Kinetic Study of the Ce(III)-, Mn(II)- or Fe(phen)₃²⁺-Catalyzed Belousov-Zhabotinsky Reaction with 2-Ketoglutaric Acid

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ABSTRACT: The Belousov-Zhabotinsky (BZ) reaction of bromate ion with 2-ketoglutaric acid (KGA) in aqueous sulfuric acid catalyzed by Ce(III), Mn(II), or Fe(phen)₃²⁺ ion exhibits sustained barely damped oscillations under aerobic conditions. In general, the reaction oscillates without an induction period. Fe(phen)₃²⁺ ion behaves differently from Ce(III) and Mn(II) ions in catalyzing this oscillating system. The gem-diol form of KGA exhibits different behavior from that of the keto form of KGA in the BZ reaction. The kinetics and mechanism of the reaction of KGA with Ce(IV), Mn(III), or Fe(phen)₃³⁺ ion was investigated. The order of relative reactivities of metal ions toward reaction with KGA is Mn(III) > Ce(IV) \gg Fe(phen)₃³⁺. Experimental results are rationalized. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 101–107, 2001

INTRODUCTION

It is well known that the catabolic pathways converge in stage III toward the Krebs citric acid cycle (tricarboxylic acid cycle) where most energy-yielding nutrients are ultimately oxidized to carbon dioxide. 2-Ketoglutaric acid is an important metabolite in the Krebs cycle and is a substrate (or product) of several enzymatic reactions. In the Krebs cycle, isocitrate is dehydrogenated to 2-ketoglutarate and CO₂ by NAD- or NADP-linked isocitrate dehydrogenase, which requires Mg(II) or Mn(II) ion. In the next step, 2-ketoglutarate undergoes oxidative decarboxylation re-

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action catalyzed by 2-ketoglutarate dehydrogenase complex to form succinyl-CoA and CO₂. In 1950, Belousov [1] studied the model catalysis in the Krebs cycle using cerium ion instead of the protein-bound metal ions and discovered the cerium-ion-catalyzed bromate ion-citric acid or malonic acid oscillation reaction. Similar oscillations were observed by Zhabotinsky [2] when the malonic acid was replaced by another organic substrate with an active methylene hydrogen atom or when the Ce(IV)/Ce(III) couple was replaced by the Mn(III)/Mn(II) couple or by the $Fe(phen)_{3}^{3+/2+}$ couple. The Belousov-Zhabotinsky (BZ) reaction has attracted much attention and has been studied most thoroughly. The first detailed mechanism of the Ce(III)-catalyzed BZ reaction with malonic acid was elucidated by Field, Körös, and Noves (FKN) [3]. Györgyi, Turányi, and Field (GTF) presented a detailed mechanism of the complete organic and inorganic chemistry of the BZ reaction with ma-

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lonic acid, which is strongly supported by the modeling computations [4]. In previous articles, we studied the BZ reactions with saccharides, mixed organic acid/ ketone substrate, and malonic acid and its derivatives (methyl-, ethyl-, butyl-, phenyl-, and dibromomalonic acids) catalyzed by Ce(III), Mn(II), or Fe(phen)₃²⁺ ion [5–10]. In this article, we demonstrate that the Ce(III)-, Mn(II)-, or Fe(phen)₃²⁺-catalyzed bromate ion-2ketoglutaric acid reaction in aqueous sulfuric acid exhibits oscillations in bromide ion concentration. The kinetics and mechanism of the reactions of 2-ketoglutaric acid with Ce(IV), Mn(III), and Fe(phen)₃³⁺ ion are investigated. The experimental results are rationalized.

EXPERIMENTAL

Materials

2- or α -Ketoglutaric acid (KGA, Lancaster), 2-ketoglutaric acid monosodium salt (NaKGA, Sigma), 2ketoglutaric acid disodium salt (Na₂KGA, Sigma), ammonium ceric nitrate (Hanawa), cerium(III) nitrate hexahydrate (Riedel de Haën), manganese(II) acetate tetrahydrate (Merck), ammonium ferrous sulfate (Merck), and 1, 10-phenanthroline (Ishizu) were used in this work. Other reagents used were of the highest grade chemicals commercially available. Solutions of ferroin (Fe(phen)₃²⁺) and ferriin (Fe(phen)₃³⁺) ions were freshly prepared as described elsewhere [7,11,12]. Deionized water from reverse osmosis (Millipore Milli-RO 20) was used.

