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Computational strategies in finding greener CFC replacements

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Abstract: For many years CFCs were used in a vast range of applications, but the adverse environmental impact of their release into the atmosphere [1,2] has led to an international effort to replace them with acceptable alternatives. The Montreal Protocol [3] led to the phase out of CFCs in industrialized countries because of their elevated ozone depletion and global warming potentials (ODP and GWP). Development of suitable replacements with lower tropospheric lifetimes thus became a priority, with HCFCs firstly selected as alternatives on the basis of their higher reactivity towards OH radicals and similar physical chemical properties with CFCs. However, besides the non-zero ODP due to the presence of chlorine, these first-generation replacements were also found to maintain a high GWP. Development of environmentally friendly second-generation replacements for CFCs and HCFCs based on fluorocarbon derivatives thus became an urgent priority, with HFCs and PFCs appearing as a preferred choice. However, because of their high GWP, they were targeted by the Kyoto Protocol on climate change [4]. Consequently, renewed efforts to design and develop useful alternatives were put into practice, with hydrofluoroethers (HFEs) and hydrofluoropolyethers (HFPEs) appearing as promising third-generation replacements because of their zero ODP and even lower GWP. Finding such replacements has become increasingly important since October 2016, when nearly 200 countries adopted the Kigali Amendment to the Montreal Protocol, which phases-down production and use of HFCs and is considered by the United Nations Environment Programme (UNEP) “the single largest contribution the world has made towards keeping the global temperature rise well below 2 degrees Celsius, a target agreed at the Paris climate conference last year.” [5]

Here, we will provide a detailed insight behind the computational strategies involved in designing and developing greener replacements according to Green Chemistry principle #10 (Design for Degradation), which states that “chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment”. We will place emphasis in two critical steps of the process: 1) cost-effective calculation of the highly multidimensional potential energy surfaces [6-9] for the reactions between the targeted replacements and the OH radical and 2) prediction of the associated forward rate constants through multiconformer transition state theory [10], where we will analyze the key factors determining their values such as a) the magnitudes of quantum tunneling corrections and barrier heights and b) the pivotal interplay between the conformational sampling of

reactants and transition states with their associated Boltzmann weight factors. These strategies will be contextualized while comparing two specific classes of the HFPEs family, a,w-dihydrofluoropolyethers (DH-FPEs) and the more recent and promising a,w-dialkoxyfluoropolyethers (DA-FPEs), in a pioneering bottom-up-like approach projected to unveil the fundamental theoretical aspects of the unestablished atmospheric chemistry of HFPEs and other compounds. Hopefully, the gained theoretical knowledge will serve as an important tool to boost the design and development of new greener CFC alternatives.

Key-words: atmospheric chemistry, conformational sampling, density functional theory, hydrofluoropolyethers, model chemistry
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