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# Linkage Photoisomerization of an Isolated Ruthenium Sulfoxide **Complex: Sequential versus Concerted Rearrangement**

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Supporting Information

ABSTRACT: Ruthenium sulfoxide complexes undergo thermally reversible linkage isomerization of sulfoxide ligands from S- to Obound in response to light. Here, we report photoisomerization action spectra for a ruthenium bis-sulfoxide molecular photoswitch,  $[Ru(bpy)_2(bpSO)]^{2+}$ , providing the first direct evidence for photoisomerization of a transition metal complex in the gas phase. The linkage isomers are separated and isolated in a tandem drift tube ion mobility spectrometer and exposed to tunable laser radiation provoking photoisomerization. Direct switching of the S,S-isomer to the O,O-isomer following absorption of a single photon is the predominant isomerization pathway in the gas phase, unlike in solution, where stepwise isomerization is observed



with each sulfoxide ligand switching in turn. The change in isomerization dynamics is attributed to rapid vibrational quenching that suppresses isomerization in solution. Supporting electronic structure calculations predict the wavelengths and intensities of the peaks in the photoisomerization action spectra of the S,S- and S,O-isomers, indicating that they correspond to metal-to-ligand charge transfer (MLCT) and ligand-centered  $\pi\pi^*$  transitions.

### INTRODUCTION

Photochromic molecules reversibly switch from one state to another in response to light, converting photonic energy into the internal molecular energy required for molecular rearrangement.<sup>1</sup> Photochromic molecules have been proposed for use as light-activated molecular switches for applications that include photopharmacology, light harvesting, energy storage, and for nonlinear optical materials.<sup>2–6</sup>

Over the past two decades, a range of photochromic ruthenium complexes have been developed, exploiting lightinduced linkage isomerization of sulfoxide ligands on a ruthenium polypyridyl core.<sup>7-10</sup> In solution, these complexes have photoisomerization quantum yields up to 0.79 with thermal half-lives extending to several hours or longer.<sup>11,12</sup> Density functional theory (DFT) calculations suggest isomerization is initiated on an excited <sup>3</sup>MLCT (metal-to-ligand charge transfer) surface and then proceeds along surfaces with predominantly MC (metal centered) character in a non-adiabatic manner.<sup>13,14</sup> Spectroscopic measurements show that the <sup>3</sup>MLCT surface is present throughout the isomerization and imply strong mixing between this surface and the MC surface, which is formally Ru–S  $\sigma^*$  (antibonding) in nature.<sup>11,12</sup> Direct comparison of theoretical predictions with experimental data is often difficult due to strong solvent perturbation of excited state energy levels in ruthenium polypyridyl complexes.<sup>15</sup> Moreover,

even simple ruthenium polypyridyls display complex photochemistry which underpins their roles as photosensitizers in dye-sensitized solar cells and as photopharmacological agents.16,17

In a step toward characterizing the inherent (solvent-free) photochemistry of a ruthenium-based photoswitch molecule, we have probed the photoisomerization of the ruthenium bissulfoxide complex  $[Ru(bpy)_2(bpSO)]^{2+}$  (Ru(bpSO), where bpy = 2,2'-bipyridine and bpSO = 1,2-bis(phenylsulfinyl)ethane) in the gas phase. As shown in Figure 1, the Ru(bpSO) complex has three stable linkage isomers, as each of the two sulfoxide groups can be either S- or O-bound, giving S,S-, S,O-, and O,O-Ru(bpSO) isomers. Earlier studies on the S,S-isomer in solution have shown two photons are required to reach the O,O-isomer; exposing the S,S-isomer solution to 355 nm light produces the S,O-isomer, and subsequent 400 nm irradiation yields the O,O-isomer.<sup>12</sup> No direct isomerization from the S,Sto O,O-isomer occurs. In contrast, we demonstrate that in the gas phase a single photon can generate the O,O-isomer directly from the S,S-isomer with minor formation of the S,O-isomer. This direct conversion has been previously observed in the related  $[Ru(bpy)_2(OSSO)]^{2+}$  (Ru(OSSO), OSSO =

