Towards New Insights into Chemistry of Group 2 Metal (Mg, Ca) Peroxides

Metal alkylperoxides play a very important role in modern coordination and bioinorganic chemistry as well as in asymmetric organic synthesis. However, the foregoing works have mainly focused on the transition metal alkylperoxide and peroxide complexes. Conversely, chemistry of main-group metal alkylperoxides is less well known, mostly due to extremely high reactivity as well as low stability of these compounds, which often prevent their isolation and thorough characterization. Only parent group ground-breaking studies have provided new insights into these unique class of compounds and convincingly demonstrated that main-group metal alkylperoxides might be easily obtained with high yields by the controlled oxygenation of the rationally desing metal alkyl complexes. Moreover, based on our further studies concerning oxygenation of organozincs, we proposed a new mechanism of the oxygenation of organometallics with redox inactive metal centers i.e. an inner sphere electron transfer mechanism (ISET). Above all, using properly designed model zinc alkyl/O_2 reaction systems, we have disclosed a hitherto overlooked decomposition pathways of zinc alkylperoxides that are mediated by homolytic cleavage of the O-O bond. Our breakthroughs in the field paved the way for the development of novel catalytic systems and initiating systems for radical organic reactions based on zinc alkylperoxide species.
On the other hand, the oxygenation chemistry of magnesium alkylperoxides still remains a highly unexplored research area, mostly owing to the higher reactivity of organomagnesium compounds as well as significantly lower stability of the resulting products compared to analogous organzinc species. However, our group recent studies convincingly demonstrated that the controlled oxygenation of (N,N)MgR compounds lead exclusively to the (N,N)MgOOR complexes, and the stability of the latter compounds strongly depends on the nature of N,N-ligand. Furthermore, these results revealed that magnesium alkylperoxides incorporating β-diketiminate ligand possess very high catalytic activity in the epoxidation of enones.

This seminal work has provided a new stimulus to further investigations on the chemistry of magnesium alkylperoxides. Moreover, in this project we decided to extend our research to hitherto unknown in literature calcium alkylperoxide complexes. A particularly novel aspect of the planned studies, which has not been essentially addressed in the literature until now, will concern the synthesis of Group 2 metal alkylperoxides by the controlled reaction of parent metal complexes with of organic hydroperoxides and an adduct $(H_2O_2)_2$·DABCO. **It should be emphasized, the proposed synthetic pathway is unprecedented for the preparation of magnesium and calcium alkylperoxides.** Moreover, the final step of the project will be dedicated to investigating catalytic activity of the resulting metal alkylperoxides in the epoxidation of enones. The research I plan to conduct will not only broaden the scope of knowledge of the chemistry of organometallic compounds of Group 2, but also pave the way for rational development of novel, efficient catalytic systems for the epoxidation of enones based on main-group metal alkylperoxides.