Procedures

Kinetic Experiment. The potentiometric traces of the BZ reaction were recorded by following the reaction with a bromide ion selective electrode (Orion 94-35) against a double junction reference electrode (Orion 90-02) [13]. The kinetics of the oxidation reactions of 2-ketoglutaric acid (KGA) by Ce(IV), Mn(III), and Fe(phen)₃³⁺ ions were studied spectrophotometrically by following [Ce(IV)], [Mn(III)], and [Fe(phen)₃³⁺] at 360 nm ($\epsilon = 3.18 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 310 nm ($\epsilon =$ $1.31 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), and 500 nm (= 1.10×10^4 M^{-1} cm⁻¹), respectively, with either a stopped-flow spectrophotometer (Photol RA-401) or a conventional spectrophotometer (Hitachi U-2000). The pseudofirst-order rate constant (k_{obs}) was calculated from the linear least-squares (LLS) fit of the plot of $\ln(A_t - A_{\infty})$ vs. time for the Ce(IV)- and Mn(III)-KGA reactions or from the plot of $\ln(A_{t+d} - A_t)$ vs. time for the $Fe(phen)_{3^{3+}}$ -KGA reaction, where the time interval d is about half of the time needed to reach the maximum absorbance.

NMR Spectra. The 1H NMR spectra of KGA, NaKGA, and Na₂KGA obtained using a Bruker AC-200 FT-NMR is shown in Figure 1. The spectrum of KGA in acetone-d₆ shows a slightly distorted A₂B₂ multiplet for the β -CH₂-group (3.11–3.18 ppm) and the γ -CH₂-group (2.58–2.68 ppm) of the nonhydrated keto-KGA (Fig. 1A). The spectrum of KGA in D₂O and D₂O containing 1 M D₂SO₄ shows both the considerably distorted A₂B₂ multiplet of the nonhydrated keto-KGA and the cyclic-KGA (lactol) (a broad peak at 2.97 ppm for β -CH₂-group and a multiplet at 2.62– 2.69 ppm for γ -CH₂-group) and the undistorted A₂B₂ multiplet of the hydrated gem-diol-KGA (2.05-2.12 ppm for β -CH₂-group and 2.37–2.45 ppm for γ -CH₂group) (Fig. 1, B-D). These results are consistent with those reported by Redfield et al. [14]. The multiplet for the β -CH₂-group (2.93–2.99 ppm) in the spectrum of NaKGA in D₂O shows significant distortion and lack of detail in contrast to that for the γ -CH₂-group (2.62-2.69 ppm) (Fig. 1E). Similar to the spectrum of KGA in acetone- d_6 (Fig. 1A), the spectrum of Na₂KGA in D₂O shows a slightly distorted A₂B₂ multiplet of the nonhydrated keto-KGA (2.89-3.10 ppm for the β -CH₂-group and 2.38–2.50 ppm for the γ -CH₂-group) (Fig. 1F).



Figure 1 ¹H NMR spectra. (A) KGA in acetone- d_6 ; (B) KGA in D₂O; (C) KGA in 1 M D₂SO₄/D₂O (<30 min); (D) KGA in 1 M D₂SO₄/D₂O (3h); (E) NaKGA in D₂O; (F) Na₂KGA in D₂O.

