

A Study of the Cerium-catalyzed Briggs-Rauscher Oscillating Reaction

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Cerium(III) catalysts can replace manganese(II) in the classic Briggs-Rauscher oscillator also containing acid, iodate, hydrogen peroxide, and malonic acid. H₂SO₄ was used as an acid; if HClO₄ is used, cerium iodate precipitates. Cerium(III) oxalate typically precipitates by the time oscillations end. Ce(III) at low concentrations is roughly three times as effective as Mn(II). At higher catalyst concentrations, there is a leveling effect for both. Oscillatory behavior with different concentrations is explored. Response to concentration change and inhibitors is similar with both catalysts. The mechanistic steps involving the catalysts must be similar. Ce(IV) is also an effective catalyst, although some cerium(IV) iodate may precipitate immediately.

Key words: Manganese-catalyzed, Cerium Oxalate, Cerium(III), Cerium(IV)

Introduction

The Briggs-Rauscher (BR) oscillating system [1], H₂SO₄ or HClO₄, NaIO₃ or KIO₃, malonic acid (MA) or other substrate, Mn(II) or cerium ions catalyst, and H₂O₂, is a well-known oscillating system, often used in lecture demonstrations and chemical 'magic' shows because of its dramatic color changes. Most previous studies have used Mn(II) catalysts, although the original paper mentioned cerium as an effective catalyst. Few studies have been reported on the cerium system [2–4]. We now present some of the trends with concentration, and compare the cerium system with the manganese system for similar concentrations. The reference concentrations have been chosen for a solution which ends oscillations in a low [I⁻] state with very little [I₂]. The ending states have been characterized by Vanag [5] as Type I (low [I⁻] and [I₂]), and Type II (high [I⁻] and [I₂]), in correspondence with flow systems [5].

There are some solubility issues with cerium ions. Ce(IO₃)₃ will precipitate if either [IO₃⁻] or [Ce(III)] is too high. Ce(IO₃)₃ precipitates more readily in the presence of perchloric acid, so in this work H₂SO₄ was used. Presumably cerium sulfate complexes help to keep the cerium in solution. Furthermore, Ce₂(C₂O₄)₃ often precipitates towards the end of the oscillatory realm since oxalic acid is one of the products of the BR reaction [6].

One reason for characterizing the Ce-based system is that the exact role of the catalyst in the BR oscillator is still open to question. We wish to compare the two catalysts to see whether there are fundamental differences in their effects. An advantage of Ce-based systems is that NMR spectra of solutions containing Ce(III) are much more well-defined than that of Mn-based solutions. We thus include a few results.

Experimental Section

Chemicals

At Bologna (B): Malonic acid, (MA) (Merck; reagent grade, > 99%), manganese(II) sulfate monohydrate (Fluka; reagent grade, ≥ 99%), cerium(III) nitrate hexahydrate (Merck; reagent grade > 99.5%), cerium(IV) sulfate tetrahydrate (Aldrich; reagent grade, ≥ 99%), and sodium iodate (Merck; reagent grade, > 99.5%) were used without further purification. Ferroin solution (25 mM) was purchased from Merck. H₂SO₄, H₂O₂ and other chemicals were of analytical grade. All stock solutions were prepared from doubly distilled deionized water. Sulfuric acid was standardized by titration *versus* standard 0.1 M NaOH (from Merck). Hydrogen peroxide was standardized daily by manganometric analysis.

At Penn State (P): Malonic acid, (Aldrich, 99%), was recrystallized from water. Manganese(II) sulfate monohydrate (Fisher, Certified ACS, 98.4%), cerium(III) nitrate hexahydrate, (reagent grade, Anachemia), cerium(IV) ammonium nitrate, (ACS Reagent Grade, 98.5%), and potassium iodate

(Baker analyzed reagent, 99.5 %) were used without further purification. H_2SO_4 , H_2O_2 and other chemicals were of analytical or reagent grade. All stock solutions were prepared from distilled deionized water, 18 Ohm-cm. Sulfuric acid was standardized by titration *versus* standard 0.1 M NaOH (from Fisher). Hydrogen peroxide was standardized regularly by manganometric analysis. I_2O was prepared by a new method [7] based on an earlier approach [8] for preparing an I(+1) solution in concentrated sulfuric acid. The I(+1) solution was extracted with CH_2Cl_2 , giving a solution of I_2O . A small amount of this solution was added with vigorous stirring to an aqueous solution of interest. The small amount of CH_2Cl_2 dissolved/evaporated, yielding HOI in solution.

Apparatus

Potential *vs.* time series were carried out in thermostatted beakers at 25 °C. Light was excluded. Electrode pairs used were an iodide-selective electrode (Orion, model 9453) or shiny Pt inlay (Corning #476060) *vs.* Ag/AgCl double junction at Penn State (P); an iodide-selective electrode (Orion, model 9453) or shiny Pt (Hamilton, model P/N 238 945) *vs.* Ag/AgCl double junction (Ingold, model 373-90-WTE-ISE-S7) at Bologna (B). Electrodes were connected to a pH multimeter (WTW, model pH 540 GLP) controlled by an IBM-compatible PC; the accuracy of the multimeter was ± 1 mV; the data acquisition program MULTI ACHAT II (by WTW) was used (B). Electrode data was acquired *via* LOGGER-PRO software, accuracy, ± 3 mV (P). UV/Vis spectra were obtained on a Shimadzu Model 1501 with a thermostatted cell compartment at 25.0 °C (P). NMR spectroscopy was performed at ambient temperature on a 300 MHz Bruker Avance Microbay spectrometer (P).

