Reaction Mechanisms

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Mechanism of Thermal Reversal of the (Fulvalene)tetracarbonyldiruthenium Photoisomerization: Toward Molecular Solar–Thermal Energy Storage**

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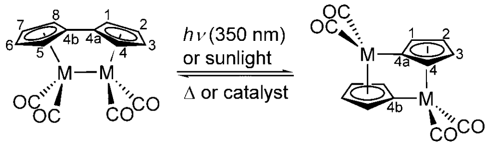
In the quest to harness solar energy for power generation, most efforts are centered around photoinduced generic charge separation, such as in photovoltaics, water splitting, other small-molecule activation, and biologically inspired photosynthetic systems.[1] In contrast, the direct collection of heat from sunlight has received much less diversified attention, the bulk devoted to the development of concentrating solar thermal power plants.[2] An attractive alternative would be to trap solar energy in the form of chemical bonds, ideally through the photoconversion of a suitable molecule to a higher energy isomer, which, in turn, would release the stored energy by thermal reversal. Such a system would encompass the essential elements of a rechargeable heat battery, with its inherent advantages of storage, transportability, and use on demand.[3] The underlying concept has been explored extensively with organic molecules (such as the norbornadiene–quadricyclane cycle),[4] often in the context of developing photoswitches,[5] although a functioning device has yet to be reported. Organometallic complexes have remained relatively obscure in this capacity.[6] A highly promising organometallic system is the previously disclosed, robust photothermal fulvalene (Fv) diruthenium couple $\mathbf{1}\rightleftarrows\mathbf{2}$ (Scheme 1).[7a] Kinetic, stereochemical, and attempted trapping experiments led, in the absence of compelling evidence to the contrary, to the postulation of concerted pathways for these isomerizations. Here we present a theoretical investigation, in conjunction with corroborating experiments, of the mechanism for the heat-releasing step of **2**→**1** and its Fe and Os relatives, painting a surprising picture.



1, M = Ru
3, M = Fe
5, M = Os

2, M = Ru
4, M = Fe
6, M = Os

Scheme 1. Photoisomerizations of (fulvalene)tetracarbonyldimetal complexes and their thermal reversal.

First-principles calculations were employed based on spin-unrestricted density functional theory (DFT) with a non-empirical gradient corrected exchange-correlation functional.[8] Ultrasoft pseudopotentials[9] were used to describe the valence–core interactions of electrons, including scalar relativistic effects of the core. Wavefunctions and charge densities were expanded in plane waves with kinetic energies up to 25 and 200 Rydberg, respectively. Reaction pathways were delineated with the string method,[10] as implemented[11a] within the Car–Parrinello approach.[11b] This procedure allows for the efficient determination of the minimum-energy path (MEP) of atomistic transitions and thus also saddle points (transition states, TSs), which are the energy maxima along the MEP. All geometries were optimized until all forces on the atoms were less than 0.02 eVÅ^{-1} (<0.01 eVÅ^{-1} for equilibrium structures). The calculated structures of **1** and **2** were in reasonable agreement with their experimental counterparts[7a] [for example (calculated/averaged experimental): **1**: Ru–Ru 2.89/2.82, cyclopentadienyl(Cp)$_{\text{centroid}}$–Ru 1.93/1.89, C$_{4a}$–C$_{4b}$ 1.45/1.46 Å; Fv bend 27.8/28.5°; **2**: Ru–Ru 3.54/3.47, Cp$_{\text{centroid}}$–Ru 1.93/1.89, C4a–C4b 2.65/2.64 Å; Cp$_{\text{centroid}}$–C$_{4a}$–Ru$_{\sigma\text{-bound}}$ 161.8/162.1°; see also the Supporting Information]. For the conversion of **2** to **1**, our calculations reveal an enthalpy difference of 20.8 kcal mol^{-1}, in excellent

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accord with the experimental value, (19.8 ± 1.4) kcal mol^{-1}.[7b,12a] This value corresponds to an energy density of approximately 0.2 MJ kg^{-1}, comparable to that of lithium ion batteries (0.5 MJ kg^{-1}).

An initial search for a concerted mechanism for the isomerization (vide supra)[7a] was executed by string-method optimization of a simple rotation of one Ru unit relative to the other. However, the string (path) evolved away from this motion, and a two-step process was uncovered, in which **2** rearranges by initial Cp−Cp coupling via TS **A** to deliver biradical intermediate **B**, which in turn progresses through TS **C** to **1** (Figure 1).[12b]

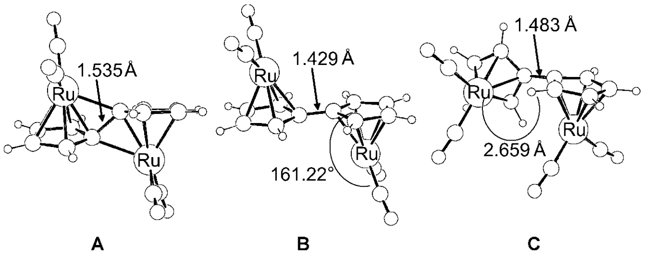

Figure 1. Key structures along the minimum-energy path for the thermal reversal reaction of **2** to **1**. Isomer **2** proceeds via transition state **A** to the *anti*-[$FvRu_2(CO)_4$] diradical intermediate **B**, which continues via transition state **C** to **1**. See the Supporting Information for key structural parameters.