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**Figure 1.** Photoinduced linkage isomerization in the Ru(bpSO) complex. Stepwise isomerization from the S,S- to the S,O- and O,O-isomers is observed in solution, whereas direct isomerization from the S,S- to the O,O-bound-isomer is the predominant process in the gas phase.

dimethylbis(methylsulfinylmethyl)silane) and  $[Ru(bpy)_2(F-bpSO)]^{2+}$  (Ru(F-bpSO), F-bpSO = 1,2-bis(2-fluorophenylsulfinyl)ethane) complexes in solution, where double isomerization was proposed to be facilitated by low barriers on the excited state triplet manifold leading to rapid quasi-statistical equilibration before nonadiabatic relaxation to the ground state.<sup>18</sup> Results from the present study suggest that solvation affects isomerization dynamics in these systems and that gas phase investigations can provide key insight into the intrinsic photochemistry of transition metal complexes.

The present investigation complements previous gas phase spectroscopic investigations of ruthenium complexes, which have mainly focused on ruthenium polypyridyl complexes such as the prototypical photosensitizer  $[Ru(bpy)_3]^{2+}$ , which has been extensively studied in solution.<sup>19,20</sup> In pioneering work, Posey and co-workers obtained an electronic spectrum of  $[Ru(bpy)_3]^{2+}$  in the gas phase observing a progressive red shift in MLCT bands with increasing microsolvation.<sup>15,21,22</sup> More recently, photodissociation action spectra have been recorded for ruthenium bipyridyl complexes in a range of oxidation states.<sup>23–25</sup> However, these earlier studies employed techniques that were not suited to following structural changes such as isomerization. To our knowledge, the present study reports the first observation of the photoisomerization of a transition metal complex in the gas phase.

#### METHODS

Experimental Procedure. The photoisomerization of Ru(bpSO) was investigated using a purpose-built tandem ion mobility-mass spectrometer coupled with a tunable optical parametric oscillator (OPO) system. The experimental apparatus has been described previously.<sup>26,27</sup> Electrosprayed ions from a 10<sup>-4</sup> M solution of S,S-Ru(bpSO) in acetonitrile were injected as 100  $\mu$ s pulses at 40 Hz into a drift tube ion mobility stage, where the ions were separated spatially and temporally on the basis of their drift mobility in 6 Torr of N2 buffer gas with an applied electric field of ≈40 V/cm. The separated isomers then passed through a quadrupole mass filter and were detected using a channeltron electron multiplier. The arrival time distribution (ATD) of the ions was built up by plotting the ion signal as a function of arrival time at the detector. In order to measure photoisomerization action (PISA) spectra, the isomer of interest was selected using a pulsed electrostatic ion gate halfway along the drift tube. Immediately after the ion gate, alternate ion packets were exposed to the output of a pulsed UV-vis OPO (EKSPLA NT342B, 20 Hz, <0.35 mJ/cm $^{-2}$  per pulse), generating laser-off and laser-on ATDs. The effect of light on the ions is manifested in the difference between the laser-on and laser-off ATDs. The photoisomerization action spectrum was generated by plotting the photoisomer yield as a function of OPO wavelength.

Isomerically pure S,S-Ru(bpSO) was synthesized according to a previously published procedure and its isomeric purity confirmed

using UV–vis and NMR spectroscopy.<sup>12</sup> The S,O-Ru(bpSO) and O,O-Ru(bpSO) ions were generated by either UV irradiation of the S,S-isomer in solution or by ion activation in the first RF ion funnel, as described below. Experiments were performed in the dark to avoid isomerization in solution prior to electrospraying.

