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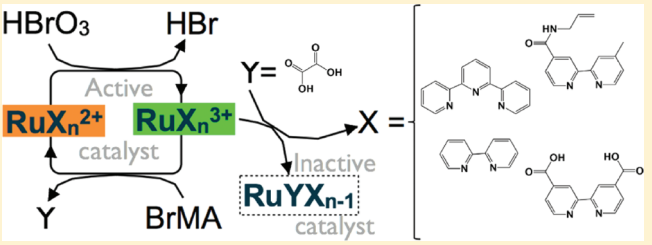
Terpyridine- and Bipyridine-Based Ruthenium Complexes as Catalysts for the Belousov−Zhabotinsky Reaction

Jorge Delgado,† Ye Zhang,† Bing Xu, and Irving R. Epstein*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02454-9110, United States

ABSTRACT: We report the successful use of Ru(II)(terpy)$_2$ (**1**, terpy = 2,2′:6′,2″-terpyridine) as a catalyst in the Belousov−Zhabotinsky (BZ) oscillating chemical reaction. We also examine several additional Ru(II) complexes, Ru(II)(bipy)$_2$(L′)$_2$ (**2**, L′ = 4-pyridinecarboxylic acid; bipy = 2,2′-bipyridine) and Ru(II)(bipy)$_2$(L″) (**3**, L″ = 4,4′-dicarboxy-2,2′-bipy; **4**, L″ = *N*-allyl-4′-methyl-[2,2′-bipy]-4-carboxamide; **5**, L″ = bipy), for catalyzing the BZ reaction. While **2** is unable to trigger BZ oscillations, probably because of the rapid loss of L′ in a BZ solution, the other bipyridine-based Ru(II)-complexes can catalyze the BZ reaction, although their catalytic activity is adversely affected by slow ligand substitution in a BZ solution. Nevertheless, the successfully tested Ru(II)(terpy)$_2$ and Ru(II)(bipy)$_2$(L″) catalysts may provide useful building blocks for complex functional macromolecules.



1. INTRODUCTION

The Belousov−Zhabotinsky (BZ) reaction, the oxidation of an organic substrate, typically a dicarboxylic acid like malonic acid, by acidic bromate, catalyzed by metal ions or complexes, is the most studied and modeled nonlinear chemical oscillator.[1] The direct oxidation of malonic acid by acidic bromate is extremely slow and monotonic, but in the presence of a suitable catalyst, like tris(2,2′-bipyridyl)-ruthenium(II) (Ru(II)(bipy)$_3$) (**5**), the reaction proceeds via cyclic oxidation and reduction of the catalyst by oxybromine species like bromous acid/bromine dioxide and bromomalonic acid, respectively.[2] Periodic production and consumption of bromous acid and bromide also take place during the BZ reaction. Despite the large number of Ru(II)-complexes described in the literature with pyridine (py), 2,2′-bipyridine (bipy), or terpyridine (terpy)-based ligands,[3,4] only one other ruthenium complex, tris(1,10-phenanthroline)-ruthenium(II) (Ru(II)(phen)$_3$), has been characterized as an effective BZ catalyst.[5] Interest in exploring similar Ru(II)-complexes as BZ catalysts arises from the fact that such species are typically photosensitive and can be incorporated into polymers, gels, or large supramolecular aggregates. Once these ligands coordinate with ruthenium, they can form materials with electroconductive, chemomechanical, or hydrophobic−hydrophilic-sensitive properties. An important example is a chemomechanically active poly isopropyl−acrylamide−Ru (PNIPAm−Ru) gel,[6] where one bipy of the original Ru(II)(bipy)$_3$ is replaced by a 4-methyl-4′-vinyl-2,2′-bipyridine. The vinyl group is then employed to covalently link the Ru(II)-center to the gel. The Ru(II)-center in the gel acts as a BZ catalyst, and the gel exhibits, in an acidic solution of bromate and malonic acid, self-sustained mechanical oscillations.

Another reaction of interest is the reported equilibrium:[7] Ru(II)(terpy)$_2$ ↔ Ru(III)(terpy) + terpy + e$^-$. Computer simulations[8] and experiments on a recently synthesized terpyridine-terminated poly(ethylene glycol) polymer[9] suggest that a gel based on a polymer with terpy-linked catalytically active ligands will undergo periodic chemo-mechanical oscillations as the density of cross-links oscillates in response to the periodic coordination and release of the Ru−BZ catalytic centers caused by the Ru(II)/Ru(III) redox oscillations. Experimental verification that unlinked Ru(II)(terpy)$_2$ indeed catalyzes the BZ reaction remains to be accomplished.

Studies of BZ catalysts[10] suggest that they must be capable of single electron transfer and have two stable oxidation states with a potential (E^0) between 1.0 and 1.5 V. In addition, E^0 is critical for understanding the BZ kinetics.[11] For instance, Rovinsky et al.[12] cite the difference between the potentials of Ce(III)/Ce(IV) and Ru(II)/Ru(III) to explain why the reaction Ru(III)(bipy)$_3$ + BrMA ↔ Ru(II)(bipy)$_3$ + BrMA· + H$^+$ is reversible, whereas the corresponding cerium reaction is irreversible. This reversible equilibrium explains the difference in shape of the BZ oscillations between the cerium-[11] and Ru(bipy)$_3$-[2] or Fe(II)(phen)$_3$-[12]catalyzed reactions. Although E^0 must lie in the appropriate range for a metal or metal complex to be able to catalyze the BZ reaction, other factors, sometimes difficult to elucidate in advance, also contribute to the efficacy of a species as a BZ catalyst.