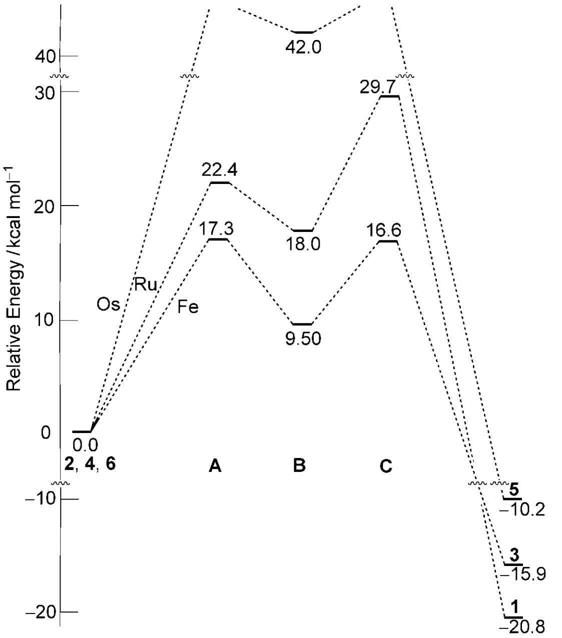

Figure 2. Calculated potential energy profiles [kcal mol^{-1}] for the thermal reversal reactions of the photoisomers **2** (Ru), **4** (Fe), and **6** (Os), all with a reference energy of 0 kcal mol^{-1}, to the corresponding fulvalene complexes **1**, **3**, and **5**. **A** and **C** correspond to transition states, while **B** is an intermediate in the reaction. See the Supporting Information for the structural evolution of **2** along the minimum-energy path.

Proceeding along this reaction coordinate, the first step defines a surprising (vide infra) preequilibrium and involves an unusual TS structure (**A**), which is 22.4 kcal mol^{-1} higher in energy than **2** (Figure 2). It can be viewed as a pseudo-triple-decker complex, in which the bridging Fv ligand contains two nearly planar Cp halves twisted by 46.3° with respect to each other. The length of the nascent C−C bond is 1.54 Å, elongated, but well on the way to that in **B** (1.43 Å). This connection, featuring two formally pentacoordinate carbon atoms, bridges the two Ru atoms unsymmetrically, each side exhibiting a short (2.21, 2.21 Å) and a long Ru−C linkage (2.39, 2.43 Å). A tantalizingly close topological analogy is the structure of the isoelectronic *anti*-[Cp_2Ru_2(μ-cyclooctatetraene)], in which the corresponding bond (1.57 Å) is also reversibly cleaved, but only on two-electron oxidation–reduction.[13] Diradical **B** lies 18.0 kcal mol^{-1} above **2**. Equating the Cp−Cp bond energy in **B** to that in biphenyl (118 kcal mol^{-1})[14] provides an estimate of the strength of the Cp−Ru σ bond of 68 kcal mol^{-1}.[15] The structure of **B** features the *anti*-[FvM_2] configuration, with a pyramidalized Ru stereochemistry [$Cp_{centroid}-Ru-(C_{C\equiv O}-C_{C\equiv O})_{centroid} = 161.2°$] that is similar to that observed in the crystallographically characterized, isoelectronic 17e [Cp*Fe(dppe)] (167.8°) (Cp* = C_5Me_5, dppe = 1,2-bis(diphenylphosphino)ethane).[16] Unexpectedly, in light of the normally diffusion-limited dimerization of 17e [CpM] species,[17] the rate-determining step of the thermal reversal of **2** is controlled by the steric hindrance of the rotation of the Cp−Cp bond,[18] 11.7 kcal mol^{-1}, before the formation of the Ru−Ru bond, as indicated by **C**. Here, the Cp−Cp distance lengthens to 1.48 Å, thus minimizing the Ru−CpH_α encumbrance, 2.66 Å, which is still well within van der Waals distance.[19]