Procedures

BR reference mixtures were prepared from stock solutions using pipets or burets. Unless stated otherwise the order of addition was MA, catalyst, NaIO_3 , H_2SO_4 , and H_2O_2 (B), or H_2SO_4 , KIO_3 , MA, catalyst, and H_2O_2 (P). The recording was started immediately after the addition of H_2O_2 .

Results and Discussion

We report induction periods (time from addition of H_2O_2 to the onset of oscillations), length of oscillations (time during which oscillations could be detected), mode of ending oscillations {low $[\text{I}^-]$ (Type I), or high $[\text{I}^-]$ (Type II)}, and time to transition (length of time from the end of oscillations until a (usually) sharp transition to lower potential (higher $[\text{I}^-]$), Type I to Type II. Recordings were made with either iodide-selective or Pt electrodes (Fig. 1).

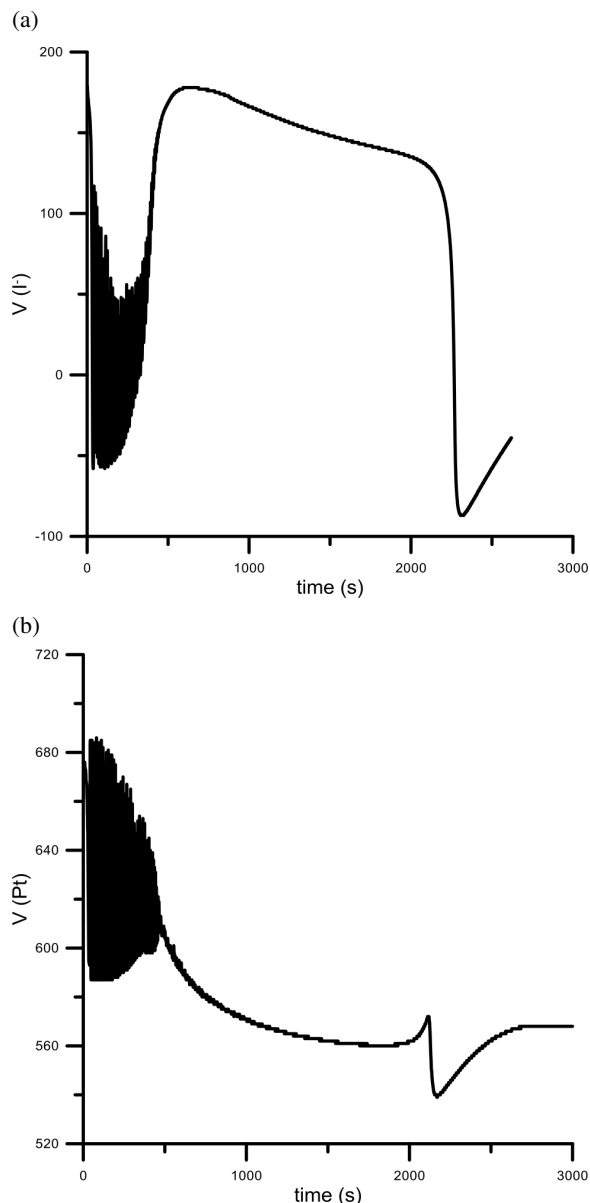


Fig. 1. (a) Recording with iodide-sensing *vs.* reference electrodes. (b) Recording with Pt *vs.* reference electrodes. Both: $[\text{MA}]_0 = 0.050$ M; $[\text{Ce(III)}]_0 = 0.0050$ M; $[\text{NaIO}_3]_0 = 0.020$ M; $[\text{H}_2\text{SO}_4]_0 = 0.10$ M; $[\text{H}_2\text{O}_2]_0 = 1.0$ M.

During oscillations, the traces with two types of electrodes are similar; however, following the oscillations, the traces are quite different. The iodide electrode potential increases, showing a decrease in $[\text{I}^-]$ (or increase in $[\text{HOI}]$), followed by a sudden transition to lower potential (higher $[\text{I}^-]$), attributed to sudden decomposition of iodinated malonic acid. The

Pt electrode responds (partly) to the $I_2 + 2 e^- \leftrightarrow 2 I^-$ couple with a potential increase for a $[I^-]$ decrease and an increase for an $[I_2]^{0.5}$ increase. The Pt electrode also responds to metal ion couples such as $M^{(n+1)} + e^- \leftrightarrow M^{n+}$ and others. The interpretation of electrode readings between the end of oscillations and the transition is unclear.

