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Review

Electron transfer triggered sulfoxide isomerization in ruthenium and osmium complexes

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Contents

Abstract

The background and achievements in the growing field of electron-transfer triggered sulfoxide isomerizations is reviewed. Starting with the original electrochemical investigations by Taube, followed by the seminal investigations by Deutsch and Meyer and concluding with the picosecond transient absorption measurements of the direct excited state S → O isomerization, this review highlights these important contributions to the field. The remarkable photochemistry exhibited by certain ruthenium sulfoxide complexes is contrasted with the more well-known medicinal chemistry of ruthenium-halo-sulfoxide complexes. This chemistry is also compared to the photochemistry of metal nitrosyl complexes.
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1. Introduction

In this journal in 2006, Bitterwolf reviewed the compelling story of the discovery and subsequent identification of linkage isomers of bound nitrosyl in a variety of metal complexes [1]. The investigation of these complexes, from inception to structural characterization, comprises more than 30 years. Gray and Manoharan first published the electronic spectrum of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, in 1965 and assigned the lowest energy visible transition as $d\pi\ Fe \rightarrow NO\ \pi^*$ MLCT transition despite an exceptionally weak intensity ($\varepsilon = 25\ M^{-1}\ cm^{-1}$) [2]. In the 1970s, Mössbauer studies revealed the presence of two metastable states (MS 1 and MS 2), which remained structurally uncharacterized until the careful work of Coppens in the late 1990s [3,4]. These studies found that MS 1 was best described as an isonitrosyl (O-bonded) and MS 2 as an η^2-NO or side-on bonded nitrosyl. Separately, photochemical investigations revealed different electronic spectra for MS 2, MS 1 and the ground state. Much effort by many researchers helped to elucidate these structures formed only in crystalline states at low temperature. Indeed, these complexes exhibit small quantum yields of isomerization and isomerize only at low temperatures. Interest in these compounds stems not only from basic coordination chemistry, but also in employing the metastable states in molecular information storage devices.

A similar story is unfolding with respect to linkage isomerizations of sulfoxide in transition metal complexes. A number

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of similarities exist between the two classes of compounds. Certain metal sulfoxides feature both S-bonded and O-bonded metastable states that can be formed from either electrochemical oxidation or MLCT irradiation. Despite the preparation of a growing number of complexes as well as high level calculations, the details of the reaction remain hidden. In contrast to the metastable states of nitrosyl compounds, there is little structural characterization of O-bonded isomers formed from irradiation of an S-bonded metal sulfoxide. However, the quantum yields of isomerization can be quite large and these reactions occur at room temperature in the solid state and in a variety of solvents. While the isomerization reactions are reversible, there has been little effort to use these complexes for information storage in a fashion similar to that of the nitrosyl complexes generally (e.g., nitroprusside) [5–7]. The purpose of this review is to remind the community of linkage isomers of sulfoxide as well as to highlight the more recent advances in this area.

2. Background

Most ruthenium sulfoxide complexes do not show evidence of isomerization. Indeed, there is a rich chemistry associated with mixed ligand ruthenium-halo-sulfoxide complexes that show remarkable anti-cancer activities [8–10]. The therapeutic action of these complexes is associated with hydrolysis of the halide and sulfoxide ligands. The origin of this chemistry is Wilkinson's minutes-long preparation of *cis*-$[RuCl_2(dmso)_4]$, where dmso is dimethylsulfoxide, a complex featuring three S-bonded sulfoxides and one O-bonded sulfoxide [11,12]. In contrast to the sulfoxide complexes that are the focus of this review, most of these ruthenium-halo-sulfoxide complexes exhibit a ground state ruthenium(III) ground state, are S-bonded on Ru^{2+}, Ru^{3+} and Ru^{4+} and only adopt an O-bonded configuration when in the presence of CO or other strong π-acid ligands [13–15]. Intramolecular isomerization chemistry is uncommon, though a number of exceptions are available. For example, in *mer*-$[RuCl_3(dmso)_3]$ reduction of Ru^{III} triggers the S → O isomerization of one of the bound dmso ligands [16,17]. This reactivity is dissimilar to that found for many ruthenium polypyridyl sulfoxide complexes and hints at the interesting chemistry associated with electron transfer triggered sulfoxide isomerizations. A number of comprehensive and informational review articles on ruthenium-halo-sulfoxide and their chemistry have appeared in recent years [13,18,19].

In 1982, the late Henry Taube and coworkers published a short paper describing the cyclic voltammogram of $[Ru(NH_3)_5(dmso)]^{2+}$ [20]. The compound and its vibrational spectra had been reported by Senoff et al. [21]. The voltammogram featured a remarkable apparent shift in oxidative and reductive waves associated with the $Ru^{3+/2+}$ couple that was ultimately interpreted as S → O and O → S linkage isomerization following Ru^{2+} oxidation and Ru^{3+} reduction, respectively (Fig. 1). Indeed, the difference in the S-bonded ($E^{\circ\prime} = 1.0$ V vs. NHE) and O-bonded ($E^{\circ\prime} = 0.1$ V vs. NHE) $Ru^{3+/2+}$ couples is ∼900 mV. The large, positive $E^{\circ\prime}$ exhibited by the ruthenium S-bonded sulfoxide is remarkable. For comparison, $E^{\circ\prime}$ for $[Ru(NH_3)_5(py)]^{2+}$ (py is pyridine) is 0.30 V vs. NHE, whereas