The reactivity of many Ru−bipy-based complexes of the form Ru(bipy)$_2$(L″), where L″ is a bidentate ligand, has been characterized in water/oxygen environments because of such species' strong oxidative power and easy electron transfer[13] and the instability of Ru−bipy-based complexes used for solar cells.[14] One also finds in the literature references to "unidentified" Ru-complex adducts arising from redox reactions.[15] As a

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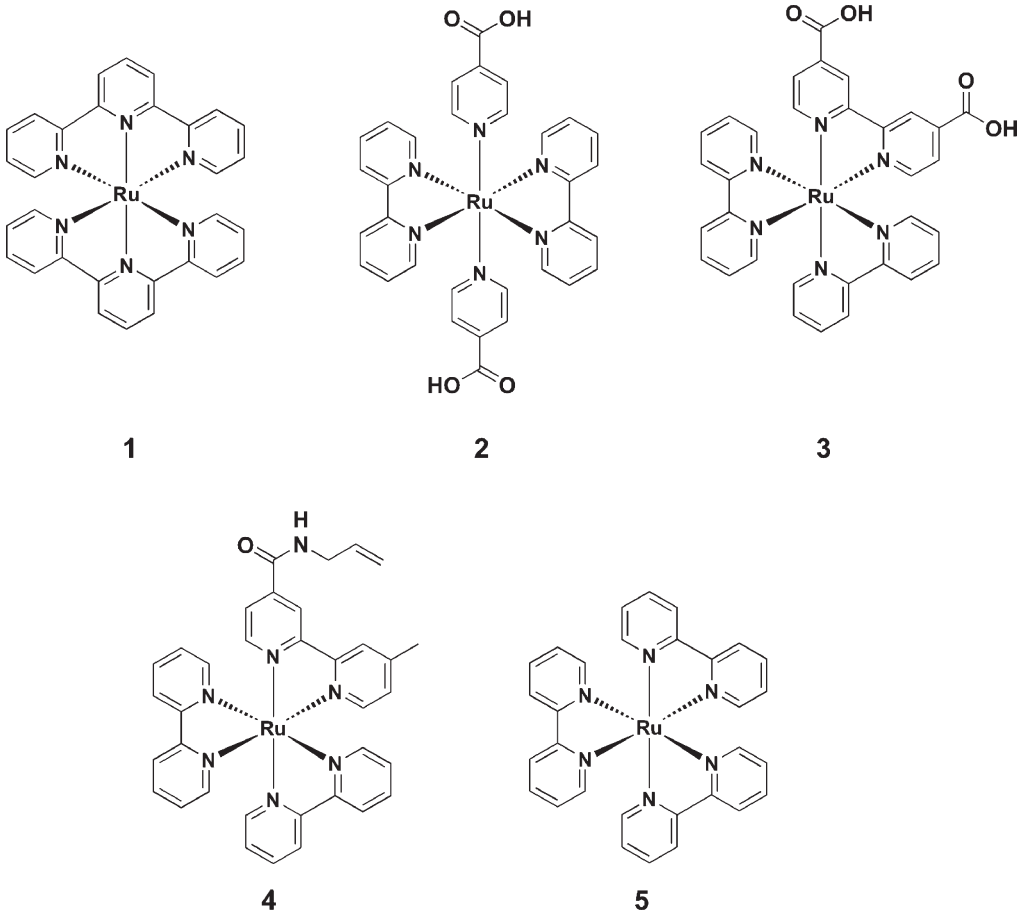

Figure 1. Ru(II)-complexes studied in this work.

consequence, it is not difficult to imagine that the same versatility of Ru(II) that allows it to form a wide variety of complexes can produce unstable or labile $Ru(bipy)_2(L'')$ species in certain environments. Formation of an insoluble Ru−bromine complex on mixing $Ru(II)(bipy)_3$ with bromine in the BZ-reaction[16] has, for example, been suggested. In addition, Ru−carboxylate complexes with citrate, oxalate, and gluconate have been reported.[17] These, frequently undesired, complexes, are difficult to characterize, and their existence is often argued for only indirectly.[16,18]

In this Article, we report the synthesis and exploration of potential BZ catalysts of the form $Ru(II)(terpy)_2$ (**1**), $Ru(II)(bipy)_2(L')_2$ (**2**), and $Ru(II)(bipy)_2(L'')$ (**3**, **4**, and **5**), where terpy = 2,2′:6′,2″-terpyridine, L′ = pyridinecarboxylic acid, and L″ = 4,4′-dicarboxy-2,2′-bipy (**3**), *N*-allyl-4′-methyl-[2,2′-bipy]-4-carboxamide (**4**), or bipy (**5**). Despite the fact that E^0 is very similar for all of the complexes synthesized, we find that only catalysts that contain exclusively bipy or terpy ligands result in BZ oscillations. $Ru(II)(bipy)_2(L')_2$ does not trigger BZ oscillations, even though it is possible to oxidize it and apparently to reduce it in the BZ environment. Facile pyridinecarboxylic acid ligand replacement in **2** likely prevents this complex from acting as a BZ catalyst. Moreover, from our examination of a wide range of conditions, we suggest that a slow bipy or terpy ligand substitution by organic derivatives of BrMA occurs as well in $Ru(II)(bipy)_2(L'')$ and $Ru(II)(terpy)_2$ catalysts during the BZ reaction, especially at high malonic acid (MA) concentrations. This substitution, which is apparently irreversible, ultimately renders the catalyst ineffective in generating BZ oscillations and can be observed even in $Ru(II)(bipy)_3$ (**5**). In light of these results, we discuss possible ligand and E^0 modifications in the catalyst over the course of the BZ reaction.

2. EXPERIMENTAL SECTION

2.1. General Synthetic Methods and Materials. The chemical structures of the Ru-molecules used here are shown in Figure 1. Complexes **1**−**4** were synthesized by us. In the syntheses, the organic solvents methylene chloride, methanol, and chloroform were HPLC grade (Fisher). Ethanol and acetone were GC grade (Fisher). Anhydrous DMF, 4,4′-dimethyl-2,2′-bipyridine (99.5%), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (99.0%), allylamine (99.0%), and dichloro(*p*-cymene)ruthenium(II) dimer were purchased from Sigma-Aldrich. Hydroxybenzotriazole (HOBt) was purchased from GL Biochem. All reagents were used without further purification. NMR spectra were recorded with a 400 MHz Varian NMR spectrometer.