During oscillations, O_2 and some CO_2 are evolved, mainly IMA is formed. Some organic component is oxidized to oxalic acid. For most of the experiments reported here, the solution is in Type I state at the end of oscillations. $[H_2O_2]$ is still in large excess. From proton NMR studies with acetic acid as an internal reference, peak integrals indicate that $[MA]$ is about 0.026 ± 0.003 M. IMA and the possible presence of tartronic acid (2-hydroxypropane-dioic acid) are obscured by the water peak. $[IO_3^-]$ is low, less than 0.004 M, determined by neutralization with sodium acetate, precipitation with silver nitrate, redissolving with ammonia, acidification, and iodometric titration with $Na_2S_2O_3$. Most iodine is in the form of IMA and a small amount of I_2MA . $[H^+]$ must have decreased by as much as $[IO_3^-]$ has decreased, and increased by two times the amount of oxalic acid formed. The total $[Ce(III)]$ is less than 0.0050 M; the amount in solution is decreasing due to formation of insoluble $Ce_2(C_2O_4)_3$. That amount was determined by neutralization with sodium acetate, filtration, and drying. The amount of oxalate found was equivalent to $\sim 0.005 \pm 0.002$ M. During the Type I state, the potential of iodide and Pt electrodes slowly decreases. Eventually there is a sharp transition to low potential (Type II state). The potential recovers somewhat as relatively high $[I^-]$ is oxidized mainly by H_2O_2 ; MA and IMA are iodinated. The platinum electrode is similar, except that the sharp transition is usually immediately preceded by an upward cusp.

Our two laboratories (P and B) had differences in some of the parameters used to describe the time series. The induction time and length of oscillations were up to 20 % shorter in Bologna compared to Penn State, although the trends were the same with different concentrations. The time to transition was especially erratic; differences of several hundred seconds were common on repeated runs in each of our labs. Taking that into account, the two laboratories were in reasonable agreement for the time to transition. This erratic behavior was previously reported [9]. We investigated stirring speed, KIO_3 vs. $NaIO_3$, H_2SO_4 vs. $HClO_4$, $Ce(NO_3)_3$,

vs. $Ce_2(SO_4)_3$, different sources of malonic acid, recrystallized malonic acid, order of addition of reagents, concentration of stock solutions, and volume of oscillating solution, and could not see any differences attributable to those factors. Other factors that could explain the differences were the sensitivity to the temperature and or different electrode pairs response. It is known that the oscillating system is very sensitive to various additives or impurities [10], but we were not able to identify and quantify all the factors affecting the system.

Cerium trends with concentration

As a reference solution, we have chosen $[H_2SO_4] = 0.10$ M, $[KIO_3]$ or $[NaIO_3] = 0.020$ M, $[MA] = 0.050$ M, $[Ce(NO_3)_3] = 0.0050$ M, and $[H_2O_2] = 1.0$ M. These solutions' end oscillations in Type I mode (low $[I_2]$ and $[I^-]$); the concentrations are similar to those recently recommended for demonstrations except the use of Mn(II) catalyst [9] (Table 1).

Except for the effect of $[H_2SO_4]$, all of the trends were in the same direction as Mn-based oscillators [9]. The Mn(II) system was studied over a much larger range in $[H_2SO_4]$.

The transition from Type I to Type II is still under investigation. The transition is not observed with other substrates, such as methylmalonic acid, which undergo single iodination. We believe that I_2MA is responsible for transition.

Oscillators can be constructed using IMA as substrate [11]. The oscillation lengths are shorter than with MA substrate, and they end typically in the Type II state. I_2MA is known to decompose and liberate I_2 and I^- in the presence of Mn(II) or Ce(III) and H_2O_2 [6].

Comparison with Mn(II)

A series of runs were made with all the same conditions as the reference solution, except in place of $[Ce(III)]$ at 0.0050 M, various concentrations of Mn(II) were used. Results are shown in Table 2.

The minimum concentration of Mn(II) which is needed to have oscillations is approximately three times higher than that of Ce(III). Likewise, for comparable induction times, $[Mn(II)]$ is a little less than three times higher than $[Ce(III)]$. In the oscillatory region, lengths of oscillation and times to transition are slightly less for Mn(II). This is in the direction to be

Table 1. Effect on oscillator of $X = \text{H}_2\text{SO}_4$, KIO_3 , MA, H_2O_2 , Ce(III) variation and trends with increase in concentration.

[X] (M)	Induction (s)	Total length of oscillations (s)	Time to transition (s)	Transition type	Description of I→II transition
$X = \text{H}_2\text{SO}_4$:					
0.050	60	592	3249	osc→I→II	sharp
0.10 ^a	56	573	1328	osc→I→II	sharp
0.20	54	515	680	osc→I→II	sharp
$X = \text{KIO}_3$:					
0.0050	no osc	N/A	none	osc→I→II	none
0.010	104	218	none (?)	osc→I→II	> 5500
0.015	80	433	none	osc→I→II	> 18000
0.020 ^a	56 ± 4	573 ± 15	1328 ± 161	osc→I→II	sharp
0.025	50			osc→II	sharp
$X = \text{MA}$:					
0.020	35			osc→II	sharp
0.030	44	143	39	osc→II	sharp
0.040	42	355	142	osc→II	sharp
0.045	50	667	756	osc→I→II	sharp
0.050 ^a	56	573	1328	osc→I→II	sharp
0.060	68	465		osc→I	
0.070	72	380		osc→I	
$X = \text{H}_2\text{O}_2$:					
0.375	119	667	2451	osc→I→II	sharp
0.50	95	667	1968	osc→I→II	sharp
0.60	62	630	1283	osc→I→II	sharp
1.0 ^a	56	573	1328	osc→I→II	sharp
1.5	42	518	735	osc→I→II	sharp
$X = \text{Ce(III)}$:					
0.00075	N/A	no osc.	3100	I→II	
0.0010	N/A	no osc.	2395	I→II	
0.0015	137	381	1672	osc→I→II	sharp
0.0020	77	427	1481	osc→I→II	sharp
0.0050 ^a	56	573	1328	osc→I→II	sharp

^a Reference mixture.