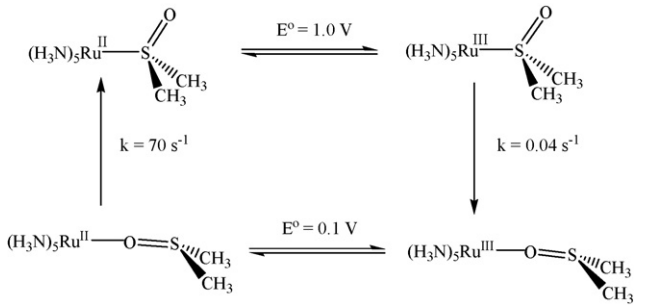

Fig. 1. Square scheme with thermodynamic and kinetic parameters describing reactivity of $[NH_3)_5Ru(dmso)]^{2+}$.

$E^{\circ\prime}$ is 0.05 V vs. NHE for $[Ru(NH_3)_6]^{2+}$ [22]. This dramatic shift in the $Ru^{3+/2+}$ couple indicates a substantial stabilization of the dπ set relative to the σ-donor NH_3 and the π-acid pyridine. Incidentally, an irreversible $Ru^{3+/2+}$ couple is observed for $[Ru(NH_3)_5(N_2)]^{2+}$ at ∼1.1 V vs. NHE [23]. Presumably, N_2 is liberated from ruthenium due to limited π-backbonding on Ru^{3+}.

Employing the equations developed by Nicholson and Shain, the isomerization rate constants were extracted assuming the now well-known ECEC square scheme mechanism [24]. The specific rate constants were $k_{S\rightarrow O} = 0.07\ s^{-1}$ on Ru^{3+} and $k_{O\rightarrow S} = 40\ s^{-1}$ on Ru^{2+} [20]. Taube did not comment on the disparity of the rate constants, despite the difference in electron count for the two complexes. This study revealed that the Ru^{3+}–S and Ru^{2+}–O bonds were thermodynamically unstable with respect to isomerization. The reactivity is determined by the preference of the polarizable, low-valent state (Ru^{II}) for the π-acceptor S-bonded sulfoxide ligand.

This work was subsequently expanded to include dinuclear complexes [25–28]. The ligand, 1,5-dithiocyclooctane, bridged two $[Ru(NH_3)_5]^{2+}$ units. Following oxidation of one of the thioether linkages, the binuclear complex featured both a reversible ($Ru–S_{thioether}$) and an irreversible couple, due to sulfoxide isomerization ($Ru–S_{sulfoxide}$). These studies demonstrated that this complex could be employed for information storage. These workers also interrogated the role of steric bulk at sulfoxide in the electron transfer triggered isomerization rates. Substitution of methyl in dmso with *s*-butyl increased $k_{S\rightarrow O}$ by a factor of 10^5 for isomerization on Ru^{3+}. These modifications did not alter $k_{O\rightarrow S}$, indicating that steric bulk is of little importance in this reaction.

In the late 1980s, the reaction chemistry and electrochemistry of ruthenium polypyridine dmso complexes was investigated [29,30]. Roeker, Meyer and coworkers discovered that reaction of $[(bpy)_2(py)Ru^{IV}=O]^{2+}$ (bpy is 2,2′-bipyridine) with dimethylsulfide gave an O-bonded Ru^{2+} dmso complex that reverted intramolecularly and spontaneously to the S-bonded isomer (Fig. 2). The O-atom transfer reaction and subsequent isomerization were characterized by UV–vis and NMR spectroscopy. Methyl resonances for both O- and S-bonded sulfoxides were observed at δ2.32 ppm and 2.61, 2.35 ppm, respectively. While the O-atom transfer reaction is rapid, the O → S isomerization occurred with a half-life ($t_{1/2}$) of 28 min, which was consistent with the results previously reported by

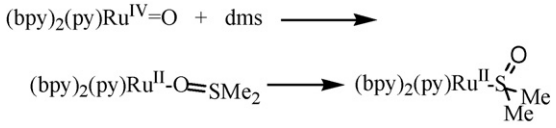

Fig. 2. Reaction of Ru^{IV}-oxo with dimethylsulfide.

Deutsch and his coworkers. Electrochemical studies revealed the O-bonded $Ru^{3+/2+}$ couple to be 1.0 V vs. SCE. A couple for the S-bonded isomer was not reported.

The electrochemistry of $[Ru(tpy)(bpy)(dmso)]^{2+}$ (tpy is 2,2′:6′,2″-terpyridine) formed following reaction of peroxide with $[Ru(tpy)(bpy)(dms)]^{2+}$ was investigated by Deutsch and coworkers. The voltammogram was qualitatively similar to that reported by Taube. He suggested that the irreversible anodic wave at 1.63 V vs. SCE was due to S → O isomerization following Ru^{2+} oxidation and that the irreversible cathodic wave was due to O → S isomerization following Ru^{3+} reduction. While the data were not fit to an ECEC square scheme mechanism, estimations of $k_{S\rightarrow O} \geq 25\ s^{-1}$ were based on the reversibility of the S-bonded couple as a function of scan rate. This paper also reports the aquation of dmso in $[Ru(tpy)(bpy)(dmso)]^{2+}$ to be of the order of $1 \times 10^{-5}\ s^{-1}$ at 50 °C. Thus, intramolecular isomerization was more rapid than bimolecular ligand substitution.