Ru(II)(2,2′:6′,2″-Terpyridine)$_2$ (***1***). To a 50 mL two-neck round-bottom flask connected to a condenser charged with dichloro(*p*-cymene)-ruthenium(II) dimer (100 mg, 0.163 mmol) and 2,2′:6′,2″-terpyridine (153 mg, 0.653 mmol) we added 2 mL of distilled water and 18 mL of ethanol. Nitrogen was bubbled through the solution for 40 min. The mixture was distilled in darkness for 3 days. After the solvent was removed, the crude mixture was purified on a Sephadex-LH 20 column. The complex was obtained in 90% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.15 (d, J = 8.4 Hz, 4H), δ = 8.89 (d, J = 8.8 Hz, 4H), δ = 8.54 (t, J = 8.4 Hz,

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2H), δ = 8.03 (t, J = 8.0 Hz, 4H), δ = 7.43 (d, J = 4.8 Hz, 4H), δ = 7.27 (t, J = 6.4 Hz, 4H) ppm. An alternative method for synthesizing **1** is described in the literature.[19]

*Ru(II)(2,2′-Bipyridine)$_2$(4-pyridinecarboxylic acid)$_2$ (**2**).* Complex **2** was prepared by refluxing a deaerated aqueous solution containing *cis*-Ru(bipy)$_2$Cl$_2$·2H$_2$O and a 10-fold molar excess of isonicotinic acid under N_2 for 8 h. The deep orange-red solution was cooled and filtered. After removal of the solvent, the product was isolated and purified on a Sephadex-LH20 column using acetonitrile and methanol as eluents. **2** was obtained in 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.78 (d, J = 8.8 Hz, 2H), δ = 8.64 (t, J = 9.6 Hz, 3H), δ = 8.55−8.50 (m, 3H), δ = 8.18−8.11 (m, 3H), δ = 7.92−7.81 (m, 6H), δ = 7.72 (t, J = 6 Hz, 1H), δ = 7.60 (d, J = 5.6 Hz, 1H), δ = 7.48 (d, J = 5.6 Hz, 2H), δ = 7.35−7.26 (m, 3H) ppm. See Abruña et al.[20] for details.

*Ru(II)(2,2′-Bipyridine)$_2$(4,4′-dicarboxy-2,2′-bipyridine) (**3**).* A mixture of 2,2′-bipyridine-4,4′-dicarboxylic acid and *cis*-bis(2,2′-bipyridine)-ruthenium(II) dichloride dihydrate in 80% acetic acid was stirred for 5 h under reflux, and the solvent was removed in vacuo. The resulting dark red solid was dissolved in a minimal amount of ethanol in the presence of concentrated hydrochloric acid. The solution was filtered through Celite, the filtrate was concentrated, and the diacid was precipitated by gradual addition of diethyl ether. After the mixture was stirred for 1 h at room temperature, the dark red product was separated, washed with diethyl ether, and dried at 60 °C. The yield was 90%. ^{1}H NMR (DMSO-d_6): δ 9.24 (s, 2H), 8.86 (m, 4H), 8.18 (m, 4H), 7.91(d, J = 5.8 Hz, 2H), 7.86 (dd, J = 5.8 and 1.1 Hz, 2H), 7.76−7.71 (m, 4H), 7.57−7.48 (m, 4H). See Beer et al.[21] for details.

*Ru(II)(2,2′-Bipyridine)$_2$(N-allyl-4′-methyl-[2,2′-bipyridine]-4-carboxamide) (**4**).* To a 25 mL round-bottom flask charged with 4′-methyl-[2,2′-bipyridine]-4-carboxylic acid (80 mg, 0.374 mmol), HOBt (129 mg, 0.75 mmol), and DCC (310 mg, 1.5 mmol) we added 8 mL of DMF. The mixture was stirred at room temperature for 1 h. Next, allylamine (0.056 mL, 0.75 mmol) was added to the mixture. The reaction was stirred at room temperature until no spot of 4′-methyl-[2,2′-bipyridine]-4-carboxylic acid showed on a TLC plate. After removal of the solvent, the crude product was purified by column chromatography using DCM and methanol as eluent. The target compound, *N*-allyl-4′-methyl-[2,2′-bipyridine]-4-carboxamide, was obtained in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 4.8 Hz, 1H), δ = 8.61 (s, 1H), δ = 8.54 (d, J = 4.8 Hz, 1H), δ = 8.28 (s, 1H), δ = 7.80 (d, J = 4.8 Hz, 1H), δ = 7.18 (d, J = 5.2 Hz, 1H), δ = 6.55 (s, 1H), δ = 5.94 (m, 1H), δ = 5.30 (d, J = 17.2 Hz, 1H), δ = 5.22 (d, J = 9.6 Hz, 1H), δ = 4.12 (t, J = 5.6 Hz, 2H), δ = 2.46 (s, 3H) ppm.

A 50 mL two-neck round-bottom flask connected to a condenser was charged with *N*-allyl-4′-methyl-[2,2′-bipyridine]-4-carboxamide (64 mg, 0.253 mmol) and dichloro-bis(dipyridyl)-ruthenium(II) dihydrate (131.5 mg, 0.253 mmol). Distilled water (2 mL) and ethanol (18 mL) were added to the flask. Nitrogen was bubbled through the solution for 40 min. The reaction mixture was refluxed in the dark for 3 days. After the solvent was removed, the crude product was purified on a Sephadex LH20 column. Methanol and acetonitrile were applied as eluents. Pure complex was obtained in 90% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.73 (s, 1H), δ = 9.50 (s, 1H), δ = 9.07 (s, 1H), δ = 8.88 (d, J = 8.8 Hz, 4H), δ = 8.18 (t, J = 7.6 Hz, 4H), δ = 7.88 (s, 2H), δ = 7.78 (d, J = 5.2 Hz, 1H), δ = 7.73 (d, J = 4.8 Hz, 3H), δ = 7.58−7.49 (m, 5H), δ = 7.41 (d, J = 5.2 Hz, 1H), δ = 5.96−5.87 (m, 1H), δ = 5.21 (d, J = 17.2 Hz, 1H), δ = 5.11 (d, J = 10.0 Hz, 1H), δ = 3.96 (t, J = 4.8 Hz, 2H), δ = 2.54 (s, 3H) ppm.