**Computational Procedure.** Supporting electronic structure calculations were performed using a combined density functional theory (DFT) and ab initio approach. Geometries and harmonic frequencies were optimized at the TPSS-D3(BJ)/def2-TZVP level of theory.<sup>28–31</sup> Single point energies were then calculated at the DLPNO-CCSD(T)/def2-TZVP level.<sup>32,33</sup> Vertical excitation energy calculations to simulate absorption spectra were performed at the PBE0/def2-TZVP and NEVPT2(14,13)/def2-TZVP levels of theory; further details are given in the Supporting Information.<sup>28,29,34</sup> All electronic structure calculations were performed using the ORCA 4.0 program package.<sup>35,36</sup>

#### RESULTS AND DISCUSSION

First, arrival time distributions (ATDs) of electrosprayed Ru(bpSO) were gathered operating the instrument as a single ion mobility drift tube under different ion source conditions; resulting ATDs are shown in Figure 2. A clear dependence on



**Figure 2.** Arrival time distributions for electrosprayed solutions of pure S,S-Ru(bpSO). (a) Low RF drive voltage for the source ion funnel. (b) High RF drive voltage for the source ion funnel. (c) Exposure of the solution to 360 nm light and low RF drive voltage on the source ion funnel. The peak labeled with an asterisk corresponds to a Ru(bpSO)–MeCN adduct that traverses the drift region intact and then dissociates to yield bare Ru(bpSO) in the exit region of the drift region prior to mass selection.

the source conditions was found: a single peak with an arrival time of 10.72 ms was observed with a low radio frequency (RF) drive voltage on the source ion funnel (Figure 2a), whereas two additional slower peaks with arrival times of 10.99 and 11.20 ms were observed when the RF drive voltage was increased (Figure 2b). As the electrosprayed solution consisted purely of the S,Sisomer, the fastest isomer can be confidently assigned to S,S-Ru(bpSO). Exposure of the S,S-Ru(bpSO) isomers in solution to UV light prior to electrospraying and with a low RF drive voltage yielded the ATD shown in Figure 2c, where three later peaks are observed, in addition to the S,S-Ru(bpSO) peak. The slower two isomers in Figure 2b with arrival times of 10.99 and 11.20 ms are assigned to the S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers, respectively, on the basis of prior studies<sup>12</sup> which found that upon exposure to UV light S,S-Ru(bpSO) in solution yields S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers. These assignments are also consistent with the appearance of S,O-Ru(bpSO) and O,O-Ru(bpSO) at higher RF drive voltages, as electronic structure calculations indicate that these isomers lie significantly higher in energy than the S,S-

Ru(bpSO) isomer (by 1800–2500 and 4200–4400 cm<sup>-1</sup> for S,O-Ru(bpSO) and O,O-Ru(bpSO), respectively; Table S2).<sup>32,33,36</sup> As discussed below, PISA spectra of the S,S- and S,O-isomers are consistent with their condensed phase absorption spectra, further supporting the ATD peak assignments.

Next, the effect of light on the gas phase S,S-Ru(bpSO) ions was investigated by exposing them to tunable radiation from the OPO (following selection with the electrostatic ion gate). As shown in Figure 3a, two slower isomers are formed from



**Figure 3.** Example light-on/light-off difference ATDs for (a) S,S-Ru(bpSO) gathered at 360 nm (red) and (b) S,O-Ru(bpSO) at 400 nm (blue) superimposed over the light-off ATDs (black). In each case, the difference ATD was generated by subtracting the light-off ATD from the light-on ATD.

S,S-Ru(bpSO) at 360 nm (near the band maximum of the condensed phase MLCT transition). Plotting the yield of these photoproducts as a function of wavelength produced the PISA spectrum shown in Figure 4. Two distinct bands are apparent with maxima at 345 nm (29 400 cm<sup>-1</sup>) and at 310 nm (32 350 cm<sup>-1</sup>). No wavelength or power dependence was observed in the photoisomerization branching ratio (Figures S1 and S2), and so the PISA spectrum corresponds to the sum of the S,O-and O,O-Ru(bpSO) isomer yields. The lower energy band



**Figure 4.** Gas phase PISA spectrum for S,S-Ru(bpSO) corresponding to aggregate S,O- and O,O-Ru(bpSO) yields as a function of wavelength (black) and calculated TDDFT absorption spectrum (red dotted). The calculated NEVPT2 absorption spectrum is plotted for reference (blue dashed, further details in the Supporting Information, Section 1.1).