In aggregate, these important observations revealed that polypyridyl ligands could also support sulfoxide isomerizations in a manner similar to that observed for the ruthenium ammine complexes. This discovery represented a major step forward since the well-known correlation between electrochemical and photochemical parameters in this class of compounds was just being fully realized. Moreover, these studies point out that the O-bonded isomers are higher in energy relative to their S-bonded isomers. While neither group employed light during their studies, these results strongly suggest the possibility that metastable O-bonded isomers could be formed through MLCT excitation. Of course, the connection lies in recognizing that MLCT irradiation yields an oxidized metal center that appears as a $17\ e^-$ metal center with an electron in a ligand-localized π* orbital. The oxidized metal center triggers S → O isomerization.

2.1. MLCT irradiation of Ru-dmso complexes

During the 1990s a number of papers appear featuring sulfoxides bound to ruthenium complexes. One of the first of these is the electrochemical and photochemical behavior of *cis*,*cis*,*cis*- and *cis*,*cis*,*trans*-$[RuCl_2(dmso)_2(tbpy)_2]$ (tbpy is *t*-butylpyridine) [31–33]. While neither of these complexes were crystallographically characterized, ^1H NMR, IR and UV–vis absorption data support the geometry of these two complexes. They can be chromatographically separated after reaction of *t*-butylpyridine with $[RuCl_2(dmso)_4]$. The geometry of the *cis*,*cis*,*trans*-isomer places the chloride ligands in a *trans*- disposition relative to the two dmso ligands (Fig. 3), though there is some controversy regarding the geometric identification of this complex [13]. The quantum yield (Φ) for this two step process is 0.13(±0.02). Interestingly, the cyclic voltammogram reveals a reversible $Ru^{3+/2+}$ couple ($E^{\circ\prime} = 1.12$ V vs. NHE) indicating that

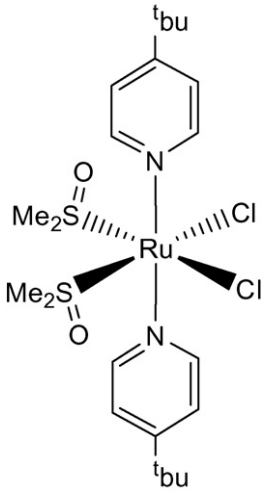

Fig. 3. Structure of *cis*,*cis*,*trans*-$[RuCl_2(dmso)_2(tbpy)]$.

isomerization is not triggered following oxidation. A scan rate dependence was not reported. The electrochemistry is similar to the majority of ruthenium-halo-sulfoxide complexes that do not isomerize, yet the couple is shifted to large positive values similar to those complexes that do feature isomerization. In contrast, the *cis*,*cis*,*cis*-isomer features S → O isomerization following oxidation of Ru^{II} to yield Ru^{III} and O → S isomerization following reduction of Ru^{III} to give Ru^{II}. There is no indication the photochemical reactivity of this isomer was investigated.

The large quantum yield deserves some comment. In the 1980s, the work from a number of laboratories demonstrated that photosubstitution of CH_3CN on $[Ru(tpy)(bpy)(CN_3CN)]^{2+}$ by pyridine in acetonitrile solution occurred with a quantum yield of 0.0014 (±0.02) [34–37]. Mechanistic studies suggested a dissociative mechanism involving population of the ligand field (LF) states. Importantly, there is no evidence of photosubstitution in the corresponding Os^{2+} complex, in support of a promoting role for the LF states in dissociation. The interpretation is that the LF states in Os^{2+} are much higher and thus inaccessible, preventing photosubstitution. The small quantum yield for photosubstitution reflects the short lifetime of ruthenium LF states. The large quantum yield observed in $[RuCl_2(dmso)_2(tpby)_2]$ is indicative of photosubstitution by a mechanism not involving LF states.

Inoue and coworkers exploited the photolability of ruthenium-dmso complexes for the preparation of enantiomerically pure ruthenium polypyridyl complexes (Fig. 4) [38–41].

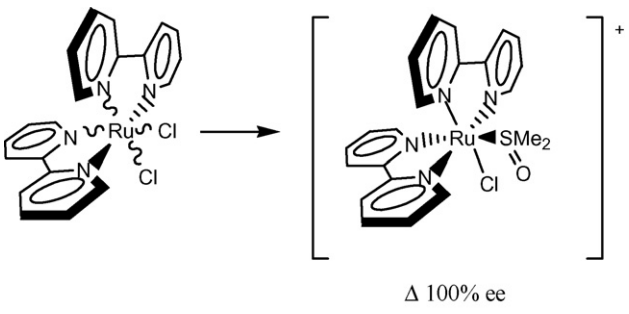

Fig. 4. Chiral production of $[Ru(bpy)_2Cl(dmso)]^+$.