2.2. BZ Experiments. Freshly prepared aqueous solutions of the various Ru(II) complexes were used for making the BZ solution. Commercially available analytical grade reagents, sodium bromate, MA, sulfuric acid, and Ru(bipy)$_3$Cl$_2$ hexahydrate, were used without further purification. The BZ reaction was performed in a closed system under constant stirring, using a spectrophotometric cell (1 cm optical path) loaded with sodium bromate, sulfuric acid, MA, and the chosen Ru(II) species in concentrations as detailed in the text. The BZ oscillations were followed by vis-spectrophotometry (Vernier Spect., Ocean Optics Inc.) at 20 °C and open to the air. Before initiation of the BZ reaction, the vis-spectrum of the Ru(II)-complex was obtained, and a convenient wavelength (λ) at or near the Ru(II)-to-bipy charge transfer peak,[22] generally around 480 nm, was chosen for recording the absorbance at 1 s intervals. From the absorbance versus time records, the oscillatory amplitude, Ψ, and period, τ, as a function of time were computed. For obtaining the UV−vis spectrum of an Ru(II)-complex before and after the BZ reaction, the solution was placed in a spectrophotometric cell (1 cm optical path) in a UV-1650 PC spectrophotometer (Shimadzu).

3. RESULTS AND DISCUSSION

With the exception of molecule **2**, all of the synthesized Ru(II)-complexes catalyzed BZ oscillations. Ru(II)-complexes were tested as BZ catalysts using [BrO_3^-] ≈ 300 mM, [H_2SO_4] ≈ 1 M, and two different [MA], ∼50 or 300 mM, referred to here as low and high [MA], respectively. Figure 2a and b shows typical experiments at low [MA] for catalysts **1**, a terpy-based catalyst, and for **4**, a bipy-based catalyst with a carboxamide group at the *para*-position of one of the bipy ligands, respectively. Despite the evident structural differences between the Ru-ligands, for all the successful Ru(II)−BZ catalysts tested at low [MA], after an induction time shorter than 5 min for all of the catalysts (not shown), the period, τ, and the amplitude, Ψ, of the BZ oscillations increase in time up to a maximum, and then Ψ decreases until the oscillations cease. After the last oscillation, the ruthenium complex remains in its oxidized form, referred to here as Ru(III). In these experiments at low [MA], depletion of MA appears to be responsible for the termination of oscillatory behavior, because it is possible to obtain a similar set of oscillations by adding MA at a level comparable to its initial concentration. Once MA is depleted, at least five new series of oscillations with similar amplitude can be obtained by adding [MA] ≤ 50 mM, as seen in Figure 2b. Note that if the entire amount of MA used in this last experiment were added initially, [MA] ≈ 250 mM would approach the aforementioned high [MA] regime. The regeneration of oscillations by adding more MA was also observed with catalysts **1** and **3**.

Oscillatory behavior at high [MA] with any of the successful Ru(II)−BZ catalysts produces larger amplitude oscillations, as shown in Figure 3a (cf., Figure 2a). Depending on the catalyst, a short induction period of small amplitude oscillations may occur, as seen in Figure 3b for **4**. Because the end of the experiment seems to be near the reduced state of the catalyst, that is, at high absorbance, we attempted, with limited success, to regenerate large amplitude oscillations by adding more bromate. One such trial is shown in Figure 3b for catalyst **4**. Adding bromate increases the amplitude to about one-half its initial value in the earlier series of oscillations, but after about 6 h the oscillations are

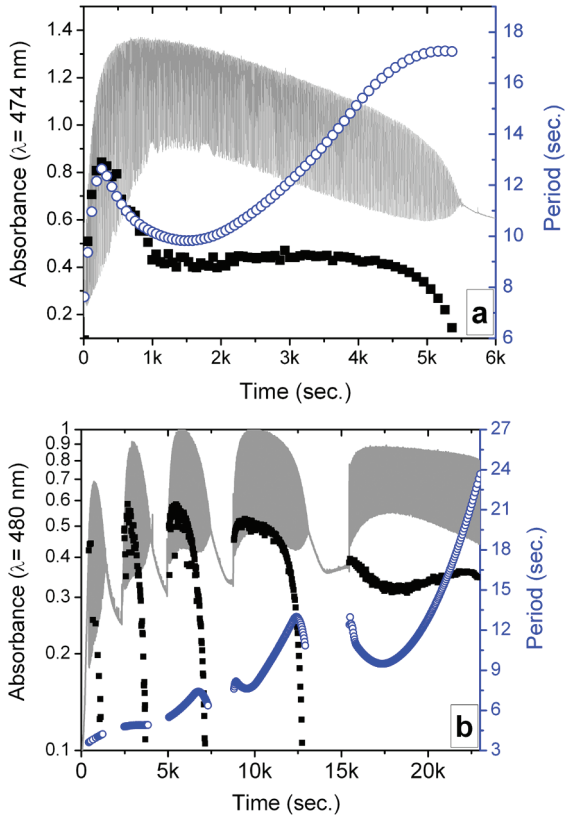

Figure 2. BZ oscillations at low [MA] with catalysts **1** (a) and **4** (b). Gray curves show absorbance of Ru(II) species versus time; "■" are amplitude (Ψ) of oscillation, and "○" are period, τ, with scale on the right-hand ordinate. Reactant concentrations: (a) [MA] = 50 mM, [BrO_3^-] = 200 mM, [H_2SO_4] = 1 M, [**1**] = 0.17 mM; (b) [MA] = 60 mM, [BrO_3^-] = 200 mM, [H_2SO_4] = 750 mM, [**4**] = 0.17 mM. The second and subsequent groups of oscillations in (b) were initiated by adding a solution containing [MA] = 2 M, [BrO_3^-] = 200 mM, and [H_2SO_4] = 750 mM. Taking into account dilution, the added [MA] corresponds to 50, 48, 47, and 46 mM for the four additions. The formal concentration of **4** at the end of the experiment is 0.15 mM.

