C; (0.811, 0.822, 0.822, 0.818, —) at 27°C; and (1.08, 1.08, 1.07, 1.09, —) at 30°C for $[BrPA]_O$ = (2.20, 4.41, 6.60, 8.79, and 11.0) × 10^{-2} M, respectively. It is interesting to observe that for this reaction the value of k_{obs} is independent of the concentration of BrPA. This result can be rationalized by invoking Eq. (2). At sufficiently high [BrPA] (K_{m1} [BrPA] $\gg 1$), k_{obs} becomes k_1'. The values of k_1' at various temperatures are given in Table I. The apparent activation energies obtained from the LLS fits of the Arrhenius plots of the preceding reactions are also shown in Table I.

The stopped-flow technique is applied to study the kinetics of the reactions of the dimerized pyruvic acid (DPA1 and DPA2) with Ce(IV) and Mn(III) ions, whereas the conventional spectrophotometric method is used for the reaction of DPA1 and DPA2 with

$Fe(phen)_3^{3+}$ ion. It was observed that the kinetics of these reactions were complicated by the compositions of the solutions of DPA1 and DPA2. However, a definite conclusion can be deduced from parallel experiments. The results indicate that the order of relative reactivity of pyruvic acids toward reaction with Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion is DPA2 > DPA1 > BrPA > PA and that of metal ions toward reaction with these pyruvic acids is Mn(III) > Ce(IV) > $Fe(phen)_3^{3+}$. These reactions are facilitated by the complex formation of metal-ion oxidant and pyruvic acids. As suggested by Leussing et al. [15], the predominant mode of chelation involves the hydroxyl and carbonyl groups attached to the asymmetric carbon of pyruvic acid.

Bromination Reactions of Pyruvic and Bromopyruvic Acids

The kinetics of the bromination reactions of PA and BrPA was studied by following $[Br_2]$ spectrophotometrically at 400 nm ($\varepsilon = 167\ M^{-1}\ cm^{-1}$) with PA and BrPA in great excess. It was found that these reactions are zero-order with respect to bromine ($(1.2-7.2) \times 10^{-4}$ M) and first-order with respect to PA or BrPA. This result is consistent with the well-known observation that halogenation of acetone in aqueous solution is zero-order with respect to halogen and the enolization of acetone is the rate-determining step when the concentration of halogen is sufficiently high [23–25]. The values of the first-order rate constant (k_{en}) of the bromination or enolization reaction of PA in 1 M H_2SO_4 are (1.55 ± 0.07, 2.55 ± 0.17, 3.10 ± 0.10, and 4.11 ± 0.21) $\times 10^{-6}\ s^{-1}$ at 22, 25, 28, and 31°C, respectively. The value of k_{en} is consistent with that reported by Burgner et al. (about $4 \times 10^{-6}\ s^{-1}$) [19]. The values of k_{en} of BrPA in 1 M H_2SO_4 are (0.70 ± 0.03, 1.02 ± 0.02, 1.46 ± 0.02, and 1.71 ± 0.05) $\times 10^{-5}\ s^{-1}$ at 20, 23, 25, and 27°C, respectively. The kinetics of the bromination reaction of BrPA was also studied by following the production of bromide ion potentiometrically. It was found that the rate of the bromide ion production is also zero-order with respect to bromine and is first-order with respect to BrPA. The value of k_{en} at 25°C is $(1.78 \pm 0.13) \times 10^{-5}\ s^{-1}$, which is consistent with that of $1.46 \times 10^{-5}\ s^{-1}$ of the spectrophotometric method mentioned above. The activation energies obtained from the LLS fits of the Arrhenius plots of k_{en} are 77 ± 11 and 89.4 ± 9.6 kJ/mol for the enolization reactions of PA and BrPA, respectively. The activation parameters ($\Delta H\neq$ and $\Delta S\neq$) obtained from the LLS fits of the Eyring plots are 75.3 ± 10.6 kJ/mol, -100 ± 35 J/(mol K) and 90.1 ± 8.2 kJ/mol, -35.8 ± 27.6 J/(mol K) for the enolization reactions of PA and BrPA, respectively. The negative value of $\Delta S\neq$ can be rationalized by invoking the solvent reorganization due to the more ionic transition state of the enolization reaction. The bromination reaction of PA produces BrPA first and then Br_2PA (Br_2CHCO-COOH). No significant amount of Br_3PA (CBr_3 COCOOH) was observed. When a sufficient amount of bromine is present, $Br_2CHCOOH$ is also produced. A similar result was observed for the bromination reaction of BrPA. A parallel study indicates that the rate of the bromination reaction of the dimerized pyruvic acid (DPA1 and DPA2) is considerably faster than that of PA, consistent with the result mentioned before that DPA2 and DPA1 are much more reactive than PA toward reaction with Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion.

Implication

According to a classification by Noyes [26], the “classical” BZ reaction is a metal-ion catalyzed oxidation and bromination of an organic substrate by acidic bromate. In the prototype BZ reaction, malonic acid is reactive toward oxidation by the oxidized form of the metal-ion catalyst and also reactive toward bromination. The brominated product of malonic acid, bromomalonic acid, is capable of reacting with the metal-ion catalyst and liberating the bromide ion. In this work, we demonstrate that the BZ system of the dimerized pyruvic acids exhibits more sustained oscillations than that of the pyruvic acid monomer. This observation can be rationalized by invoking that the dimerized pyruvic acids are more reactive toward bromination or oxidation by Ce(IV), Mn(III), or $Fe(phen)_3^{3+}$ ion, as mentioned earlier. The higher reactivity of dimerized pyruvic acids also supports that parapyruvate blocks the citric acid cycle by specifically inhibiting the oxidative decarboxylation of α-ketoglutarate to succinate [27–28]. Similar to the BZ reactions of malonic acids [7,9–10], $Fe(phen)_3^{2+}$ ion behaves differently from Ce(III) or Mn(II) ion as a catalyst for the BZ reactions of pyruvic acids. This result can be rationalized by invoking the different reactivity of $Fe(phen)_3^{3+/2+}$ couple from Ce(IV)/Ce(III) or Mn(III)/Mn(II) couple toward reaction with pyruvic acids and with bromine species (BrO_3^-, $HBrO_2$, $BrO_2\cdot$, HOBr, and Br_2) [29].

SUMMARY

In a stirred batch experiment, the reaction of bromate ion with pyruvic acid monomer (PA) or dimer (DPA) catalyzed by Ce(III), Mn(II), or Fe(phen)$_3^{2+}$ ion in aqueous H_2SO_4 exhibits damped oscillations. Both the open-chain (DPA1) and the cyclic-form (DPA2) dimers show more sustained oscillations than PA monomer. The characteristics of the oscillations depend on the concentrations of organic substrate, bromate ion, metal-ion catalyst, and sulfuric acid. Fe(phen)$_3^{2+}$ ion behaves differently from Ce(III) and Mn(II) ions in catalyzing these oscillating reactions. The results of the kinetic study indicate that the order of relative reactivity of pyruvic acids toward reaction with Ce(IV), Mn(III), or Fe(phen)$_3^{3+}$ ion is DPA2 $>$ DPA1 $>$ 3-bromopyruvic acid (BrPA) $>$ PA and that of metal ions toward reaction with pyruvic acids in Mn(III) $>$ Ce(IV) $>$ Fe(phen)$_3^{3+}$. The rates of bromination reactions of pyruvic acids are independent of the concentration of bromine and the order of reactivity toward bromination is (DPA1, DPA2) $>$ BrPA $>$ PA.

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