Enantiomerically pure Δ or Λ $[Ru(bpy)_2(sulfoxide)Cl]^+$ may be obtained through heating of the dichloride starting material in the presence of a chiral sulfoxide followed by HPLC resolution. Broad band irradiation of the ruthenium sulfoxide complex in the presence of bases such as halides, pseudo-halides or bridging pyridyl ligands yields the enantiomerically pure complex with expulsion of the sulfoxide. The reaction occurs with retention of stereochemistry. Presumably, photosubstitution of dmso follows excited state S → O isomerization. This important result not only provides a methodology for isolation of chiral $[Ru(bpy)_2]^{2+}$ units, but also demonstrates selective bond photocleavage, a long-standing goal in photochemistry. These reports complement the few known procedures for isolating enantiomerically pure ruthenium polypyridyl complexes.

In 2000, Smith et al. published a report regarding the structure and photochemistry of $[Ru(bpy)_2(dmso)_2]^{2+}$ [42]. They found that both dmso ligands would isomerize under white light illumination in two sequential steps. The S-bonded isomer was reformed in the dark. Careful ^1H NMR studies demonstrated that the dark reversion reaction was bimolecular, occurring following isomerization to the O-bonded isomer. The ^1H NMR resonance for the bound sulfoxides (δ2.56 ppm) is lost following irradiation. Again, substitution occurs following excited state isomerization to yield the O-bonded isomer. The S-bonded isomer reformed after irradiation does not reveal the resonance characteristic of bound dmso. Consistent with previous reports, the O → S isomerization rates were slow ($k = 4.0 \times 10^{-3}\ s^{-1}$ and $1.1 \times 10^{-4}\ s^{-1}$). This slow rate did not change dramatically in a nitromethane-dmso mixture, indicating a unimolecular/intramolecular pathway in addition to the more prominent bimolecular isomerization pathway. This work not only demonstrated that two dmso ligands could isomerize on a single metal, but also that the chemistry may be made reversible in the proper environment.

3. Recent studies

In accord with the photochemistry of $[Ru(bpy)_2(dmso)_2]^{2+}$, MLCT irradiation of $[Ru(tpy)(bpy)(dmso)]^{2+}$ resulted in dramatic changes in the absorption spectrum with the lowest energy absorption transition shifting from 419 to 490 nm [43]. In the presence of donor solvents such as acetonitrile or methanol, dmso was displaced as evidenced by the formation of the bis solvento complexes as the absence of a reversion to the starting material. However, in weakly basic solvents such as halocarbons or propylene carbonate, the absorption changes were found to be reversible at room temperature. Mechanistic studies revealed the forward (S → O) and reverse (O → S) reactions to be first order in ruthenium indicating these reactions were intramolecular. In conjunction with electrochemical studies and the prior literature, the reversible absorption changes were assigned to the S-bonded and O-bonded isomers. The high energy absorption maximum was ascribed to the S-bonded complex while the low-energy absorption maximum was attributed to the O-bonded complex. Indeed, the difference in $E^{\circ\prime}$ for the $Ru^{3+/2+}$ couple (0.63 V) is similar in energy to the difference in absorption maxima (3400 cm^{-1}) for the S- and O-bonded isomers of $[Ru(tpy)(bpy)(dmso)]^{2+}$.

Table 1
Properties of $[Ru(tpy)(L2)(dmso)]^{n+}$ complexes

L2	λ_{abs} (nm)	$E^{\circ\prime}$ (V)	$\Phi_{S\rightarrow O}$
bpy	419	1.60	0.024 (1)
pic	421	1.38	0.25 (1)
Me-pic	413	1.30	0.79 (1)
tmen	433	1.27	0.007 (1)
acac	468	0.95	$<10^{-4}$
mal	502	0.82	–

Substitution of the π-acid bipyridine ligand in $[Ru(tpy)(bpy)(dmso)]^{2+}$ by other bidentate ligands provides a means of exploring the limits of this reactivity [44–46]. The ligands, 2-pyridine carboxylate (pic), 6-methyl 2-pyridine carboxylate (Me-pic), tetramethylethylene diammine (tmen), acetylacetonate (acac) and malonate (mal) were chosen to tune the spectroscopic features in hope of determining both electrochemical and photochemical limits for S → O isomerization. In Table 1 are shown $E^{\circ\prime}$ values and absorption maxima for this family of complexes. These data show $E^{\circ\prime}$ ranges almost 0.80 V and nearly 100 nm (~4600 cm^{-1}), indicating synergistic bonding between dmso and the ancillary ligands. For comparison, the corresponding aquo complexes show a range of 0.33 V for $E^{\circ\prime}$, suggesting the range exhibited by the dmso complexes is quite large.