Trends with increase in concentration for Ce(III)-based oscillators.

Species	Induction	Length oscillations	Time to transition
$[\text{H}_2\text{SO}_4]$	slight decrease	decrease	decrease
$[\text{IO}_3^-]$	decrease	increase	decrease
[MA]	increase	increase, decrease	increase
[Ce(III)]	decrease	increase	decrease
$[\text{H}_2\text{O}_2]$	decrease	decrease	decrease

Table 2. Effect on oscillator of Mn(II) variation.

[Mn(II)] (M)	Induction (s)	Total length of oscillations (s)	Time to transition (s)	Transition type	Description of I→II transition
0.0030	N/A	no osc	2060	I→II	
0.0045	110	346	1324	osc→I→II	sharp
0.0060	62	365	1283	osc→I→II	sharp
0.0090	48	344	1275	osc→I→II	sharp
0.012	42	335	1210	osc→I→II	sharp
0.015	37	322	1373	osc→I→II	sharp

expected due to the lowering of effective [Ce(III)] with time as oxalate builds up. MnC_2O_4 is much more soluble than $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ and is not seen as a precipitate. In the oscillatory region, increasing either [Mn(II)] or [Ce(III)] shortens the induction period, but otherwise has rather little effect.

Precipitation of $\text{Ce}_2(\text{C}_2\text{O}_4)_3$

Oxalate is a breakdown product of malonic acid in the BR oscillator, probably produced *via* iodomalonic acid (IMA) and diiodomalonic acid (I_2MA) as intermediates [6]. $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ is rather insoluble.

Usually, at the conditions reported herein, colorless $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ is visible in the solution when oscillations end. Since Ce(III) is a catalyst for iodine production, a precipitation process or complexation process should slow iodine production and affect oscillations. Indeed, $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ begins to appear as the amplitude of oscillations decreases towards zero.

We have investigated the solubility of $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ by spectrophotometric means. We lowered the concentrations of Ce(III) and $\text{H}_2\text{C}_2\text{O}_4$ in 0.10 M H_2SO_4 until no turbidity was seen (as broad absorbance). A solution with 0.10 M H_2SO_4 , 0.0016 M Ce^{III} , and 0.0024 M $\text{H}_2\text{C}_2\text{O}_4$ had close to the maximum concentrations which could remain turbidity-free for more than 30 min. We calculated an apparent K'_{sp} for $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ as 4.7×10^{-25} , compared to 3.2×10^{-26} for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ [12]. K'_{sp} includes the effects of cerium-sulfate complexation.

Iodine production subsystems

Ce(III) and Mn(II) are catalysts for iodine production. The subsystems without malonic acid can be studied separately, spectrophotometrically, following I_2 absorption. The rate of iodine production is sensitive to $[\text{Ce}(\text{III})]$ from about 1×10^{-4} M to 1×10^{-3} M (Fig. 2(a)). Above 1×10^{-3} M there is a saturation effect; additional increases in catalyst have little effect (Fig. 2(b)).

Mn(II) is an effective catalyst above approximately 1×10^{-4} M. The saturation effect sets in above approximately 2×10^{-3} M (Fig. 3 (a) and 3(b)).

The various curves show that in the range of approximately 2×10^{-4} M to 2×10^{-3} M, $[\text{Mn}(\text{II})]$ has roughly the same effect as $[\text{Ce}(\text{III})]$, but about 3 times lower.

Oscillations are first seen at roughly concentrations of catalyst where saturation effects are observed in the iodine producing solutions.

Effect of inhibitors

Several types of compounds are known to be inhibitors of oscillations [13]. Polyphenols have been reported to mainly act by reaction with HO_2^\bullet radicals. Some of them are also known to be easily iodinated by HOI [10]. Addition of the inhibitor to an oscillating system causes oscillations to cease, then, after an interval dependent on the inhibitor concentration, the oscillations restart. Resorcinol, benzene-1,3 diol, (*Re*),

