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Predicting arene rate coefficients with respect to hydroxyl and other free radicals in the gas-phase: a simple and effective method using a single topological descriptor

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Abstract. The reactivity of aromatic compounds is of great relevance to pure and applied chemical disciplines, yet existing methods for estimating gas-phase rate coefficients for their reactions with free radicals lack accuracy and universality. Here a novel approach is taken, whereby strong relationships between rate coefficients of aromatic hydrocarbons and a Randić-type topological index are investigated, optimized and developed into a method which requires no specialist software or computing power.

Measured gas-phase rate coefficients for the reaction of aromatic hydrocarbons with OH radicals were correlated with a calculated Randić-type index, and optimized by including a term for side chain length. Although this method is exclusively for use with hydrocarbons, it is more diverse than any single existing methodology since it incorporates alkenylbenzenes into correlations, and can be extended towards other radical species such as $O(^3P)$ (and tentatively NO_3, H and Cl). A comparison (with species common to both techniques) is made between the topological approach advocated here and a popular approach based on electrophilic subsituent constants, where it compares favourably.

A modelling study was carried out to assess the impact of using estimated rate coefficients as opposed to measured data in an atmospheric model. The difference in model output was negligible for a range of NO_x concentrations, which implies that this method has utility in complex chemical models.

Strong relationships (e.g. for OH, R^2=0.96) between seemingly diverse compounds including benzene, multisubstituted benzenes with saturated, unsaturated, aliphatic and cyclic substitutions and the nonbenzenoid aromatic, azulene suggests that the Randić-type index presented here represents a new and effective way of describing aromatic reactivity, based on a quantitative structure-activity relationship (QSAR).

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