Cyclic voltammograms of $[Ru(tpy)(pic)(dmso)]^+$ and $[Ru(tpy)(tmen)(dmso)]^{2+}$ are qualitatively similar to that observed for $[Ru(tpy)(bpy)(dmso)]^{2+}$ and $[Ru(NH_3)_5(dmso)]^{2+}$ (Fig. 5) [44,46]. The voltammograms are well modeled by the ECEC mechanism in which S → O and O → S isomerization follow oxidation of Ru^{2+} and reduction of Ru^{3+}, respectively. Remarkably, while these ligand substitutions shifted the observed $E^{\circ\prime}$ values, they did not alter the rates of isomerization on either Ru^{3+} or Ru^{2+}. That is, for the compounds studied, $k_{S\rightarrow O} \geq 50\ s^{-1}$, whereas $k_{O\rightarrow S} \sim 10^{-3}\ s^{-1}$. Consistent with the early Taube report, the S-bonded Ru^{3+} and O-bonded Ru^{2+} complexes were thermodynamically unstable, but a Linear Free Energy Relationship (LFER) was not observed for these ligand substitutions. Interestingly, $k_{S\rightarrow O}$ for these com-

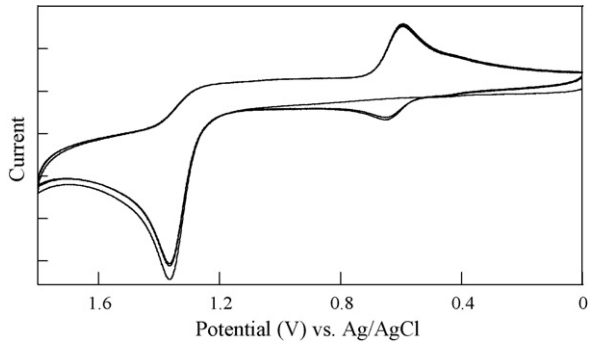

Fig. 5. Cyclic voltammogram of *trans*-$[Ru(tpy)(pic)(dmso)]^+$. The geometry label refers to the disposition of the sulfoxide relative to the carboxylate oxygen of the pic ligand.

plexes is significantly greater than that originally observed for $[Ru(NH_3)_5(dmso)]^{2+}$ $k_{S\rightarrow O} = 0.07\ s^{-1}$ by Taube. In contrast, cyclic voltammograms of $[Ru(tpy)(acac)(dmso)]^{+}$ and $[Ru(tpy)(mal)(dmso)]^{+}$ show reversible one-electron Nernstian behavior with no evidence of isomerization at any scan rate [44,46]. The observed difference in the peak potentials (ΔE_{pk}) are no greater than that seen for an arbitrary transition metal complex, indicating little molecular rearrangement following electron transfer. Thus, the substitution of bpy with π-donor ligands such as acac or mal serves to completely turn off the electron transfer triggered dmso isomerization.

In accord with the electrochemical results, irradiation of $[Ru(tpy)(pic)(dmso)]^{+}$ and $[Ru(tpy)(tmen)(dmso)]^{2+}$ features changes in the absorption spectrum similar to that of $[Ru(tpy)(bpy)(dmso)]^{2+}$. In contrast, irradiation of $[Ru(tpy)(acac)(dmso)]^{+}$ and $[Ru(tpy)(mal)(dmso)]^{+}$ shows no evidence of isomerization. As stated earlier, the absorption changes are reversible in halocarbon solvents and propylene carbonate, indicating the isomerization is intramolecular. The $k_{O\rightarrow S}$ is 1.4×10^{-3}, 1.0×10^{-3} and $1.8 \times 10^{-3}\ s^{-1}$ for the bpy, pic and tmen complexes, respectively. Kinetic studies verify the first order dependence of the ruthenium complex on this reaction. The observation of the photochromic effect in polymer films, crystals and microcrystalline solids further supports the intramolecular nature of this reaction.

We noticed during these studies that the irradiation time required to fully convert to the O-bonded complex from the S-bonded complex was shorter for $[Ru(tpy)(pic)(dmso)]^{+}$ than for the other complexes, notably $[Ru(tpy)(bpy)(dmso)]^{2+}$. Naturally, this prompted the determination of the quantum yields of isomerization ($\Phi_{S\rightarrow O}$) for these complexes (Table 1). The work of Ford, McMillin and others suggest that the quantum yield should be similar to those found for photosubstitution, reflecting the presumed role of the LF states in this process [34–37,47]. For $[Ru(tpy)(bpy)(dmso)]^{2+}$, $\Phi_{S\rightarrow O} = 0.024(\pm 0.02)$ in propylene carbonate. This value is an order of magnitude increase over the value determined for photosubstitution of CH_3CN by pyridine in $[Ru(tpy)(bpy)(CH_3CN)]^{2+}$ [35,36]. This value increases another order of magnitude to $\Phi_{S\rightarrow O} = 0.25(\pm 0.01)$ for $[Ru(tpy)(pic)(dmso)]^{+}$. These large quantum yields are consistent with *cis*,*cis*,*trans*-$[RuCl_2(dmso)_2(tbpy)_2]$ and are indicative of a different mechanism for isomerization relative to photosubstitution. It is interesting to note that Silva's compound and $[Ru(tpy)(pic)(dmso)]^{+}$ both feature relatively large quantum yields of isomerization and a π-donor ligand (Cl^{-}) *trans* to the sulfoxide.