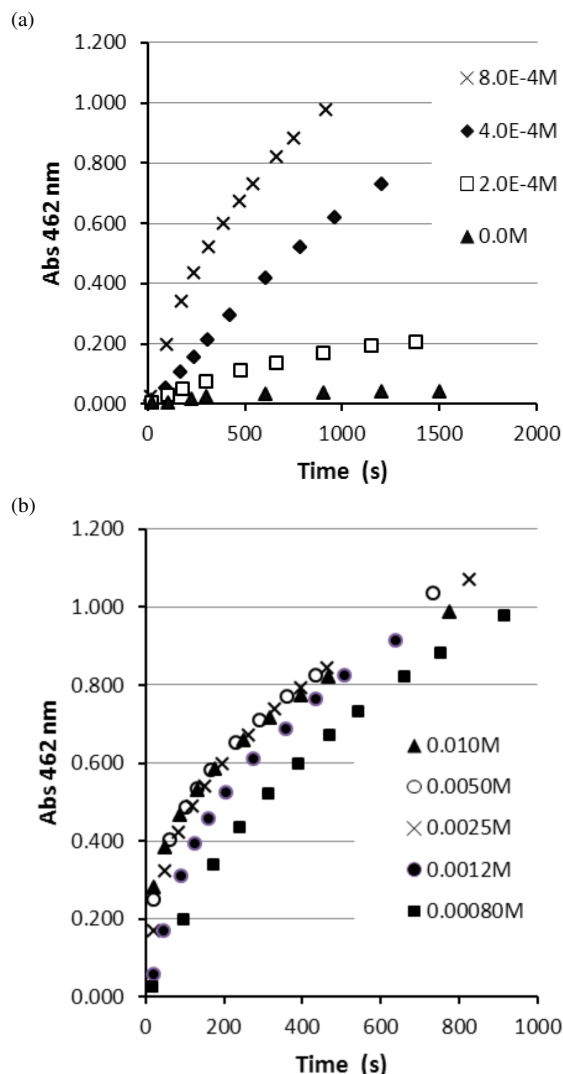


Fig. 2. (a) Iodine production with Ce(III), lower range. $[\text{KIO}_3]_0 = 0.020$ M; $[\text{H}_2\text{SO}_4]_0 = 0.10$ M; $[\text{H}_2\text{O}_2]_0 = 1.0$ M; $[\text{Ce}(\text{III})]$ in legend. (b) Iodine production with Ce(III), higher range. Same except $[\text{Ce}(\text{III})]$, in legend.

at 7.9×10^{-6} M added to a reference mixture after the fourth oscillation, stopped oscillations for 44 s. The inhibition period is the time for the inhibitor to be degraded (oxidized or iodinated), after which oscillations can restart.

Ferriin inhibition has been previously studied [14]. The reaction of BR oscillators with ferriin is very similar to that of polyphenols such as *Re*. It was concluded that ferriin interacts with the oscillator by a similar mechanism, *i.e.* with HO_2^\bullet radicals. Ferriin (added before H_2O_2) is more than 30 times more effective

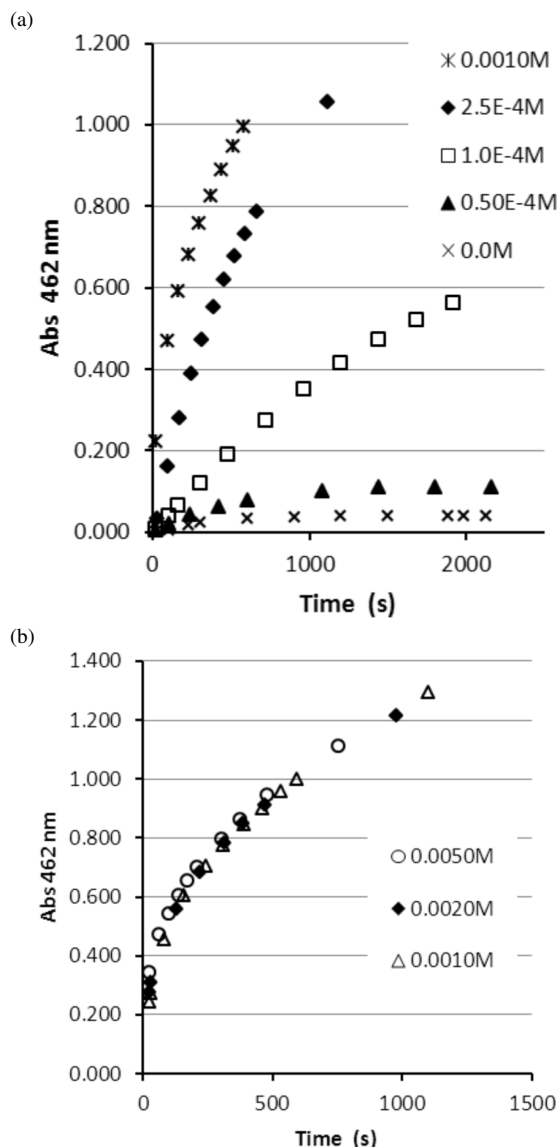


Fig. 3. (a) Iodine production with Mn(II), lower range. $[\text{KIO}_3]_0 = 0.020 \text{ M}$; $[\text{H}_2\text{SO}_4]_0 = 0.10 \text{ M}$; $[\text{H}_2\text{O}_2]_0 = 1.0 \text{ M}$; [Mn(II)] in legend. (b) Iodine production with Mn(II), higher range. Same except [Mn(II)], in legend.

than *Re*. Ferriin at $2.5 \times 10^{-7} \text{ M}$ suppressed oscillations for 357 s.

Oxalic acid is a product in the oscillatory system [6]. Addition of sufficient oxalic acid before H_2O_2 prevents oscillations. Unlike ferriin or *Re* inhibition, there is no restart of oscillations. The inhibition by oxalic acid is related to precipitation (and/or complexation) of Ce(III) by oxalate and to oxalic acid as a reducing agent for oxyiodine species.