RESULTS AND DISCUSSION

The BZ Reaction with 2-Ketoglutaric Acid

Under stirred aerobic conditions, the reaction of bromate ion with 2-ketoglutaric acid (KGA) in aqueous sulfuric acid catalyzed by Ce(III), Mn(II), or Fe(phen)₃²⁺ ion exhibits sustained barely damped oscillations in bromide ion concentration. Typical oscillatory responses of the bromide ion selective electrode are shown in Figure 2 (A–C). In general, the reaction oscillates without an induction period. The frequency of oscillations follows the sequence of Mn(II) system > Ce(III) system > Fe(phen)₃²⁺ system. Figures 2D-F show the oscillatory patterns under anaerobic conditions (deaerated with N2). For the Mn(II)or Ce(III)-catalyzed system, the oscillating reaction is catalyzed by the presence of oxygen molecules, and the oscillatory behavior depends on the degree of deaeration of the solution with nitrogen gas (Figs. 2E and 2F). In contrast, under anaerobic conditions the Fe(phen)₃²⁺-catalyzed system exhibits a higher frequency of oscillations (Fig. 2D). The concentration of sulfuric acid, which is 0.6-1.2 M for the Ce-(III)- and Mn(II)-catalyzed systems and 0.3-0.6 M for the Fe(phen)₃²⁺-catalyzed system, also plays an important role in generating the oscillations. As shown in Figures 2G and 2H, the Ce(III)-catalyzed system using NaKGA or Na2KGA initially instead of KGA exhibits an oscillating pattern quite similar to that of the KGA system except that it exhibits an induction period and a smaller amplitude of oscillations during the initial stage of reaction.

Kinetics and Mechanism

The stopped-flow technique was applied to study the kinetics of the Mn(III)-KGA reaction. The kinetics of the Ce(IV)-KGA and Fe(phen)₃³⁺-KGA reactions were studied by using a conventional spectrophotometric method. Typical plots of $\ln(A_t - A_{\infty})$ or $\ln(A_{t+d} - A_t)$ vs. time are shown in Figure 3. For the Ce(IV)-KGA reaction, the value of the observed pseudo-first-order rate constant (k_{obs}) measured under aerobic conditions is not significantly different from that measured under deaerated conditions. Under similar reaction conditions, no significant effect on the value of k_{obs} is observed if using NaKGA or Na₂KGA initially instead of KGA. The kinetics of the Fe(phen)₃³⁺-KGA reaction was studied under deaerated conditions since it was observed that oxygen molecules exhibited an inhibitory effect on the reaction rate. For both the Ce(IV)-KGA and Mn(III)-KGA reactions, the plot of k_{obs} vs. [KGA]₀ is linear, which

indicates that these reactions follow a second-order kinetics (Figs. 4 and 5). The values of the second-order rate constant ($k' = k_{obs}/[KGA]_0$) obtained at various temperatures are shown in Table I. For the Mn(III)-KGA reaction, the plot of k_{obs}^{-1} vs. [KGA]₀⁻¹ is linear (Fig. 6). As shown below (Eq.(1)), k_{obs} can be expressed as $k_{obs} = k[KGA]_t / (1 + K_m[KGA]_t)$. The values of k and $K_{\rm m}$ obtained from the LLS fits of the plot of k_{obs}^{-1} vs. [KGA]₀⁻¹ at various temperatures are given in Table I. The apparent activation energies calculated from the LLS fits of the Arrhenius plots are also given in Table I. The order of relative reactivities of metal ions toward reaction with KGA is $Mn(III) > Ce(IV) \gg Fe(phen)_3^{3+}$. The mechanism proposed to explain these kinetic results is shown in Scheme I. If initially $[KGA]_0 \gg [M^{(n+1)+}]_0$, the rate law (Eq. (1)) can be derived by applying the steadystate approximation to three metal-ion complexes.

$$k-KGA + H_2O \xleftarrow{k_1}_{k_{-1}} d-KGA \qquad K_1 \qquad (M1)$$

$$c-KGA + H_2O \Longrightarrow k-KGA \qquad K_2 \qquad (M2)$$

$$\mathbf{M}^{(n+1)+} + \mathbf{k} \cdot \mathbf{KGA} \xleftarrow{k_3}_{k_{-3}} [\mathbf{M}^{(n+1)+} \mathbf{k} \cdot \mathbf{KGA}] \quad (\mathbf{M3})$$

$$\mathbf{M}^{(n+1)+} + \mathbf{d} \cdot \mathbf{KGA} \xleftarrow{k_4} [\mathbf{M}^{(n+1)+} d \cdot \mathbf{KGA}] \quad (\mathbf{M4})$$

$$\mathbf{M}^{(n+1)+} + \mathbf{c} \cdot \mathbf{KGA} \underbrace{\overset{k_{5}}{\underset{k_{-5}}{\longrightarrow}}} [\mathbf{M}^{(n+1)+} \ \mathbf{c} \cdot \mathbf{KGA}] \quad (\mathbf{M5})$$