As stated earlier, it was observed that photosubstitution did not occur on osmium(II) centers presumably due to the much larger LF energy gap [35]. For reasons of synthetic simplicity, $[Os(bpy)_2(dmso)_2]^{2+}$ was investigated for evidence of electron-transfer triggered isomerization in order to further probe the role of ligand field states in this photochemistry [48]. The structurally characterized complex features a bis S-bonded configuration and an absorption maximum at 355 nm, similar to that observed for $[Ru(bpy)_2(dmso)_2]^{2+}$ [42,49]. The electrochemistry and photochemistry are consistent with isomerization, although it is apparent that only one dmso ligand isomerizes. An irreversible

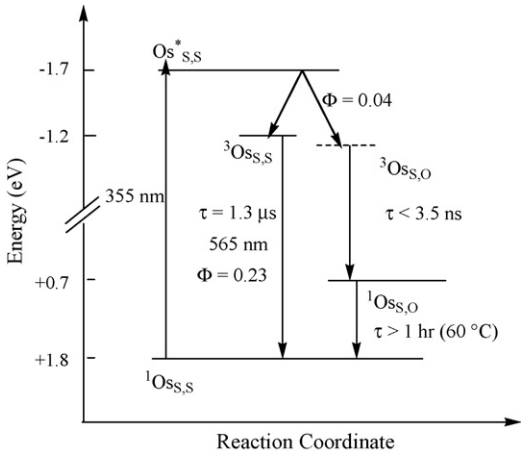

Fig. 6. State diagram for $[Os(bpy)_2(dmso)_2]^{2+}$.

oxidation assigned to the bis S-bonded $Os_{SS}^{3+/2+}$ couple is observed near +1.8 V vs. Ag/AgCl. The mixed S,O-isomer $Os_{SO}^{3+/2+}$ couple is found at +1.0 V vs. Ag/AgCl. Irradiation of the bis S-bonded complex revealed both emission with a maximum at 565 nm and isomerization in propylene carbonate. Excitation with 355 nm showed an emission lifetime of 1.3 μs with a quantum yield of 0.23 ± 0.02. Steady state irradiation resulted in a decrease in absorbance at 355 nm with a concomitant increase at 403 nm. The reversion to the bis S-bonded isomer is not observed at room temperature and requires modest heating for reversion ($T = 60\ ^{\circ}C$). The isomerization quantum yield was determined to be 0.042 ± 0.001. Transient absorption studies suggest that isomerization does *not* occur from the emissive charge-transfer state, but rather from a higher-lying charge transfer state. Shown in Fig. 6 is a state energy diagram of $[Os(bpy)_2(dmso)_2]^{2+}$. From these studies, it is clear that the LF states are not involved in isomerization. That the $\Phi_{S\rightarrow O}$ are similar for ruthenium and osmium complexes indicates that isomerization involves different states than those used for photosubstitution.

3.1. Excited state sulfoxide isomerization

Consistent with the large quantum yields of isomerization, picosecond transient absorption spectroscopy of $[Ru(tpy)(bpy)(dmso)]^{2+}$ and $[Ru(tpy)(pic)(dmso)]^{+}$ in propylene carbonate reveal fast isomerization rate constants [50]. Shown in Fig. 7 are selected traces at time delays ranging from 5 to 242 ps for *S*-$[Ru(tpy)(bpy)(dmso)]^{2+}$ ($\Phi_{S\rightarrow O} = 0.024$). For the S-bonded data, the first trace at 5 ps shows a weak bleach or negative peak near 450 nm which corresponds to the red-edge of the ground state absorption of the S-bonded isomer. This trace also features a sharp absorption near 550 nm and a broad less-intense absorption at longer wavelengths ($\lambda > \sim 600$ nm). From 5 to 14 ps, the bleach near 450 nm becomes more pronounced and the sharp absorption at 550 nm shifts to lower energy and becomes indistinguishable from the broad, featureless low energy absorption ($\lambda > \sim 600$ nm). From 14 to 242 ps, the spectra show a loss of the bleach feature near 450 nm as well as subtle changes in

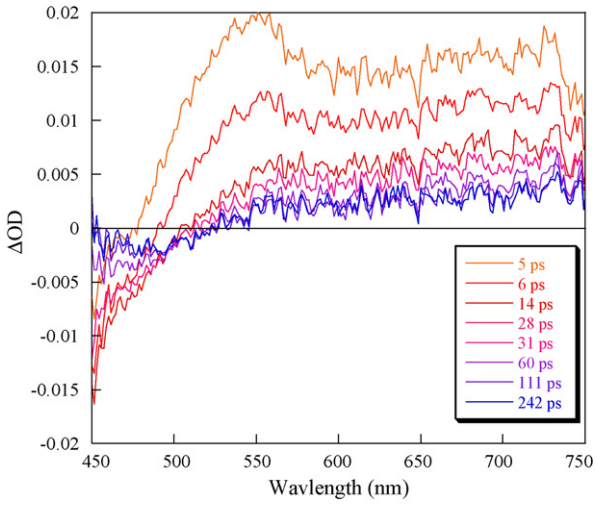

Fig. 7. Picosecond transient absorption spectra of $[Ru(tpy)(bpy)(dmso)]^{2+}$ in propylene carbonate solution.