The measured barrier for the thermal reversal reaction from **2** to **1** is (29.9 ± 2) kcal mol^{-1}. To address this quantity computationally, we solved numerically a set of rate equations for **2**$\rightleftarrows$**B**$\rightleftarrows$**1**, using the calculated reaction energetics (see the Supporting Information). The preequilibrium **2**$\rightleftarrows$**B** was found to be established extremely rapidly, and the effective barrier from **2** to **1** computed at 29.7 kcal mol^{-1},[12a] corresponding to the energy difference between **2** and **C**. Conversely, the barrier for Ru−Ru bond dissociation in **1** is calculated at 50.5 kcal mol^{-1}, consistent with the extraordinary thermal stability of this compound (m.p. 288–290 °C), and the computed Ru−Ru bond strength (estimated from the energy difference between **B** and **1**) is 38.8 kcal mol^{-1}, close to a value previously suggested (35 kcal mol^{-1}).[7a]

An important consequence of the computed mechanism is the presence of a preequilibrium **2**$\rightleftarrows$**B** on the way to **1**, a facet that explains some peculiar experimental observations.[7a] Thus, the observed accelerated disappearance of **2** with added CCl_4 and concomitant appearance of [$FvRu_2(CO)_4Cl_2$] as a product can now be rationalized by the competitive trapping of **B** with the additive. Indeed, a reinvestigation of this reaction in toluene charged with increasing amounts of CCl_4 at 70 °C revealed saturation kinetics from which $\Delta G^{\neq}_{70°C} = (25.6 \pm 0.5)$ kcal mol^{-1} was obtained. This value is consistent with the calculated barrier of $\Delta H^{\neq}_{DFT} = 22.4$ kcal mol^{-1} for the preequilibrium step (**A**; Figure 1 and Figure 2). Finally, one notes that the barrier for the conversion of **B** to **2** is only 4.4 kcal mol^{-1}, reviving the initially discounted possibility that the photochemical step from **1** to **2** also proceeds through the intermediacy of **B**.[7a] The finding that CCl_4 as a solvent does not affect this step may simply be due to noncompetitive intermolecular trapping kinetics at room temperature.[20] This extraordinary labilization of the normally strong Fv linkage by the homolysis of a metal–metal bond has been an unrecognized feature in this class of compounds.

To further explore the scope of the photothermal system, in particular the possibility of using the cheaper and environmentally and economically more favorable Fe analogues, the potential energy manifold of **3**⇄**4** and, for completion of the triad elements, briefly also **5**⇄**6**, were scrutinized (Scheme 1, Figure 2). For the former, the photochemical energy storage potential (15.9 kcal mol^{-1}) is diminished relative to that of its Ru relative. In addition, the rate-determining transition state is now that of the first step leading to the biradical and the computed effective barrier is much smaller (17.3 kcal mol^{-1}). Consequently, the nature of the thermal reversal reaction changes for the Fe case, likely the combined result of the weaker metal–Cp σ bond in **4** and the diminished Fe–CpH$_\alpha$ interaction (2.76 Å) in **C** relative to the corresponding values for Ru. The significantly lower kinetic and thermal stability of photoisomer **4** might preclude its isolation. Experimentally, the 2,3,6,7-tetra-*tert*-butyl derivative of **3** was observed to be (seemingly) photoinert, possibly because of fast thermal reversal at the ambient temperatures employed.[21] Indeed, the computed rate for this process is several orders of magnitude larger at room temperature than that of its Ru analogue (see the Supporting Information).

The computations also give an estimate of the Fv(Fe–Fe) bond strength, 25.4 kcal mol^{-1}, which is comparable to that in $[CpFe(CO)_2]_2$, 26.9 ± 2.7 kcal mol^{-1}.[22] In comparison, the Os system is estimated to be an even poorer photoenergy storage molecule (10.2 kcal mol^{-1}) and appears to traverse a prohibitively energetic reversal manifold, as judged from the high energy of the diradical intermediate (42 kcal mol^{-1} above **6**; approximate Os–Os bond strength 52.2 kcal mol^{-1}).[23] Given these findings, an MEP for the Os case was not addressed. Preliminary experiments reveal that the 2,3,6,7-tetra-*tert*-butyl derivative of **5**, while it photoisomerizes to the correspondingly substituted **6**, cannot be regenerated thermally even at temperatures as high as 275 °C (phenyloctane solvent).[21]

In conclusion, we have investigated the detailed mechanism of the thermal reversal reaction of the photoisomer **2** of $[FvRu_2(CO)_4]$ (**1**), a representative of a promising platform for storing solar energy using organometallic molecules. In contrast to earlier suggestions, our first-principles calculations predict the existence of a diradical intermediate **B** with a surprisingly low barrier for Cp–Cp bond rupture to furnish **2** and an equally unexpected high barrier to rotation to (re)generate **1**. The new mechanism uncovered by the calculations is consistent with all experimental findings. An extension to the Fe and Os relatives of this system reveals quantitatively very different thermodynamic and kinetic aspects, also corroborated by preliminary experiments. These results may be of relevance to other topologically related rearrangements.[24] We are currently constructing a proof-of-principle device, based on derivatives of **1** and the discovery of catalysts obviating thermal activation of **2**,[25] to demonstrate the feasibility of the concept.

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