A fully automated tool for estimating atmospheric oxidation reaction rates of unsaturated volatile organic compounds with OH, NO$_3$, O$_3$ and Cl

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Large quantities of various unsaturated volatile organic compounds (UVOCs) are emitted into the atmosphere, where they rapidly undergo electrophilic addition of OH, Cl, NO$_3$ or O$_3$. Upon oxidation, products of these reactions may also engage in oxidation reactions. This leads to extremely large numbers of rate coefficients, k_{add}, for which no measurements exist. Accordingly, structure-activity relationships (SARs) are used to parametrize reactivity. For electrophilic addition, the types, degree and distance of substitution attached to the double-bond result in wide ranges of reactivity exhibited by UVOCs. We provide a quick and easy-to-use automated tool to predict k_{OH}, k_{Cl}, k_{NO3} and k_{O3} for various UVOCs, and predictions were compared to Atkinson's group-additivity approach,[1] recent SARs,[2],[3] and perturbation frontier molecular orbital theory.[4] To our knowledge, k_{Cl} is not predicted by any automated technique. Here, orbital energies and a steric descriptor are correlated with experimental k_{add} at room temperature. Additional factors account for electron delocalization as observed in aromatics or conjugated systems. The parameters are calculated using density functional theory and a computationally cheap semi-empirical PM6 method. Despite its comparative cheapness, PM6 doesn't reduce estimation accuracy. Predicted k_{OH}, k_{Cl} and k_{NO3} are in good agreement with experiments and predictions from other techniques if existing, while k_{O3} predictions remain the most challenging using this method and require further consideration, which was expected due to the complexity of the mechanism compared to OH or Cl addition. Compared to existing approaches, our tool improves the general accuracy for estimating k_{add} for a variety of UVOCs. Based on the underlying calculation, our approach contains more information than many traditional SARs, and we therefore posit that it may perform more reliably when extrapolated to new and unfamiliar species. This tool will be online and open-access for general use and will facilitate the screening of large databases of molecules for atmospheric modelers, policymakers, or industrials.

[1] Kwok & Atkinson (1995), *Atm. Env. 29*, 1685-1695.

[2] Kerdouci, Picquet–Varrault & Doussin (2010), *Chem. Phys. Chem. 11*, 3909-3920.

[3] Michelat *et al.* (2022). *ACS Earth and Space Chem. 6*, 3101-3114.

[4] King, Canosa-Mas & Wayne (1999). *Physical Chemistry Chemical Physics 1*, 2231-2238.