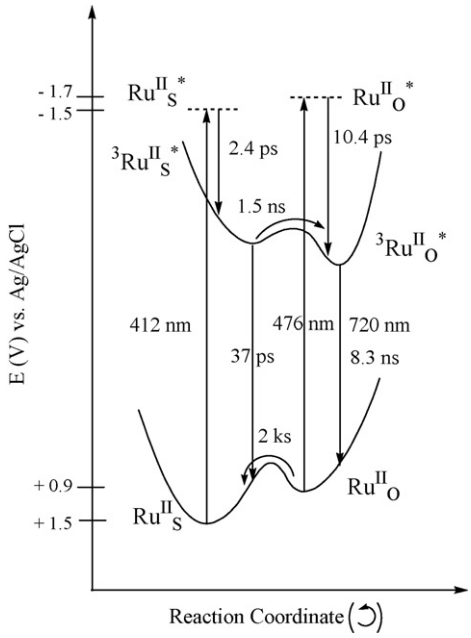

Fig. 8. Electronic state diagram and rate constants for photochromic $[Ru(tpy)(bpy)(dmso)]^{2+}$.

the intensity of the low energy absorption. The final spectrum of weak intensity shows a shallow bleach centered near 475 nm and a broad absorption at low energy ($\lambda > 550$ nm). Interestingly, an isosbestic point at 500 nm becomes apparent in the spectra from 14 to 242 ps. Monitoring the spectral changes at 454 and 530 nm reveals a biexponential decay with time constants of 2.4 ± 0.2 and 36 ± 0.2 ps.

The picosecond transient absorption data of $[Ru(tpy)(bpy)(dmso)]^{2+}$ reveals features attributable to both *S*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$ and *O*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$ states. The lifetime of *O*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$ was independently determined to be 8.3 ± 0.1 ns. The S-bonded ground state is not observed as it serves as the background absorption. The early time traces (up to 14 ps) show both the growing intensity of the bleach near 450 nm and the red-shifting of this feature. In addition, the sharp peak at 550 nm diminishes in intensity and shifts to lower energy. The features in the bleach region correspond to formation of the ^{3}MLCT state, whereas the absorptions in the red are attributable to $\pi^* \leftarrow \pi^*$ transitions on the reduced ligand and LMCT transitions [34,51,52]. The early time progression affects both of these spectral regions and it seems reasonable to assign this 2.4 ± 0.2 ps time constant to intramolecular vibrational relaxation following the ^{1}MLCT to ^{3}MLCT intersystem crossing.

The longer time (14–250 ps) transient data for *S*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$ shows that further changes are evident. The intense bleach near 450 nm diminishes in intensity and yields to a spectrum having a shallow minimum centered near 475 nm with a long, broad featureless absorption in the red. The red portion of the spectrum is nearly identical to that observed for $[Ru(tpy)_2]^{2+*}$ on a 50 ps timescale produced from 532 nm excitation [53]. It is also comparable to the spectrum obtained following bulk electrolysis of $[Ru(tpy)(bpy)(dmso)]^{2+}$ at -1.3 V vs. Ag/AgCl. In the absence of $S \rightarrow O$ isomerization, it is expected that the negative peak near 450 nm will return to the zero line or background absorbance, indicating relaxation to the ground state S-bonded isomer. The changing transient spectra in conjunction with an isosbestic point suggests direct formation of a new complex from relaxed ^{3}MLCT *S*-$[Ru(tpy)(bpy)(dmso)]^{2+}$. The most reasonable assignment for the new complex is *O*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$. This assignment is affirmed upon examination of the transient absorption spectra of the *O*-$[Ru(tpy)(bpy)(dmso)]^{2+}$. These spectra show a mono-exponential decay on a short timescale ($\tau = 10$ ps) to yield the O-bonded excited state. The similarity of the 250 ps time traces in both experiments is compelling. In consideration of the observed time constant (36 ps) for *S*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$ decay and the quantum yield for isomerization ($\Phi_{S\rightarrow O} = 0.024$), the $S \rightarrow O$ isomerization time constant must be 1.5 ± 0.2 ns ($k_{S\rightarrow O} = 6.67 \pm 0.04 \times 10^8\ s^{-1}$). This analysis reveals relaxation from *S*-$[Ru(tpy)(bpy)(dmso)]^{2+*}$ to *S*-$[Ru(tpy)(bpy)(dmso)]^{2+}$ occurs in ~35 ps at room temperature in propylene carbonate solution. Incidentally, these rates are in agreement with our original estimate determined from low temperature single crystal emission experiments [43]. Despite the low quantum yield of isomerization ($\Phi_{S\rightarrow O} = 0.024$), the spectrum observed at 242 ps is attributable to excited state *O*-$[Ru(tpy)(bpy)(dmso)]^{2+}$.

The absorption and emission data as well as the electrochemical and transient absorption data for $[Ru(tpy)(bpy)(dmso)]^{2+}$ are compiled in an electronic state diagram (Fig. 8). The energy scale is in reference to Ag/AgCl(V) and the *x*-axis is the isomerization coordinate. The ground states are shown at the appropriate energy as determined from cyclic voltammetry. Absorption maxima are shown for both *S*- and *O*-$[Ru(tpy)(bpy)(dmso)]^{2+}$. Following formation of the initial S-bonded excited state ($Ru^{II}_S{}^*$), this complex relaxes to a thermally equilibrated excited-state ($^3Ru^{II}_S{}^*$) in 2.4 ps. The complex may surface jump to ground state *S*-$[Ru(tpy)(bpy)(dmso)]^{2+}$ or isomerize to yield the O-bonded excited-state ($^3Ru^{II}_O{}^*$), with a time con-

stant of 1.50 ns. For *O*-[Ru(tpy)(bpy)(dmso)]$^{2+}$, direct excitation yields thermally equilibrated $^{3}Ru^{II}{}_{O}$* from an initial excited state with a time constant of 10 ps. The O-bonded excited state relaxes to the ground state in 8.3 ns, as measured by nanosecond transient absorption spectroscopy. Finally, metastable *O*-[Ru(tpy)(bpy)(dmso)]$^{2+}$ relaxes to *S*-[Ru(tpy)(bpy)(dmso)]$^{2+}$ in approximately 700 s ($k = 1.4 \times 10^{-3}$ s^{-1}).