$$[\mathbf{M}^{(n+1)+} \text{ k-KGA}] \xrightarrow{k_{3}'} \mathbf{M}^{n+} + \mathbf{R1} + \mathbf{CO}_{2} + \mathbf{H}^{+} \quad (\mathbf{M6})$$

$$[\mathbf{M}^{(n+1)+} \text{ d-KGA}] \xrightarrow{k_4'} \mathbf{M}^{n+} + \mathbf{R2} + \mathbf{CO}_2 + \mathbf{H}^+ \quad (\mathbf{M7})$$

$$[\mathbf{M}^{(n+1)+} \text{ c-KGA}] \xrightarrow{k_{3}'} \mathbf{M}^{n+} + \mathbf{R3} + \mathbf{CO}_{2} + \mathbf{H}^{+} \quad (\mathbf{M8})$$

$$\mathbf{M}^{(n+1)+} + \mathbf{R}\mathbf{1} + \mathbf{H}_2\mathbf{O} \longrightarrow \mathbf{M}^{n+} + \mathbf{S}\mathbf{A} + \mathbf{H}^+ \quad (\mathbf{M}\mathbf{9})$$

$$\mathbf{M}^{(n+1)+} + \mathbf{R}\mathbf{2} \longrightarrow \mathbf{M}^{n+} + \mathbf{S}\mathbf{A} + \mathbf{H}^{+} \qquad (\mathbf{M}\mathbf{10})^{n+1}$$

$$\mathbf{M}^{(n+1)+} + \mathbf{R3} + \mathbf{H}_2\mathbf{O} \longrightarrow \mathbf{M}^{n+} + \mathbf{SA} + \mathbf{H}^+ \quad (\mathbf{M11})$$

 $M^{(n+1)+}:Ce(IV), Mn(III), or Fe(phen)_{3}^{3+};$ k-KGA = keto-KGA; d-KGA = gem-diol-KGA; c-KGA = cyclic-KGA; R1 = .COCH_2CH_2CO_2H; R2 = .C(OH)_2CH_2CH_2CO_2H;

$$R3 = OH;$$

SA = HO₂CCH₂CH₂CO₂H
Scheme I



t/h

Figure 2 Potentiometric traces of $\log[Br^{-}]$ vs. time for the oscillating reaction of bromate ion and 2-ketoglutaric acid catalyzed by Ce(III), Mn(II), or Fe(phen)₃²⁺ ion at 25°C. (A): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.020 M, [KGA]₀ = 0.170 M, [H₂SO₄]₀ = 0.800 M; (B): [Mn(II)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.020 M, [KGA]₀ = 0.170 M, [H₂SO₄]₀ = 1.00 M; (C): [Fe(phen)₃²⁺]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.020 M, [KGA]₀ = 0.400 M; (D): (C) deaerated with N₂ gas; (E): (B) deaerated with N₂ gas; (F): (A) deaerated with N₂ gas; (G): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.015 M, [NaKGA]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.180 M, [H₂SO₄]₀ = 1.00 M; (H): [Ce(III)]₀ = 1.00 × 10⁻³ M, [BrO₃⁻]₀ = 0.015 M, [H₂SO₄]₀ = 0.180 M.

$$- d[\mathbf{M}^{(n+1)+}]/dt = k[\mathbf{KGA}]_t [\mathbf{M}^{(n+1)+}]_t / (1 + K_{\mathrm{m}} [\mathbf{KGA}]_t) = k_{\mathrm{obs}} [\mathbf{M}^{(n+1)+}]_t$$
(1)

In Eq. (1), $[M^{(n+1)+}]_t$ is the total concentration of $M^{(n+1)+}$ species, $[KGA]_t$ is the total concentration of KGA species,

$$\begin{split} k &= (k'_3 K_{\rm m3} K_2 + k'_4 K_{\rm m4} K_1 K_2 + k'_5 K_{\rm m5}) / \\ &\qquad (1 + K_2 + K_1 K_2) \end{split}$$

$$K_m &= (K_{\rm m3} K_2 + K_{\rm m4} K_1 K_2 + K_{\rm m5}) / \\ &\qquad (1 + K_2 + K_1 K_2) \end{split}$$