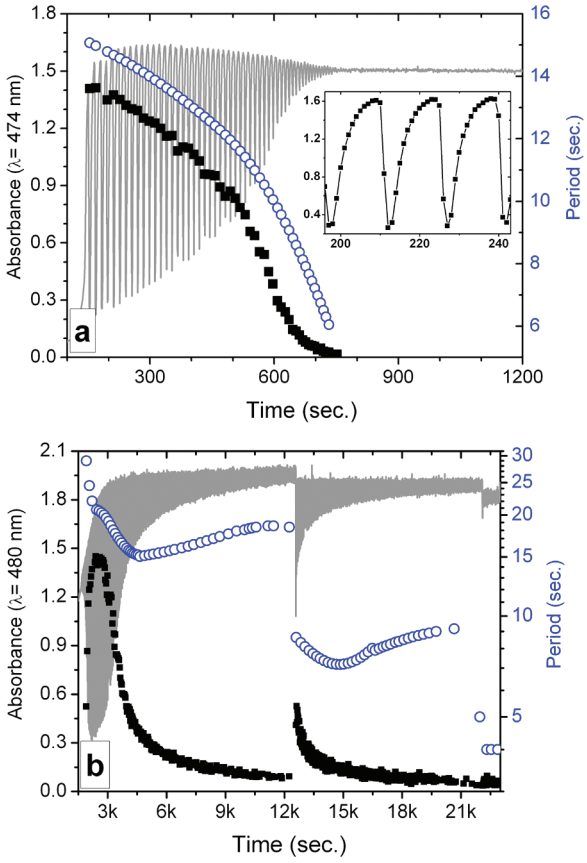

Figure 3. BZ oscillations at high [MA] with catalysts **1** (a) and **4** (b). Gray curves and inset in (a) show absorbance of Ru(II) species versus time; "■" are amplitude (Ψ) of oscillation, and "○" are period (τ) with scale on the right-hand ordinate and abscissa. Axes of the inset in (a) correspond with left-hand ordinate and abscissa. Reactant concentrations: (a) [MA] = 450 mM, [BrO_3^-] = 200 mM, [H_2SO_4] = 750 mM, [**1**] = 0.17 mM; (b) [MA] = 460 mM, [BrO_3^-] = 200 mM, [H_2SO_4] = 1.4 M, [**4**] = 0.16 mM. At about 12 000 and 22 000 s, both [BrO_3^-] and [MA] were increased by 200 and 250 mM, respectively.

again small, and additional bromate or MA fails to regenerate large amplitude oscillations, as observed in a third trial at ca. 22 000 s in Figure 3b. In this experiment, [MA] was increased together with [BrO_3^-], so that the cessation of oscillations cannot be accounted for by depletion of MA. Note that, for a similar experimental time, ~22 000 s, oscillations in Figure 2b, where roughly the same total [MA] is added, but the maximum level never rises above about 50 mM, we still have an amplitude similar to that at the beginning of the experiment. For high [MA], once oscillations cease only the addition of more catalyst is able to retrigger large amplitude oscillations, as observed in Figure 4. In this experiment, although addition of fresh catalyst **5** at ca. 19 000 s restores Ψ to about 2/3 of its value in the early stages, the oscillations after this time are not as smooth as they were initially, as shown in the lower panel in this figure. Apparently, at high [MA], it is not possible to regain smooth oscillations in our closed system for longer times.

In an attempt to gain insight into the differences between the behaviors at high and low [MA], we performed the experiment illustrated in Figure 5. A solution containing complex **3**, 1.0 M sulfuric acid, and 300 mM MA was stirred for 9 h. After this time, we added [BrO_3^-] = 160 mM to initiate the BZ oscillations. The oscillatory behavior was the same as that observed in a BZ solution of the same composition with the bromate added initially to the other reactants. This result implies that MA does not react directly with the Ru(II)−BZ catalyst, but rather that some brominated MA derivative produced during the BZ reaction, and/or ligand substitution between MA and a bipy in the Ru(III)−BZ catalyst, leads to the loss of catalytic activity. In addition, although Ru−Br complexes are usually insoluble in water,[16,17] we never observed the formation of precipitates in our reactions, nor could we detect them at the end of the experiments. Introduction of high levels of [MA] at any time during the reaction eventually lowers irreversibly the amplitude of oscillation as shown in Figure 6a and b for catalysts **3** and **4**, respectively.

A hint about how high [MA] can destroy the activity of Ru(II)−BZ catalysts was obtained during our unsuccessful attempts to use **2** as a BZ catalyst. In acetonitrile (AN), Ru(II)-$(bipy)_2(py)_2$, a complex very similar to **2**, has a half-wave Ru(III)/Ru(II) reduction potential ($E_{1/2}$) of −1.28 V.[23] The same authors report $E_{1/2}$ = −1.30 V for **5**. It is known that additional *N-para*-subtituents in the bipyridine rings do not appreciably modify the redox potential of a Ru(II)-complex.[22] Also, the reduction and oxidation peak potentials (redox E_p) for

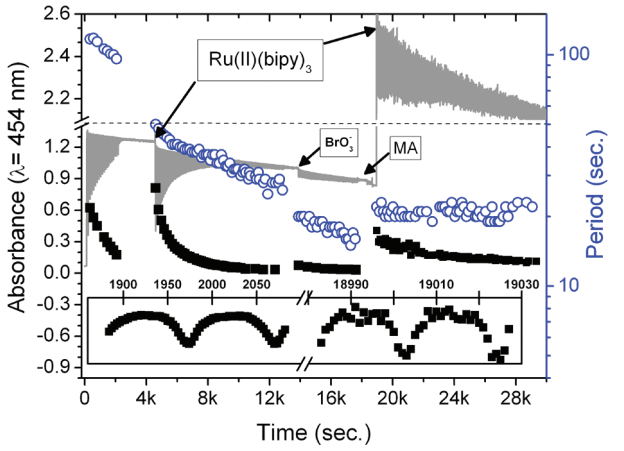

Figure 4. BZ oscillations obtained with catalyst **5**. Initial concentrations: [MA] = 200 mM, [BrO_3^-] = 10 mM, [H_2SO_4] = 700 mM, and [**5**] = 0.1 mM. At ca. 4600 and 19 000 s, [**5**] was increased by 0.1 mM. At ca. 14 000 and ca. 18 000 s, [BrO_3^-] and [MA] were increased by 10 and 57 mM, respectively. The lower panel shows the shape of oscillations of similar amplitude at two different times during the experiment: near the beginning (1885 s) and after the second addition of more catalyst (18 980 s).