An analysis of the picosecond transient absorption spectra of [Ru(tpy)(pic)(dmso)]$^{+}$ yields similar information. The quantum yield of S → O isomerization is larger ($\Phi_{S\rightarrow O} = 0.25$) than that determined for [Ru(tpy)(bpy)(dmso)]$^{2+}$ ($\Phi_{S\rightarrow O} = 0.024$) indicating that the S → O isomerization rate constant should be greater. Indeed, an excited state S → O isomerization time constant of 473 ± 3 ps and direct *S*-^{3}MLCT decay to ground state of 157 ± 3 ps was determined. Both sets of data indicate that isomerization occurs following intersystem crossing and ^{3}MLCT formation. Attempts to make complexes that isomerize faster must be mindful of the apparent slow ^{3}MLCT formation.

4. Future considerations

Monodentate ligands are notoriously labile relative to the chelating ligands and thus there is some motivation to determine if this chemistry will occur with chelating sulfoxides. We have recently published a study involving a chelating sulfoxide and the excited state reactivity is retained [54]. Collin and coworkers have also employed a tethered sulfoxide in the design of rotaxane-like bistable molecules [55]. Further investigations will likely reveal new excited state reactivity related to light-to-potential energy conversion. It is envisioned that these studies will play an important role in the continued development of these molecules in molecular logic gates.

Additional studies involving X-ray absorption spectroscopy are also welcome for the field. The sulfur K-edge has been well-examined in a number of small molecule and protein structures [56,57]. Indeed, a recent XAS study of [Ru(bpy)$_3$]$^{2+}$ illustrates the contributions this technique can make to our understanding of the structural changes that accompany electronic excitations [58]. Interrogation of photochromic sulfoxide complexes should reveal further electronic structural details of these compounds. Lastly, structural information of the O-bonded metastable structures is needed.

Computational studies should identify important bonding interactions as well as details of the potential energy surface. An interesting question overlooked at present involves why the phototriggered excited state S → O isomerization reaction occurs approximately 10^5 times faster than the electrochemically triggered isomerization reaction on Ru^{3+}. In contrast, it is obvious why the isomerization on Ru^{3+} is much faster than on Ru^{2+}, as the latter is an 18e$^-$ complex and substitutions on 17e$^-$ metal centers are known to be rapid [59,60]. Additional questions may center on the nature of the thermally equilibrated excited state as well as evolution of this state. These studies gain importance as the rate for isomerization increases. If the rate of isomerization becomes competitive with intramolecular vibration, then the factors affecting vibrational energy flow during excited state formation must be further examined. While the present studies indicate a separation of these events, chelating sulfoxide compounds may exhibit isomerization rates where this separation is no longer convenient. Moreover, these studies would complement other electronic structural techniques and provide forward paths in the design of other complexes. At present only few such papers exist, indicating this is a fruitful area for research [61,62].

5. Photochemical linkage isomerization in organometallic complexes

Photochemical bistability has been observed a number of other species. For example, linkage isomerization in Cp*Mn(CO)$_2$L, where L is 3-cyanomethylpyridine, has been investigated by UV–vis spectroscopy. The two isomers are associated with cyano vs. pyridyl coordination [63]. Both unimolecular and bimolecular pathways for isomerization were observed. This work was followed up by an ultrafast chelation study of [Cr(η^6-C$_6$H$_5$R)(CO)$_3$], where R is a pendant thioether, and the manganese compound [64–67]. Time resolved IR spectroscopy reveals both a solvent dependent and solvent free pathway for CO displacement by the thioether on the picosecond to nanosecond timescale. Similarly, photolysis of M(CO)$_6$ (M = Cr, Mo, W) in the presence of excess 2,3- or 2,5-dihydrofuran (DHF) yields the O-bonded [M(CO)$_5$(DHF)] [68–70]. This complex reverts intramolecularly to a η^2-DHF on a slow timescale (10^0 s^{-1}). Presumably, the isomerization is due to the preference of the polarizable, low-valent metal for the olefin relative to the furan oxygen. Recently, ruthenium bipyridine complexes containing hemilabile ligands was reviewed [71]. These complexes alter the coordination environment in the presence of certain ions. All three of these examples involve displacement of a bound ligand prior to the isomerization.

6. Conclusions

This paper provides a narrative of the progress in this field over the last 20 years and highlights the needs in this field. There are opportunities in synthesis, spectroscopy and computation to make valuable contributions. The concept of excited state isomerization is both experimentally and intellectually challenging as a field of study. There are obvious applications for these materials in sensing and detection, light-to-potential energy conversion and information and energy storage. For these reasons, it is hoped that this paper serves as motivation for others to enter this field.

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