peaking at 345 nm is close to the analogous band maximum in solution at 335 nm (29 850 cm<sup>-1</sup>), which has been assigned to a MLCT transition from the ruthenium center to the bipyridyl ligands.<sup>12</sup> Similarly, the higher energy band peaking at 310 nm is close to the band assigned to bipyridyl-localized  $\pi\pi^*$  transitions for S,S-Ru(bpSO) in solution (319 nm, 31 350 cm<sup>-1</sup>).<sup>12</sup> It was not possible to measure below 290 nm due to background signal caused by photoionization of trace contaminants in the drift region. Overall, the gas phase PISA spectrum is similar to the absorption spectrum of S,S-Ru(bpSO) in solution,<sup>12</sup> reinforcing assignment of the earliest ATD peak in Figure 2 to the S,S-Ru(bpSO) isomer.

In order to confirm band assignments, excited state calculations were performed using time-dependent density functional theory (TDDFT, details in the Supporting Information).<sup>28-30,37</sup> The TDDFT-simulated spectrum is shown below the experimental PISA spectrum in Figure 4, along with a spectrum generated using multireference NEVPT2 theory to confirm that TDDFT provides at least a qualitatively correct description for the present system (see the Supporting Information for computational details).<sup>34</sup> As shown in Figure 4, the TDDFT calculations predict two major absorption bands for S,S-Ru(bpSO) at 340 nm (29 440 cm<sup>-1</sup>) and 290 nm  $(34640 \text{ cm}^{-1})$ . The calculated electronic character of the transitions agrees well with previous assignments,<sup>12</sup> with the low-energy transition at 340 nm corresponding to MLCT associated mainly with the bipyridyl ligands with a minor component connected with the bpSO phenyl rings and the higher energy transition at 290 nm corresponding to bipyridylcentered  $\pi\pi^*$  transitions. Kohn-Sham orbitals responsible for the calculated transitions are depicted in Table S4.

The NEVPT2 calculations are able to treat MLCT excited states accurately.<sup>38</sup> The discrepancy of <1000 cm<sup>-1</sup> between the TDDFT and NEVPT2 calculations for the MLCT bands suggests that TDDFT performs reasonably at least for this system (vertical excitation energies are tabulated along with a quantitative discussion of relative performances in the Supporting Information). There is poorer agreement between TDDFT and NEVPT2 calculations for the higher energy band, with a difference of around 30 nm (~3000 cm<sup>-1</sup>). For reasons of economy, and because the TDDFT approach provides a reasonable qualitative description of the excited state character, for the S,O-Ru(bpSO) isomer only the TDDFT approach was used.

Given that  $\pi\pi^*$  excitation leads to isomerization, there must be efficient conversion from the initial  ${}^1\pi\pi^*$  state to the <sup>3</sup>MLCT state from which photoisomerization occurs.<sup>13</sup> However, it is unclear whether internal conversion (IC) to a <sup>1</sup>MLCT state precedes intersystem crossing (ISC), which is known to occur on a femtosecond time scale in ruthenium polypyridyls,<sup>19,20</sup> or whether rapid ISC yields a  ${}^3\pi\pi^*$  state before internal conversion to the <sup>3</sup>MLCT manifold. To elucidate the mechanism, we are presently performing wavelength-dependent transient absorption studies to probe the dynamics following  $\pi\pi^*$  excitation.

Significantly, whereas direct isomerization is observed from the S,S-isomer to the O,O-isomer in the gas phase, stepwise isomerization via the S,O-isomer was observed in solution.<sup>12</sup> Power dependence studies (Figure S1) indicate that in the gas phase the branching ratio between the S,O- and O,O-Ru(bpSO) photoproducts does not depend on light fluence at both band maxima, and therefore both single and double isomerizations are triggered by absorption of a single photon.