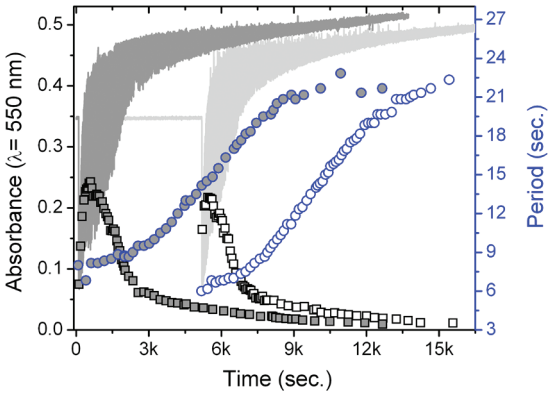

Figure 5. Oscillatory traces from two experiments with catalyst **3**. Initial concentrations: [MA] = 300 mM, [BrO_3^-] = 160 mM, [H_2SO_4] = 1 M, and [**3**] = 0.4 mM. In the experiment corresponding to the trace on the left, all components were mixed initially. To obtain the trace at the right, which is arbitrarily displaced in time for clarity, a solution with MA, sulfuric acid, and catalyst **3** was stirred for 9 h. After this time, BrO_3^- was added to initiate the BZ reaction. For both traces, squares are amplitude (Ψ) of oscillation, and circles are period (τ) with scale on the right-hand ordinate.

5 and **1** in AN are quite similar:[15] 1.35 and −1.33 V redox E_p for **5** versus 1.28 and −1.43 V redox E_p for **1**. There is thus no evident thermodynamic reason why **2** should not act as a BZ catalyst. Also, a 0.35 M solution of bromate in 1 M sulfuric or nitric acid is able to oxidize **2**, probably to the Ru(III) form of the complex, because the solution becomes green (the **1**, **3**, **4**, and **5** Ru(III)-complexes are green). Once MA is added, this green complex appears to be slowly reduced to **2**, the original Ru(II)-complex, as observed in Figure 7, but this reduction is irreversible and does not produce oscillations between the Ru(II) and Ru(III) forms of the complex. Attempts to obtain oscillations with different concentrations of the catalyst, lower bromate, and/or higher acidity also failed.

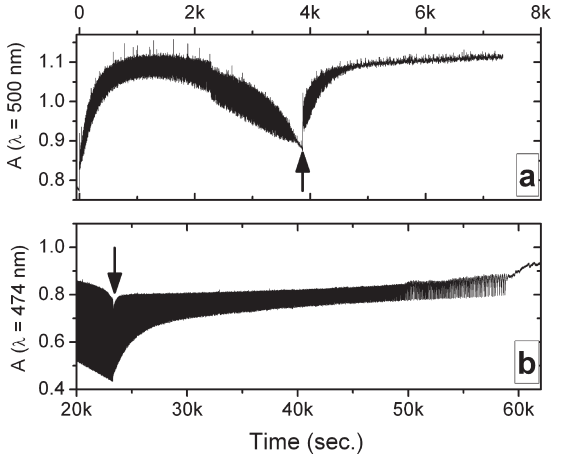

Figure 6. Oscillatory traces with catalysts **3** (a) and **4** (b). (a) BZ oscillatory traces obtained with **3** with initial concentrations [MA] = 50 mM, [BrO_3^-] = 300 mM, [H_2SO_4] = 1.3 M, and [**3**] = 0.19 mM. At the time marked by the arrow, [MA] was increased by 250 mM. (b) Continuation of Figure 2b. At the time marked by the arrow, [MA] was increased by 380 mM.

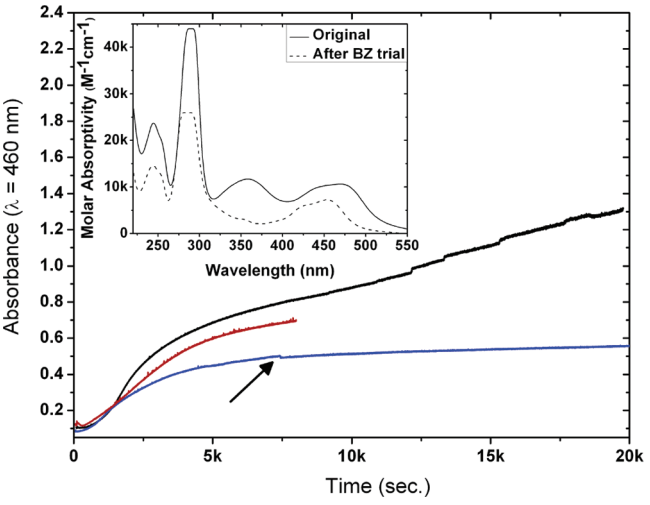

Figure 7. Attempts to generate BZ oscillations using complex **2** and [MA] = 20, 40, and 300 mM in the upper, lower, and middle traces, respectively. In all cases, MA was added at $t = 0$ to a solution previously loaded with BrO_3^-, H_2SO_4, and **2**. [BrO_3^-] = 276 mM, [H_2SO_4] = 920 mM, and [**2**] = 0.12 mM in all the experiments. At the time marked by the arrow in the middle trace, [BrO_3^-] was increased by 300 mM. [**2**], formal after this time, was 0.11 mM. Inset shows spectra of the original complex **2** (solid line) and of the solution 1 week after the end of the unsuccessful BZ experiment (dashed line).