With reference solution concentrations except for [Ce(III)] at 0.0015 M, $[\text{H}_2\text{C}_2\text{O}_4]$ at 0.0050 M is enough to shorten the length of oscillations by about 2/3 and double the delay to transition. With 0.0060 M $\text{H}_2\text{C}_2\text{O}_4$, there is only one excursion from high to low $[\text{I}^-]$ and return, and no transition. With reference solutions ([Ce(III)] at 0.0050 M), the number of oscillations gradually diminishes to four as $[\text{H}_2\text{C}_2\text{O}_4]$ is increased to 0.010 M. The delay to transition gradually lengthens with increasing $[\text{H}_2\text{C}_2\text{O}_4]$ to about 95 min, and the transition becomes more gradual.

In all the measurements in the above paragraph, K_{sp} for $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ was exceeded when Ce(III) was added to a solution containing sufficient amounts of oxalic acid. Precipitation was not immediate when concentrations were low, but passed through a colloidal state on a time scale of a few seconds to a few minutes. Ce(III) was added last so that the potential traces were more reproducible. If H_2O_2 was added last, $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ had more (variable) time to coagulate and withdraw more Ce(III) from solution.

The shortening of the oscillation state and lengthening of the delay to transition are mainly due to the lowering of [Ce(III)] by precipitation as the oxalate. Calculations using the measured K_{sp} for $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ have shown that for $[\text{Ce(III)}]_0 = 0.0050 \text{ M}$, $[\text{H}_2\text{C}_2\text{O}_4]_0$ of 0.010 M would lower free [Ce(III)] below 0.0010 M, the oscillation limit in Table 1. For $[\text{Ce(III)}]_0 = 0.0015 \text{ M}$, $[\text{H}_2\text{C}_2\text{O}_4]_0$ of 0.005 M would also lower free [Ce(III)] below 0.0010 M.

Some effects of oxalic acid are due to reduction of oxyiodine species by oxalic acid. When I(I) (as $1 \times 10^{-4} \text{ M I}_2\text{O}$ [7]) was added to 0.0020 M $\text{H}_2\text{C}_2\text{O}_4$ in 0.10 M H_2SO_4 , most of the I_2O was hydrated to HOI and disproportionated to I_2 and IO_3^- . But when the same amount of I_2O was added to 0.020 M $\text{H}_2\text{C}_2\text{O}_4$ reduction to I_2 was complete in $\sim 75 \text{ s}$. $\text{H}_2\text{C}_2\text{O}_4$ at 0.020 M is a fairly effective scavenger of I(I) or HOI.

Comparison of resorcinol addition to the Ce(III) and Mn(II) systems

Re is a potent free radical scavenger. In the BR mixture used for relative antioxidant activity measurements ($[\text{HClO}_4] = 0.0226 \text{ M}$, $[\text{NaIO}_3] = 0.0667 \text{ M}$, $[\text{MA}] = 0.050 \text{ M}$, $[\text{Mn}(\text{SO}_4)] = 0.00667 \text{ M}$, and $[\text{H}_2\text{O}_2] = 1.20 \text{ M}$) [13c], the addition of $5.86 \mu\text{M Re}$ after the third oscillation caused an inhibition time

Table 3. Effect of resorcinol on a Mn(II)- or Ce(III)-based oscillator.

$[Re]_{\text{mix}}$ (M)	Induction (s)	Inhibition (s)	Total length of oscillations (s)	Time to transition I→II (s)	Electrode	ΔV (%)
$[MnSO_4] = 0.012 \text{ M}^{a,b}$:						
0	35	–	335	1280	Pt	0
3.60×10^{-6}	38	34	362	1540	Pt	1.0
5.96×10^{-6}	40	44	390	1820	Pt	1.67
8.28×10^{-6}	35	65	425	2260	Pt	2.33
$[MnSO_4] = 0.0050 \text{ M}^a$:						
0	85	–	355	1780	Pt	0
3.60×10^{-6}	86	57	379	1860	Pt	1.0
5.96×10^{-6}	85	76	400	2155	Pt	1.67
8.28×10^{-6}	87	123	438	recorded until <i>ca.</i> 3000 s	Pt	2.33
$[Ce(III)] = 0.0050 \text{ M}^a$:						
0	40	–	420	1790	Pt	0
3.60×10^{-6}	38	24	440	2062	Pt	1.0
5.96×10^{-6}	40	36	480	2830	Pt	1.67
8.28×10^{-6}	39	53	431	recorded until <i>ca.</i> 3500 s	Pt	2.33

^a All solutions: $[MA]_0 = 0.050 \text{ M}$; $[NaIO_3]_0 = 0.020 \text{ M}$; $[H_2SO_4]_0 = 0.10 \text{ M}$; $[H_2O_2]_0 = 1.0 \text{ M}$; ^b ΔV (%): Percent change in volume on addition of *Re* to 30 mL of the reference mixture.

Table 4. Synthetic mixtures to replicate approximate conditions at end of the oscillations^a.