Figure 5. Schematic potential energy surfaces for S,S-Ru(bpSO) isomerization in the gas phase (left) and in solution (right). Relaxation time scales in solution are taken from King et al.<sup>12</sup>

Likewise, the branching ratio for formation of S,O-Ru(bpSO) and O,O-Ru(bpSO) does not vary with wavelength (Figure S2). Together, these results suggest that the thermal reversion barriers are sufficiently high on the ground state potential energy surface to prevent back-isomerization of the S,O- and O,O-isomers under the present experimental conditions.<sup>39</sup> Support for this interpretation comes from DFT calculations on the closely related  $[Ru(bpy)_2(dmso)_2]^{2+}$  complex (dmso = dimethyl sulfoxide), which predict that barriers to thermal reversion on the ground state potential energy surface are ≥85 kJ/mol compared to barriers on the triplet MC and MLCT surfaces of ≈20 kJ/mol.<sup>14</sup> Although the present system differs from this model system through presence of a chelating linker between the sulfoxides, the electronic character of the triplet state surfaces should be comparable.

Schematic potential energy surfaces (PESs) shown in Figure 5 illustrate the proposed mechanisms for isomerization dynamics for S,S-Ru(bpSO) in the gas phase and in solution. They are based on the experimental results from the present study and from King et al.<sup>12</sup> as well as DFT calculations of Boggio-Pasqua and co-workers on the closely related [Ru- $(bpy)_2(dmso)_2]^{2+}$  complex.<sup>13,14</sup> Although the previous theoretical work considered the MC and MLCT states to be distinct, we discuss the lowest triplet surface in Ru(bpSO) as a mixed surface with varying MC and MLCT character for the following reasons: the two states are similar in energy, multiconfigurational character has been predicted in low-lying triplet states of ruthenium coordination complexes,<sup>40</sup> and Kohn-Sham density functional theory has difficulty describing such mixed states.<sup>41</sup> Future computational studies using appropriate multireference methods may be able to elucidate the electronic character of the triplet surface. Note that for simplicity the reaction coordinate is depicted as being onedimensional, whereas in reality a multidimensional reaction coordinate likely exists along which direct S,S- to O,Oisomerization can occur.

The different rates of vibrational quenching in solution and in the gas phase are probably responsible for the difference in isomerization dynamics. Specifically, vibrational energy transfer to the solvent (i.e., thermalization) is usually complete on a sub-200 ps time scale, although the rate is solvent dependent. This time scale is on the same order as the time scale for isomerization of the present system in solution,<sup>12</sup> as illustrated in Figure 5. Assuming S,S- to O,O-Ru(bpSO) photoisomerization occurs on the excited state surface in a sequential manner, vibrational energy transfer to solvent causes excited state molecules in the S,O geometry to be trapped before they can further isomerize to O,O-Ru(bpSO). In contrast, vibrational energy quenching in the present gas phase experiment is much slower, taking place through ion-molecule collisions occurring every few nanoseconds, with hundreds of collisions required to thermalize the ions. Gas phase ions therefore remain vibrationally energized on the excited state surface, allowing the excited state population to sequentially propagate through the transient S,O-isomer to form O,O-Ru(bpSO). This is consistent with studies on Ru(OSSO) and Ru(F-bpSO) in solution, which suggested a mixture of S.O- and O.O-isomers results from a quasi-statistical equilibrium on the <sup>3</sup>MLCT surface, where interconversion between excited state isomers is rapid compared to deactivation to the singlet electronic ground state.<sup>18</sup>

The direct S,S- to O,O-Ru(bpSO) isomerization in the gas phase might also be related to the strength of the Ru-S bond on the triplet surface. As discussed above and illustrated in Figure 5, the triplet states of Ru(bpSO) are thought to have mixed MC and MLCT character. MC character is formally antibonding toward the sulfoxide ligands and should induce weaker Ru-S bonds, while MLCT character should have no significant impact on the Ru-S bond strength. One might expect that the MC character of the lowest triplet state should be enhanced relative to MLCT character in the gas phase because there is no solvent to stabilize the separated charges associated with MLCT.<sup>42</sup> For these reasons we hypothesize that weaker Ru-S bonds on the isomerizing triplet surface in the gas phase should promote formation of the S,O- and O,O-Ru(bpSO) isomers, while suppressing recovery of S,S-Ru-(bpSO). We note that this hypothesis is consistent with previous solution studies considering changes in Ru-S bond strengths following incorporation of electron-withdrawing groups (EWGs) into the bpSO ligand, such as fluorination of the phenyl groups or insertion of a silane group in the alkyl linker.<sup>18</sup> EWGs decrease the electron donating character of the sulfur atoms, leading to longer, weaker Ru-S bonds, allowing direct S,S- to O,O-Ru(bpSO) conversion.<sup>18</sup>

