Oxo Complexes

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# Comment on “A Low-Spin Ruthenium(IV)–Oxo Complex: Does the Spin State Have an Impact on the Reactivity”**

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In their recent Communication,[1] Kojima et al. describe C–H and C–C bond activations of three simple test substrates by two closely related ruthenium(IV)-oxo complexes and conclude that “… the spin state of the $Ru^{IV}$-oxo complexes does not affect their reactivity…”. While the preparative work is of high quality, the general concept appears reminiscent of the seminal work of Detrich et al. entitled “Can Spin State Change Slow Organometallic Reactions?”[2] and the parallel development of the concept of “two-state reactivity”.[3] Specifically, in the Communication by Kojima et al.,[1] several aspects have been considered insufficiently in addressing the role of spin states in chemical reactivity.

- Owing to non-negligible spin-state coupling in transition-metal compounds, different spin states can only be isolated in substance if the compounds themselves differ, for example, by having different ligands such as species **3** and **4** in reference [1]. Any observed difference would hence be the result of the coupled changes in ligand environment and spin state, the differentiation of which is nontrivial.
- As noted by the authors, compound **4** has a singlet ground state only when two water molecules are coordinated to the oxo ligand, and even then the triplet state is calculated to be only 0.77 $kcal\,mol^{-1}$ higher in energy (Table S1 in the Supporting Information of reference [1]). Without the water molecules, the triplet state is lower by 14.1 $kcal\,mol^{-1}$.[4] Owing to spin–orbit coupling, an efficient equilibration of the two spin states is thus to be expected, with specific solvation favoring the low-spin state, as found experimentally.[1]
- The influence of spin states on chemical reactivity is gradual, which is most pronounced in competing reactions on the way from the reactants to the transition structure and subsequently to the product(s).[3,5] The substrates chosen in reference [1] do not offer such competition.
- As pointed out earlier, molecular symmetry plays a central role with regard to the reactivity of different spin states.[3] In this respect, the ligand in compound **3** of reference [1] is quasi $C_3$-symmetric, whereas that in **4** has $C_s$ symmetry.
- With regard to the kinetic experiments, questions about the magnitude of the expected differences and the precision of the experiments arise. Thus, are selectivities of 100 and 88 %, respectively (Table 1 of Ref. [1]), to be considered as “identical”? If significant, is such a difference to be assigned to the difference in spin states or ligand structures?
- Kojima et al. note that kinetic analysis of the oxidation of 1-propanol by the title compounds shows a pre-equilibrium involving a catalyst–substrate complex.[1] With the two spin states of **4** being so close in energy and the strong dependence of the state splitting on the presence of water molecules, the $S$ 0 ground state of **4** is in fact a precursor, or a “loaded gun”, with a more reactive $S$ 1 state. Even if the spin-state separation is somewhat larger owing to DFT inaccuracy,[4] this situation can still be the case, much as the ground state of FeO serves as a precursor for the $S$ 3/2 states that lie approximately 8 $kcal\,mol^{-1}$ higher[3a,b] and the ground state of nonheme oxo iron reagents acts as a “loaded gun” with a more reactive $S$ 2 state.[3d] The most likely scenario is that **3** and **4** in fact pass through the same spin surface, which would account for the similar kinetic parameters found experimentally. Indeed, most closed-shell metal-oxo reagents are unreactive and require open-shell excited states to mediate the oxidation reactions.[6]
- As a note of further caution, in general, and specifically in the case of catalytic reactions, the interpretation of intermolecular, rather than intramolecular, isotope effects can be quite misleading.[7]

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In conclusion, Kojima et al. report a nice piece of work,[1] but the title is not properly chosen and the implications may thus be misleading, because compounds **3** and **4** appear as inadequate probes to address the influence of the spin state on chemical reactivity. Moreover, when the spin states are close in energy, as in compound **4**, not too much can be inferred from the identity of the ground state about the spin state of the energetically most favorable transition structure.

After having read the authors' response,[9] we agree that the spin state of the reactants may not have any relevance for the reactivity in the transition structure, since the latter may have a different spin state owing to spin crossover along the reaction path. Further, we note that the strongest evidence for the occurrence of two-state reactivity indeed comes from experiment.[8]

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[1] T. Kojima, Y. Hirai, T. Ishizuka, Y. Shiota, K. Yoshizawa, K. Ikemura, T. Ogura, S. Fukuzumi, *Angew. Chem.* **2010**, *122*, 8627 – 8631; *Angew. Chem. Int. Ed.* **2010**, *49*, 8449 – 8453.

[2] a) J. L. Detrich, O. M. Reinaud, A. L. Rheingold, K. H. Theopold, *J. Am. Chem. Soc.* **1995**, *117*, 11745 – 11748; see also: b) D. W. Keogh, R. Poli, *J. Am. Chem. Soc.* **1995**, *117*, 2516 – 2523; c) J. L. Carreón-Macedo, J. N. Harvey, *J. Am. Chem. Soc.* **2004**, *126*, 5789 – 5797.

[3] a) S. Shaik, D. Danovich, A. Fiedler, D. Schröder, H. Schwarz, *Helv. Chim. Acta* **1995**, *78*, 1393 – 1407; b) D. Schröder, S. Shaik, H. Schwarz, *Acc. Chem. Res.* **2000**, *33*, 139 – 145; c) J. N. Harvey, P. Poli, K. M. Smith, *Coord. Chem. Rev.* **2003**, *238*, 347 – 361. For multi-state scenarios, see: d) S. Shaik, H. Hirao, D. Kumar, *Acc. Chem. Res.* **2007**, *40*, 532 – 542.

[4] It should be added, however, that there remains a significant challenge for theory to improve accuracy in the prediction of spin states, see: a) F. Neese, *Coord. Chem. Rev.* **2009**, *253*, 526 – 563; b) S. Ye, F. Neese, *Inorg. Chem.* **2010**, *49*, 772 – 774; c) F. Neese, *J. Biol. Inorg. Chem.* **2006**, *11*, 702 – 711.

[5] N. Strickland, J. N. Harvey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 331 – 343.

[6] a) S. P. de Visser, D. Kumar, R. Neumann, S. Shaik, *Angew. Chem.* **2004**, *116*, 5779 – 5783; *Angew. Chem. Int. Ed.* **2004**, *43*, 5661 – 5665; b) C. Q. Wang, K. V. Shalyaev, M. Bonchio, T. Carofiglio, J. T. Groves, *Inorg. Chem.* **2006**, *45*, 4769 – 4782; c) S. J. Yoon, S. A. Wilson, Y. K. Jang, M. S. Seo, K. Nehru, B. Hedman, K. O. Hodgson, E. Bill, E. I. Solomon, W. Nam, *Angew. Chem.* **2009**, *121*, 1283 – 1286; *Angew. Chem. Int. Ed.* **2009**, *48*, 1257 – 1260.

[7] P. J. Derrick, K. F. Donchi in *Comprehensive Chemical Kinetics, Vol. 24* (Eds.: C. H. Bamford, C. F. H. Tipper), Elsevier, Amsterdam, **1983**, pp. 53 – 247.

[8] C. Rue, P. B. Armentrout, I. Kretzschmar, D. Schröder, J. N. Harvey, H. Schwarz, *J. Chem. Phys.* **1999**, *110*, 7858 – 7870.

[9] T. Kojima, S. Fukuzumi, *Angew. Chem.* **2011**, *123*, 3936 – 3937; *Angew. Chem. Int. Ed.* **2011**, *50*, 3852 – 3853.