From the UV−vis spectra taken before and after the BZ reaction, shown in the inset of Figure 7, we obtained evidence of 4-pyridinecarboxylic acid substitution in the Ru coordination sphere: The peak at $\lambda < 300$ nm corresponds to intraligand $\pi-\pi^*$ bipy transitions,[24] while the band at ~470 nm corresponds to metal-to-ligand charge transfer (MLCT) for bipy.[22] The peak at 360 nm is an intraligand $\pi-\pi^*$ bipy transition observed in particular when the Ru-atom has two bipy ligands and a mono-coordinated pyridine-based ligand.[24] The lack of this peak after the BZ reaction demonstrates the removal of the 4-pyridinecarboxylic acid ligands in **2**. Because the E^0 of **2** is similar to that of

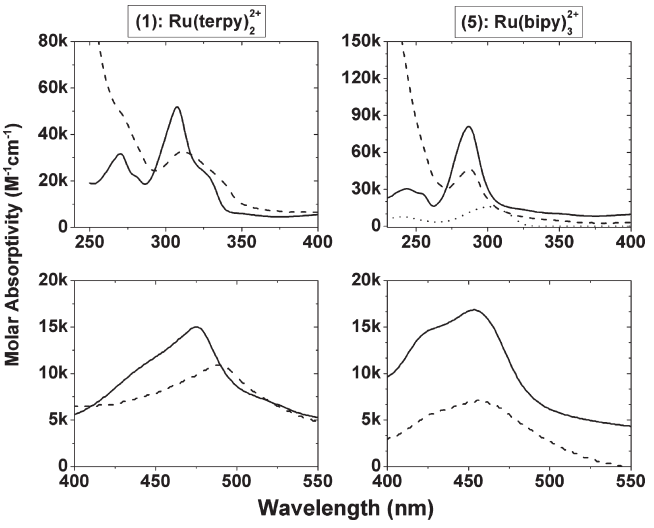

Figure 8. Molar absorptivity of BZ solutions containing **1** (left) and **5** (right) before and after reaction at high [MA]. Solid line, initial spectra; dashed line, spectra from solutions at least 1 week after the end of the BZ experiment. The dotted line in the upper right plot shows the molar absorptivity of free bipy in 1 M H_2SO_4 solution. The spectrum with **1** after reaction was taken after the experiment shown in Figure 3a. For the BZ system with **5**, [MA] = 255 mM, [BrO_3^-] = 200 mM, [H_2SO_4] = 750 mM, and [**5**] = 0.19 mM.

the other Ru(II)-complexes, we infer that during the reduction of **2**, a new Ru-complex is formed, which is not oxidized by BrO_3^-, as observed in Figure 7.

It is known that Ru(II)-py-based ligands are labile toward py-ligand substitution,[25] and that substitution of ligands in the Ru-coordination sphere can shift the redox E_p potentials of the Ru(II)/Ru(III) redox pair by as much as 0.7 V.[26] The above observations suggest why it is not possible to use **2** as a BZ catalyst: once **2** is oxidized by acidic bromate to the Ru(III) form, it effectively oxidizes BrMA, and a product of the BrMA oxidation, or perhaps MA itself, quickly replaces the labile 4-pyridinecarboxylic acid *cis*-ligands in **2**, producing a new, kinetically inert redox complex or a complex with an E^0 such that it cannot be directly oxidized by bromate. Our results suggest the likelihood of irreversible damage of all Ru(II)−BZ catalysts, including Ru(II)(bipy)$_3$, when the BZ reaction is carried out at sufficiently high [MA]. This phenomenon has not previously been reported.

The decomposition of these species may be difficult to detect, because in many Ru−bipy-based catalysts the main absorbance peak in the vis-spectrum, the MLCT peak at ∼450 nm, does not undergo a shift after the BZ reaction at high [MA], as illustrated for **5** in Figure 8. The **3** and **4** MLCT peaks also remain unshifted. Interestingly, it is known that the replacement of one bipy-ligand in Ru(II)(bipy)$_3$ by many different kinds of ligands, including halogens, π-basic ligands, and py, does not shift the MLCT peak.[27] Only in the case of **1**, as shown in Figure 8, do we observe a clear shift in the MLCT peak, from λ_{max} = 475 nm to λ_{max} = 490 nm, following the BZ reaction at high [MA], evidencing formation of a new species. In the literature, the MLCT peak for complexes of the form Ru(II)(terpy)L(dmso), where L = oxalate or malonate, is shifted to lower energies with respect to the MLCT peak of complexes of the same form where L = bipy or 2-pyridine carboxylate.[28] However, the most important differences between the spectra of the Ru(II)-complexes before and after the high [MA] BZ reaction occur in the absorbance peaks at 240−270 nm and at 290−310 nm. The intensity of these bands, which correspond to an intraligand $\pi-\pi^*$ bipy transition, decreases dramatically after the BZ reaction at high [MA], as seen in Figure 8 for **5** and for **1**. The molar absorptivity of intraligand $\pi-\pi^*$ bipy transitions is enhanced when bipy coordinates with ruthenium[29] and decreases when the bipy ligand is not coordinated,[27] as observed in Figure 8. We therefore conclude that some organic derivative of BrMA oxidation slowly replaces bipy and terpy ligands during the course of the BZ reaction at high [MA].

