Unfolding mysteries of metal-dioxygen and metal-TEMPO chemistry

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Exceptional reactivity of metal-alkyl bonds towards dioxygen has lain at the heart of organometallic chemistry since Frankland's pioneering studies.[1] In turn, the behavior of TEMPO and the related nitroxyl radicals as ligands is a topic of significant interest as their bonding and reactivity provide mechanistic insights into various chemical transformations. Nevertheless, reports on the reactivity of both dioxygen and free organic radicals towards metal alkyls has remained contradictory and vague for decades. For example, nitroxyl radicals were commonly used as inhibitors or radical traps in metal alkyls/O_2 reactions, and in 1968 Davies and Roberts concluded, misleadingly, that "galvinoxyl apparently reacts with Et_2Zn (in the presence of O_2) to give a product which has little effect on the rate of oxidation of the first ethyl-zinc bond, but strongly inhibits the oxidation of the second".[2] In recent year, our group has marked important milestones in a deeper understanding of the oxygenation of non-redox-active metal alkyls[3-7] as well as dispelled the widely held myth about the non-innocent behavior of nitroxyl radicals towards organometallics.[4,8-10]

Herein, we will provide a new look at the reactivity of both O_2 and free stable radicals towards organometallic compounds and demonstrate synergy of electronic and steric effects in turning the reactivity in deceptively simple organometallic M-O_2 and M-TEMPO systems.

References

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