$[H_2SO_4]_0$ (M)	$[MA]_0$ (M)	$[IMA]_0$ (M)	$[IO_3^-]_0$ (M)	$[H_2C_2O_4]_0$ (M)	No. of oscillations	Time to transition (s)
0.10	0.022	0.018	0.0020	0.010	none	1000 (average)
0.083	0.024	0.018	0.0020	0.0080	3 small	1490
0.083	0.022	0.018	0.0020	0.0080	1 small	1500
0.084 ^b	0.024	0.018	0.0020	0.0060	2 small	1306
0.084 ^b	0.024	0.018	0.0020	0.0060	none	1295

^a $[H_2O_2]$ was 0.90 M in these mixtures; ^b these solutions also contained 0.0020 M tartronic acid.

of 660 s. In the present Mn(II)-based reference mixtures, the effect is less evident, but inhibition is still seen, as can be seen from Table 3. The effect on the Ce(III)-catalyzed reference mixture is reported for comparison.

For these reference mixtures, it seems that the effect of increasing *Re* has little effect on inhibition time and duration of oscillations either in Mn(II)- and Ce(III)-catalyzed reaction, while the effect is especially evident in lengthening the time from the end of oscillations to transition.

Simulation of spent oscillator

We have attempted to replicate the conditions at the end of the oscillations (synthetic mixtures) by mixing a solution containing similar $[H_2SO_4]$ and $[Ce(III)]$, lower $[IO_3^-]$, lower $[MA]$, and lower $[H_2O_2]$ compared to the reference mixture, in addition to $H_2C_2O_4$ and IMA. There are constraints on possible concentrations. The major organic species in solution at the end of the oscillations are MA, IMA, and $Ce_2(C_2O_4)_3$, CO_2 having escaped. Thus $[MA]_0 = [IMA]_{\text{end}} + [MA]_{\text{end}} + 3 Ce_2(C_2O_4)_3$, where the subscript “end” denotes

the amount at the end of the oscillations. For synthetic mixtures where oxalic acid was added, $[MA]_0 = [IMA]_{\text{end}} + [MA]_{\text{end}} + 2H_2C_2O_4 = 0.0050 \text{ M}$. Essentially all the iodine is either in IO_3^- or in IMA, so $[IO_3^-]_0 = [IO_3^-]_{\text{end}} + [IMA] = 0.020 \text{ M}$. To maintain charge balance, $\Delta[H^+] = \Delta[IO_3^-] + 2H_2C_2O_4$. The $[H^+]$ balance with $H_2C_2O_4$ occurs after precipitation of $Ce_2(C_2O_4)_3$.

Trial synthetic mixtures are shown in Table 4, using a range of estimated concentrations at the end of oscillations.

These solutions had few or no oscillations. The ratio of $[IMA]$ to $[MA]$ (and the lowering of $[IO_3^-]$) is an important parameter in oscillation prevention. Trial mixtures which had $[MA] > 0.024 \text{ M}$ or $[IO_3^-] > 0.0020 \text{ M}$ (not shown) had more oscillations. In the first three mixtures, $[H_2C_2O_4]$ was significantly higher than the amount of oxalate measured by weighing the $Ce_2(C_2O_4)_3$ precipitate (0.0050 M). Some of the initial organic matter may be present as intermediates such as tartronic acid, which was added in the last two solutions to bring the total organic to 0.050 M. $[H_2O_2]_{\text{end}}$ was not measured but estimated to be 0.9 M. All solutions shown underwent Type I → Type II transitions

[NaIO ₃] (M)	Induction (s)	Total length of oscillations (s)	Time to transition (s)
0.010	–	none	infinite
0.0150	–	none	1020
0.0175	350	100	600
0.020	351	182	152
0.025	200	340	110

Table 5a. Effect of variation of [NaIO₃] on mixtures with Ce(IV)^a.^a All solutions: [H₂SO₄], 0.20 M; [MA], 0.050 M; [H₂O₂], 1.0 M, [Ce(IV)], 0.0025 M.

[H ₂ SO ₄] (M)	Induction (s)	Total length of oscillations (s)	Time to transition (s)
0.050	225	170	infinite
0.10	225	195	775
0.15	260	150	215
0.20	351	182	152

Table 5b. Effect of variation of [H₂SO₄] on mixtures with Ce(IV)^a.^a All solutions: [NaIO₃], 0.020 M; [MA], 0.050 M; [H₂O₂], 1.0 M; [Ce(IV)], 0.0025 M.

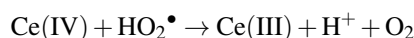
[Ce(IV)] (M)	Induction (s)	Total length of oscillations (s)	Time to transition (s)
0.0010	–	cusp at 1705 (ave)	not meas
0.00125	–	cusp at 1480	not meas
0.0014	1130	170	not meas
0.0015	1045	201	not meas
0.0025	200	340	110

Table 5c. Effect of variation of [Ce(IV)] on mixtures with Ce(IV)^a.^a All solutions: [H₂SO₄], 0.20 M; [NaIO₃], 0.025 M; [MA], 0.050 M; [H₂O₂], 1.0 M.

from 1000 s to ~ 1500 s after mixing, similar to reference oscillators after oscillations cease. We conclude that the synthetic mixtures are at least a fair approximation to the BR solutions at the end of the oscillations.

Cerium(IV) catalyst

Cerium(IV) is rapidly reduced to cerium(III) by H₂O₂.