 $K_{m3} = k_{3}/(k_{-3} + k'_{3})$ $K_{m4} = k_{4}/(k_{-4} + k'_{4})$ $K_{m5} = k_{5}/(k_{-5} + k'_{5})$ $K_{1} = [diol-KGA]/[keto-KGA]$ $K_{2} = [keto-KGA]/[cyclic-KGA]$ $k_{obs} = k[KGA]_{t}/(1 + K_{m} [KGA]_{t})$

This rate equation (Eq. (1)) is similar to the Michaelis-Menten-like kinetics as suggested by Kasperek and Bruice [15]. The kinetics of the Mn(III)-KGA reaction is consistent with Eq. (1). However, under the



Figure 3 Plots of $\ln(A_t - A_x)$ (A, B) or $\ln(A_{t+d} - A_t)$ (C) vs. time for the Ce(IV)-KGA (A), Mn(III)-KGA (B), and Fe(phen)_3^{3+}-KGA (C) reactions in 1 M H₂SO₄. (A): [Ce(IV)]_0 = 3.00 × 10^{-4} M, [KGA]_0 = 3.00 × 10^{-3} M, 20^{\circ}C, 360 nm; (B): [Mn(III)]_0 = 5.00 × 10^{-4} M, [KGA]_0 = 0.0100 M, 25^{\circ}C, 310 nm; (C): [Fe(phen)_3^{3+}]_0 = 1.50 × 10^{-4} M, [KGA]_0 = 0.0240 M, 25^{\circ}C, 500 nm, deaerated with N₂ gas.

present reaction conditions, this reaction is quite insensitive to the change in [KGA] due to the relatively large value of K_m (Table I). On the other hand, if the value of K_m is small, then at sufficiently low [KGA] $(K_m [KGA]_t \ll 1)$, k_{obs} reduces to $k_{obs} = k [KGA]_t$ and a second-order kinetics is obtained, as observed in the Ce(IV)-KGA and Fe(phen)₃³⁺-KGA reactions.

Discussion

It is well known that α -keto acids (XCH₂COCO₂H) are of major importance in intermediary metabolism. If the X group in XCH₂COCO₂H is a simple aliphatic group or is linked through one or more methylene groups (e.g., as in KGA), the enol form is quantitatively unimportant in neutral or acidic solutions [16]. Most α -keto acids in aqueous solution exist in equilibrium with the hydrate (gem-diol) form (as in step (M1)). The position of equilibrium favors the nonhydrated keto form at neutral pH, whereas at low pH values (below the pK_a value of the α -carboxylic acid group) the hydrate form predominates.



Figure 4 Plots of k_{obs} vs. $[KGA]_0$ for the Ce(IV)-KGA reaction at various temperatures. $[Ce(IV)]_0 = 3.00 \times 10^{-4}$ M, $[H_2SO_4] = 1.00$ M, 360 nm. (A): 15°C, (B): 18°C, (C): 20°C, (D): 23°C, (E), 25°C.



Figure 5 Plots of k_{obs} vs. [KGA]₀ for the Fe(phen)₃³⁺-KGA reaction at various temperatures. [Fe(phen)₃³⁺]₀ = 1.50 × 10⁻⁴ M, [H₂SO₄] = 1.00 M, 500 nm, deaerated with N₂ gas. (A): 15°C, (B): 17°C, (C): 20°C, (D): 23°C, (E): 25°C.

Ce(IV)–KGA Reaction		Fe(phen) ³⁺ -KGA Reaction	
<i>T</i> /°C	$k'/M^{-1} s^{-1}$	T/°C	$k'/M^{-1} s^{-1}$
15	2.76	15	1.20
18	3.85	17	1.42
20	4.46	20	1.66
23	5.37	23	1.97
25	6.59	25	2.16
$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	59.3 ± 3.7		41.2 ± 1.9
	Mn(III)-KGA Reaction		
<i>T</i> /°C	$k/M^{-1} s^{-1}$	K_m/M^{-1}	
15	89.6	340	
20	110	222	
23	174	265	
25	164	184	
28	163	115	
$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	38.0 ± 10.9		

Table IRate Constants and Apparent Activation Energies of the Reactions of 2-Ketoglutaric Acid with Ce(IV),Mn(III), and $Fe(phen)_{3}^{+}$ lons

