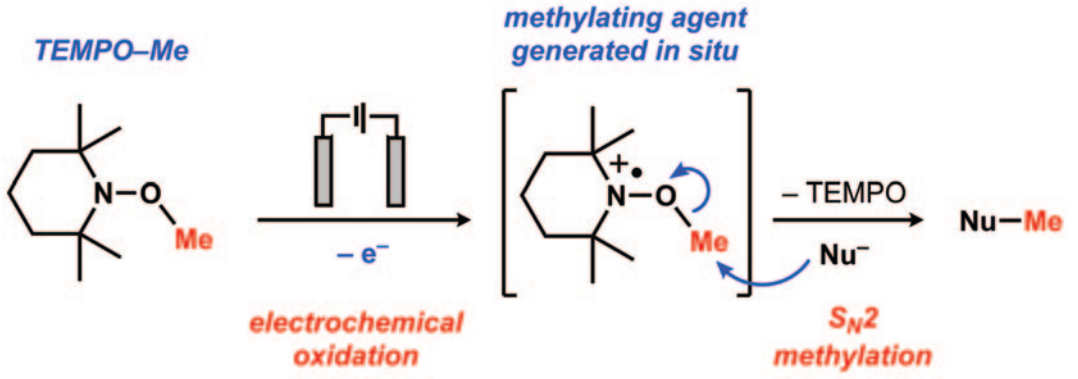
Electrophilic methylating agent activated by electrochemistry



Alkoxyamines are important compounds in polymer synthesis due to their ability to form a persistent nitroxide and a carbon-centred radical at elevated temperatures, thus facilitating controlled radical polymerisation. However, using a combination of experimental and computational chemistry, researchers at the Australian National University recently showed that, by electrochemically oxidising these molecules, they can instead generate carbocations. Building on this work, and in collaboration with researchers from the University of Tasmania, they have now demonstrated that the simplest of these alkoxyamines, TEMPO–Me, becomes a powerful electrophilic methylating agent when oxidised by electrochemistry (Norcott P.L., Hammill C.L., Noble B.B., Robertson J.C., Olding A., Bissember A.C., Coote M.L. *J. Am. Chem. Soc.* 2019, **141,** 15 450–5). Rather than generating a carbocation, the methylation proceeds via an S_N2 mechanism when combined with an appropriate nucleophile. Conventional methylating agents such as iodomethane, dimethyl sulfate or diazomethane suffer from acute toxicity, and often can be volatile and/or explosive. Using this new electrochemical methylation process, the reactive species is generated and consumed in situ, completely eliminating the need to handle hazardous reagents. This chemistry can be conducted at room temperature, open to the air, in a simple undivided electrochemical cell set-up.