The S,O-isomer also undergoes photoisomerization in the gas phase. As shown in Figure 3b, irradiation of isolated S,O-Ru(bpSO) yields a light-on/light-off difference ATD in which depletion of the S,O-Ru(bpSO) peak is matched by growth in a later peak with an arrival time consistent with O,O-Ru(bpSO). Notably, formation of the S,S-isomer was not observed. The

lack of reverse photoisomerization is consistent with the PES presented in Figure 5, as the S,S-Ru(bpSO) isomer lies energetically uphill on the excited triplet surface, while barriers on ground state singlet surface are sufficiently large to prevent thermal reversion before thermalization by buffer gas. The PISA spectrum, generated by monitoring the O,O-isomer yield as a function of wavelength, is plotted in Figure 6 along with a



**Figure 6.** Gas phase PISA spectrum of S,O-Ru(bpSO) corresponding to O,O-Ru(bpSO) yield as a function of wavelength (black) and the TDDFT-simulated absorption spectrum (red). Further details of the calculation are given in the Supporting Information.

TDDFT-simulated spectrum. The PISA spectrum exhibits a lower energy band with a maximum at  $\approx$ 395 nm (MLCT) and another band with an onset at 330 nm and increasing in intensity to shorter wavelength (bpy-centered  $\pi\pi^*$  transition). Over the measured region, the gas phase PISA spectrum is again very similar to the solution absorption spectrum.<sup>12</sup>

Finally, no photoisomerization was observed for O,O-Ru(bpSO) over the 295–600 nm range, and hence no PISA spectrum could be measured. This is consistent with solution studies that demonstrated thermal but not photochemical reversion from O,O-Ru(bpSO) to S,O-Ru(bpSO) and S,S-Ru(bpSO).<sup>12</sup> Although we have no estimate for the barrier height for reversion in this system, the barriers must be sufficiently large that thermal isomerization rate following return to the ground electronic state is much less than  $10^8-10^9$  s<sup>-1</sup>, the collision rate of ions with the buffer gas molecules in our experiment. As with S,O-Ru(bpSO), these observations are consistent with the proposed potential energy surfaces.

#### CONCLUSIONS

We report gas phase photoisomerization action spectra for the S,S- and S,O-Ru(bpSO) photoswitching complexes. The two isomers display ligand-centered electronic transitions in the UV and MLCT transitions in the visible, which both lead to photoisomerization via a triplet surface. In the gas phase, absorption of a single photon induces isomerization directly from the S,S- to the O,O-bound isomer, whereas in solution double linkage isomerization is likely suppressed by a combination of solvent-mediated vibrational quenching and increased Ru-S bond strength in the excited state. We aim to continue these gas phase studies by examining the roles of the chelate linker and of metal-centered excited states in the photoisomerization of metal-sulfoxide complexes, in similar ruthenium complexes and in analogous osmium com-pounds.<sup>18,43,44</sup> Comparison of condensed and gas phase PISA spectra should allow us to directly assess the effect of solvation on photoisomerization.<sup>45</sup> Additionally, studies of osmium

polypyridyl complexes, which, due to strong spin–orbit coupling, have bright  $T_1 \leftarrow S_0$  transitions, may allow direct optical access to the <sup>3</sup>MLCT surface and provide an alternative route to initiating photoisomerization.<sup>46</sup>

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00871.

Full details of the computational methods used in this study, a description of the reference NEVPT2 calculation, a listing of relative energies and collision cross sections for each isomer, and a discussion of the branching ratio dependence on light fluence and wavelength (PDF)

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#### Notes

The authors declare no competing financial interest.

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