A third equilibrium form (cyclic-KGA or lactol) was observed for KGA in contrast to 2-ketoadipic acid (HO₂CCH₂CH₂CH₂COCO₂H). As reported by Fisher et al. [17], the cyclic-KGA \rightleftharpoons keto-KGA interconver-



Figure 6 Plots of k_{obs}^{-1} vs. $[KGA]_0^{-1}$ for the Mn(III)-KGA reaction at various temperatures. Mn(III)]_0 = 5.00 × 10^{-4} M, [H_2SO_4] = 1.00 M, 310 nm. (A): 15°C, (B): 20°C, (C): 23°C, (D): 25°C, (E): 28°C.

sion (step (M2)) is extremely rapid, which leads to the broad peak for β -CH2-group shown in Figure 1B–D. The cyclic-KGA ≓ gem-diol-KGA interconversion is very slow in the NMR time scale. The rate constants of solvent-catalyzed hydration (k_1) and dehydration (k_{-1}) of KGA at 25°C are 0.34 s⁻¹ and 0.19 s⁻¹, respectively [18]. Furthermore, the equilibria of steps (M1) and (M2) can be maintained under the present reaction conditions, since $[KGA]_0 \gg$ $[M^{(n+1)+}]_0$. The enol form of KGA is negligible and the keto-KGA \rightleftharpoons enol-KGA interconversion is very slow. No deuteration of the β -carbon atom was observed in 1 M DCI after one day at 25°C, and enolization of keto-KGA appeared to be base-catalyzed but not acid-catalyzed [14]. However, the results in Figures 1C and 1D indicate that the rate of isotope exchange (or bromination) reaction of the gem-diol-KGA is faster than that of the keto- or cyclic-KGA. The appearance of the induction in the Ce(III)-catalyzed BZ reaction with NaKGA or Na2KGA (Figs. 2G and 2H) supports this argument, since initially the amount of the hydrate form in NaKGA or Na2KGA solution is less than that in KGA solution. As reported by Fisher et al. [17], the keto form of 2-ketoglutarate is the substrate for the enzyme, bovine liver glutamate dehydrogenase, and the gem-diol form is not, which becomes a substrate only after nonenzymatic conversion to the keto form. In this work, we demonstrate that gem-diol-KGA exhibits different behavior from keto-KGA in the BZ reaction. The presence of gemdiol-KGA shortens the induction period and increases the amplitude of oscillations during the initial stage of the Ce(III)-catalyzed BZ reaction with KGA. However, we are not in a position to differentiate the reactivities between keto-KGA and gem-diol-KGA toward reaction with Ce(IV), Mn(III), and Fe(phen)₃³⁺ ions by using the present kinetic results. Similar to the BZ reaction with malonic acids [7,9,10], Fe(phen)₃²⁺ ion behaves differently from Ce(III) or Mn(II) ion as a catalyst for the BZ reaction with KGA. This result also can be rationalized by invoking the different reactivity of the Fe(phen)₃^{3+/2+} couple from the Ce(IV)/Ce(III) or Mn(III)/Mn(II) couple toward reaction with KGA and with bromine species (BrO₃⁻, HBrO₂, ·BrO₂, HOBr, and Br₂) [19].

SUMMARY

In a stirred batch experiment, the reaction of bromate ion with 2-ketoglutaric acid (KGA) in aqueous sulfuric acid catalyzed by Ce(III), Mn(II), or Fe(phen)₃²⁺ ion exhibits sustained barely damped oscillations under aerobic conditions. In general, the reaction oscillates without an induction period. The presence of oxygen molecules catalyzed the oscillations in the Ce(III)or Mn(II)-catalyzed BZ system. In contrast, the Fe(phen)₃²⁺-catalyzed system exhibits a higher frequency of oscillations under anaerobic conditions than under aerobic conditions. Fe(phen)₃²⁺ ion behaves differently from Ce(III) and Mn(II) ions in catalyzing this oscillating system. The order of relative reactivities of the metal ions toward reaction with KGA is Mn(III) > Ce(IV) \gg Fe(phen)₃³⁺. We thank the National Science Council of the Republic of China for the financial support of this work (NSC85-2113-M-006-011, NSC86—2113-M-006-011, and NSC87-2113-M-006-011).

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