

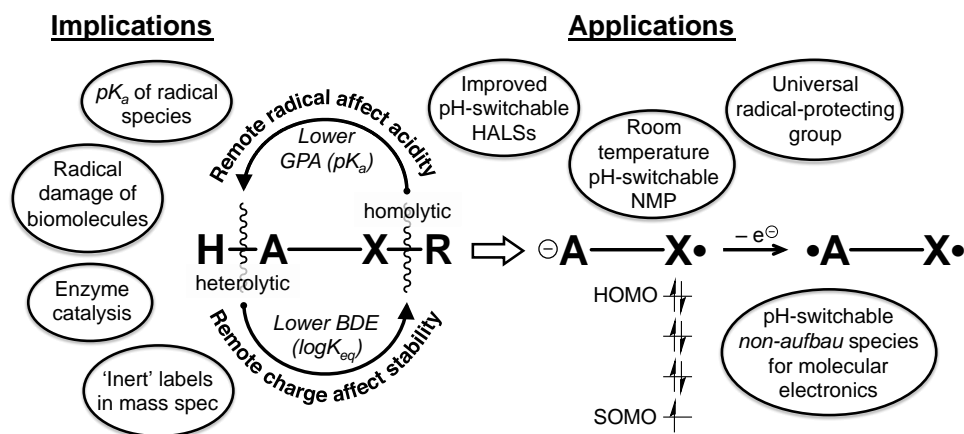
Manipulating Stability and Orbital Configuration of Free Radicals with pH

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Polar effects on radical stability are traditionally attributed either to resonance effects or to dipole effects. Resonance involves donor-acceptor interactions between specific functional groups that are conjugated or hyperconjugated with one another; dipole effects involve through-space electrostatic interactions between charged functional groups and/or partially charge-separated (polarised) fragments. Very recently, we have discovered a third type of polar effect that is in principle non-directional and does not require σ - or π -conjugation or permanent dipoles [1,2]. Specifically, when a relatively localised anion, such as COO^- , is placed in the vicinity of a delocalised radical, *e.g.*, nitroxyl $\text{R}_2\text{NO}\cdot$ or 1,4-pentadienyl $\cdot\text{CH}(\text{CH}=\text{CH}_2)_2$, the radical experiences additional stabilisation, surprisingly large and long-range compared with its corresponding non-radical analogues. The effect arises in the enhanced polarisability (*i.e.*, ability to redistribute the electron density in response to an external electric field) of delocalised radicals compared with their corresponding closed-shell counterparts. In this way, the destabilising Coulombic repulsion between a remote negative charge and an unpaired electron is minimised and a greater overall stabilisation of the species (through charge-nuclei attraction) is achieved. Moreover, in distonic radical anions, this stabilisation is generally accompanied by a so-called SOMO-HOMO energy level conversion – a molecular orbital configuration violating the *aufbau* principle. As a result, the one-electron oxidation of such compounds produces high-spin species with potential applications in molecular electronics. Importantly, both the extra radical stabilisation and the orbital conversion disappear upon removal of the negative charge, *e.g.*, upon protonation of the acid-base group, and are therefore pH-switchable. These findings are likely to be useful in polymer and small-molecule synthesis and may be harnessed in enzyme catalysis.



References

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- G. Gryn'ova and M. L. Coote, *Journal of the American Chemical Society*, 135, 2013, 15392-15403.