One would expect that starting with Ce(IV) would be equivalent to starting with Ce(III). A brief report [15] mentions the use of Ce(SO₄)₂ in producing an oscillator. However, another previous trial of Ce(IV) as a BR catalyst [3] was unsuccessful due the very low solubility of Ce(IO₃)₄ and immediate precipitation if Ce(IV) is added to a BR mixture containing iodate, with H₂O₂ being added last. If Ce(IV) is added last to a BR mixture containing H₂O₂ but no catalyst, the solution becomes turbid, but much less precipitation takes place. Reduction to Ce(III) is much slower than with “free Ce(IV)”, so there is an induction period as Ce(III) increases, and then oscillations begin. Table 5 summarizes several runs with Ce(IV) catalyst. Fig. 4 shows a comparison of Ce(III) with Ce(IV).

Ce(IV) is an effective BR catalyst. The differences from Ce(III)-based oscillators can be attributed partly to the insolubility of Ce(IO₄)₄, and to slow reduction of colloidal Ce(IV) complexes to Ce(III), leading to a longer induction period. In parallel runs using

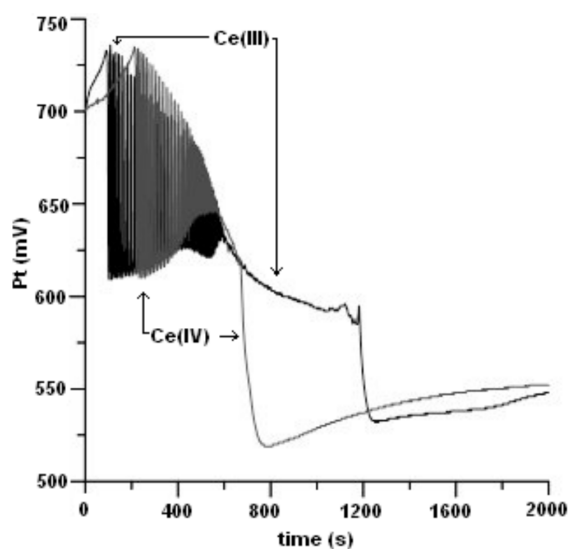
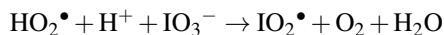


Fig 4. Comparison of Ce(IV) with Ce(III) as a catalyst. [H₂SO₄], 0.20 M; [NaIO₃], 0.025 M; [MA], 0.050 M; [H₂O₂], 1.0 M; (darker) [Ce(III)], 0.0025 M; (lighter) [Ce(IV)] 0.0025 M.

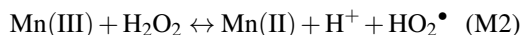
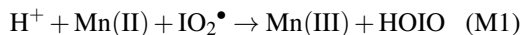
[H₂SO₄], 0.10 M; [NaIO₃], 0.020 M; [MA], 0.050 M; [H₂O₂], 1.0 M; [Ce(IV)], 0.0014 M, one in the spectrophotometer to watch turbidity, and one in the apparatus with electrodes to measure oscillations, the oscillations began at nearly the same time that turbidity disappeared. The [Ce(IV)] value of 0.0014 M is near the lower limit for oscillations with either Ce(III) or Ce(IV).

Another effect of Ce(IV) is on the reactions of HO₂[•], a product of H₂O₂ oxidation by Ce(IV). Some

of the radicals may either disproportionate to give H_2O_2 and O_2 , having a limited effect on oscillations. Some may reduce iodate, leading to faster production of IMA and I_2MA , thus shorter length of the oscillatory period and shorter delay to transition.



The radical IO_2^\bullet is a key intermediate in the proposed reaction mechanisms [16–18]. The metal catalyst supposedly is oxidized by IO_2^\bullet then reduced by H_2O_2 via the reactions



For cerium, only a one electron exchange is possible. Manganese has several possible oxidation states; Mn(III) species were identified by EPR [19] in the BR oscillator but Mn(IV) has not been reported in the oscillator. The forward rate of reaction (M2) with Mn(III) is $3.2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ [20]. The comparable rate, with Ce(IV) in 0.8 M H_2SO_4 , is $1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ [21]. Both are fast enough to keep (M1) very low. The trends

of oscillator characteristics with concentration and the effects of inhibitors are qualitatively similar for both metal catalysts.

Conclusion

Cerium is an effective catalyst for BR oscillators over a wide range of component concentrations. Because of the precipitation of $\text{Ce}_2(\text{C}_2\text{O}_4)_3$, the oscillating mixture becomes heterogeneous, and some of the free Ce(III) is removed. Ce(IV) is also an effective catalyst, although $\text{Ce}(\text{IO}_3)_4$ may precipitate immediately, and cerium-iodate complexes require some time for the cerium to be reduced to Ce(III).

At low limiting concentrations for oscillations, cerium is roughly three times more effective than manganese.

Essentially all the comparisons of Ce-based systems with Mn-based systems (trends with concentrations of all components, effects of inhibitors) showed qualitative similarity. The reduction potentials of Ce(IV) and Mn(III) are both in the neighborhood of 1.4 to 1.6 V. We believe that these oxidized forms are key intermediates in the metal-catalyzed BR oscillator.

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