The BZ reaction generates a variety of MA derivatives.[30,31] Thus, there are many candidates to replace the ligands initially hosted in our Ru(II)-complexes. One likely possibility is oxalate (OX), a common intermediate in the BZ reaction.[30] Like bipy, OX is a bidentate ligand that can form a 1:3 complex with Ru(III).[17] Oxalate can also form a complex replacing chlorine in Ru(III)Cl$_2$(bipy)$_2$, where oxalate has a dual effect: as a chelating agent and as a reductant of Ru to the +2 state.[32] A high concentration of OX in a Fe(II)(phen)$_3$-catalyzed BZ batch reaction at intermediate times has been reported,[31] as well as high concentrations of mesoxalic and tartronic acids. Because the E^0 values of Fe(II)(phen)$_3$ and Ru(II)(bipy)$_3$ are similar, we may expect that the BZ mechanism with these catalysts or any other Ru(II) catalyst having a similar E^0 is also similar.[2] Accumulation of these dicarboxylic acid intermediates thus probably occurs in our experiments, providing candidates to replace some or perhaps all of the bipy and terpy ligands in the Ru-complexes. When a high [OX] is added under our reaction conditions, production of CO_2 bubbles[30] hampers spectrophotometric recording of BZ oscillations, although we can easily observe changes in the color of the solution. In experiments using **5**, [OX] between 100 and 200 mM, and low [MA], low amplitude oscillations that become smaller and more erratic with time can be observed. At the end of these experiments, the color of the solution is quite different from the usual deep-orange associated with Ru−bipy-based complexes. The final colors range from pale orange to pale pink, which matches the pink color reported for the Ru(II)(bipy)$_2$OX complex.[32] The spectra of two solutions after the **5**-catalyzed BZ reaction in the presence of OX are shown in Figure 9a. Although these spectra do not unambiguously establish the existence of Ru−oxalate complexes, in both cases, the intensity of the MLCT peak for **5** at ca. 450 nm decreases, suggesting replacement of at least one of the bipy ligands on Ru, probably by OX or by carboxylic acid derivatives. We also tested the replacement of pyridinecarboxylic acid ligands by OX in complex **2**. Figure 9b shows the extinction coefficient for a solution of **2** stirred at 40 °C for 2 days in the presence of [OX] = 0.4 M. As previously seen in the inset of Figure 7, the peak at 360 nm, arising from bipy when py ligands are present, vanishes. This result implies replacement of the pyridinecarboxylic acid at the metal center, and accordingly the MLCT peak for bipy also decreases.

The above observations suggest why the destruction of the Ru(II)−BZ catalyst is greatly enhanced at high [MA]. Dicarboxylic acids, like OX, are eliminated only via direct oxidation by oxybromine molecules.[30,31] The consumption of these dicarboxylic acids, which can replace bipy ligands in the Ru-catalyst, occurs sufficiently rapidly when they are produced in low concentrations, that is, at low [MA] and high [BrO_3^-], preserving the catalyst activity. However, at sufficiently high [MA], this removal is not fast enough, and the Ru−BZ catalyst is deactivated. Here, we have illustrated how a high [OX] can deactivate

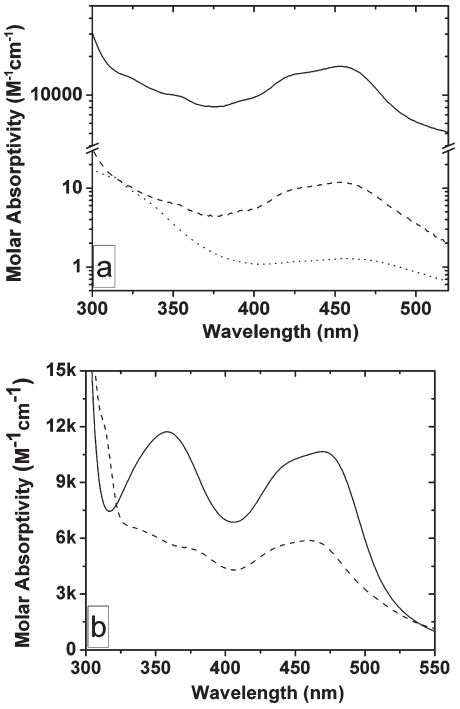

Figure 9. (a) Molar absorptivity of BZ solutions containing **5** before and after oscillations during which a high [OX] was present. BZ solutions had [MA] = 50 mM, [BrO_3^-] = 60 mM, [H_2SO_4] = 700 mM, [**5**] = 0.1 mM, [OX] = 200 mM (dashed line), and 100 mM (dotted line). Solid line is the original spectrum of **5**. (b) Dashed line: Molar absorptivity of **2** after 48 h of reflux in the presence of [OX] = 0.4 M. Solid line: Original spectrum of **2**.

5. Similar studies to identify other possible candidates among the species generated from MA for bipy replacement in the BZ reaction are necessary. Ru−carboxyl complexes, however, equilibrate slowly,[18] or can decompose easily,[28,33] which may make it difficult to characterize the precise composition of the Ru-complex(es) formed in the BZ reaction.

Our results demonstrate that bipy-based Ru(II)-complexes are far more stable in a BZ batch solution than are py-based Ru(II)-complexes. In general, ligands with more coordination sites should produce more stable complexes by virtue of the chelate effect, so that a terpy-based Ru(II)-complex should be more stable than a bipy-based one. However, the stability of Ru(II)$(terpy)_2$ versus that of a bipy-based Ru(II)-complex may not follow this rule because of the possible equilibrium:[7] Ru(II)-$(terpy)_2$ ↔ Ru(III)(terpy) + terpy + e^-. Our results with py (complex **2**) and bipy-based complexes (complexes **3**, **4**, **5**) suggest that once a dicarboxylic acid replaces a ligand in these Ru-complexes, this replacement is not reversible.

4. CONCLUSIONS

We have demonstrated for the first time that Ru(II)$(terpy)_2$ (**1**), a species suggested as the basis for chemomechanically active polymer gels,[8] can be used as a BZ catalyst. In contrast, we found that Ru(II)−py-based complexes are not effective as BZ catalysts, probably because of rapid ligand exchange during their reduction by BrMA. We have also obtained evidence of the slow displacement of bipy and terpy in Ru(II)-catalysts during a BZ batch reaction at high [MA]. The Ru-complexes generated by this substitution may be incapable of catalyzing the BZ reaction either for thermodynamic reasons, that is, E^0 is no longer in the appropriate range, or for kinetic reasons; for example, the new complex undergoes a conformational change between its oxidized and reduced states that renders it unsuitable for "fast redox" reactions.[13] If the BZ reaction coupled to redox-sensitive polymers is to be used as a building block for actuators, sensors, and other practical devices,[34] it is essential to understand (and overcome or control) the factors that curtail the lifetime of the catalyst. Further experiments, perhaps involving the introduction of different carboxylic compounds into BZ reaction mixtures as we did here with oxalic acid, may shed more light on this important question. Nonetheless, our finding that a variety of Ru(II)bipy and terpy-based catalysts support oscillatory behavior in the BZ reaction is encouraging for the future development of Ru-containing macromolecules for use in novel applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: epstein@brandeis.edu.

Author Contributions

†These authors contributed equally to this work.

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