

Reply

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We have reported on the formation of the first low-spin ($S = 0$) ruthenium(IV)-oxo complex in water by proton-coupled electron transfer (PCET).^[1] The Ru^{IV}-oxo complex (**4** in Ref. [1]) bears a derivative of tris(2-pyridylmethyl)amine (TPA) with a carboxy group at the 6-position of one of the three pyridine rings of TPA. DFT calculations suggested that the novel low-spin Ru^{IV}-oxo complex should have a seven-coordinate, pentagonal-bipyramidal structure involving the coordination of one water molecule and that the structure can be stabilized by hydrogen bonding with one or more water molecules. In 2008, we also reported the characterization of an intermediate-spin ($S = 1$) Ru^{IV}-oxo complex bearing the TPA ligand and one aqua (H₂O) ligand (**3** in Ref. [1]) and described its catalytic activity in water.^[2] In the recent publication,^[1] we compared the reactivity of the two Ru^{IV}-oxo complexes in oxidation reactions of organic substrates in water in light of catalytic activities and kinetic parameters. The conclusion obtained from our experimental results is that the spin states of Ru^{IV}-oxo complexes in the ground state do not affect their reactivity. This finding should be very important to consider the reactivity of high-valent metal-oxo complexes as reactive species in catalytic oxidation reactions.

Schröder and Shaik^[6] comment on our discussion of the data, our conclusion, and a part of the title of the Communication, “Does the Spin State Have an Impact on the Reactivity?”^[1] We appreciate, without doubt, the contribution of theoretical chemistry to a broad range of chemical disciplines, as can be also seen in our publications. Based on our results and on the literature, we present our reply to the comments by Schröder and Shaik.

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1. Here we would like to make it clear that the spin state mentioned here is that determined at room temperature, neither that in the transition state nor that of the excited state. The ¹H NMR spectrum of **4** in D₂O exhibits well-resolved signals in the normal region, thus clearly demonstrating that its spin state is $S = 0$ at room temperature. To explain its diamagnetism, we applied DFT calculations to reveal that it is plausible the seven-coordinate, pentagonal-bipyramidal structure involving one aqua ligand and the hydrogen bonding with one or more water molecules is indispensable for the stabilization of the low-spin state. As all the reactions and analytical measurements were performed in water, it should be reasonable to consider the hydrogen bonding with water molecules (i.e., hydration). Regardless of the size of the energy difference between the singlet and triplet states suggested by calculations, the NMR spectrum of **4** indicates that the spin state is $S = 0$ at room temperature—the temperature at which the reactions were examined.
2. We have chosen appropriate substrates to compare the reactivity of the Ru^{IV}-oxo complexes in the three different types of reactions (Table 1 in Ref. [1]). The reactivity of **3** and **4** toward the substrates should be concluded to exhibit no significant differences, as listed in the table, even though the turnover numbers are not exactly the same.
3. Of course, the spin state of a metal complex depends on its molecular symmetry. More importantly, it also depends on the ligand-field splitting, which is mainly governed by the characteristics of the ligand. However, the reactivity in oxidation reactions may not be significantly dependent on the molecular symmetry if the energy levels of isomers with different symmetries are similar.
4. The “loaded gun” scenario is interesting to consider; however, experimental evidence to support it has yet to be obtained. According to the kinetic analysis on the oxidation of 1-propanol with both **3** and **4**, the activation parameters are nearly the same, thus indicating that the corresponding transition states should be similar, regardless of slight structural differences between the complexes.
5. Closed-shell ($S = 0$) Ru^{VI} dioxo complexes, especially in the *cis* configuration, have been well known to be reactive enough to oxidize organic substrates, even methane.^[3] Moreover, the Sharpless dihydroxylation of olefins has been effectively performed by closed-shell OsO₄.^[4] No evidence has been provided to demonstrate the requirement of open-shell excited states to perform the oxidation reactions by those metal-oxo complexes.

6. We have discussed the kinetic isotope effect (KIE) in the oxidation of 1-propanol by **3** and **4** to ascertain the reaction mechanism of the hydrogen abstraction. The KIE values have been determined properly on the basis of the second-order rate constants. The results simply indicate that the rate-limiting hydrogen abstraction occurs at the α -position, not at the hydroxy group. There is no doubt about the conclusion obtained by these experiments.

In conclusion, the comments by Schröder and Shaik are quite interesting, but they need to be verified by careful calculations and, more importantly, by experiments. We believe that our title, “Does the Spin State Have an Impact on the Reactivity?” is appropriate from the experimental point of view, which deals with the ground state, because there seems to be general belief that a difference in spin state always affects reactivity. We have shown clearly in our Communication that there is a case in which the difference in the spin state does not affect the reactivity.^[1] Of course, our

conclusion does not undermine the great concept of “two-state reactivity”^[5] in the transition state.

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