

H-migration in Alkylperoxy Radicals in the Atmosphere: Theory-based SAR Development

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The fate of alkylperoxy radicals, RO₂, in the troposphere is traditionally thought to be governed by their reactions with HO₂ and RO₂ in pristine conditions, and by NO in polluted areas. H-migration reactions in RO₂ radicals, forming hydroperoxide alkyl radicals, are well-known in combustion where they play an important role in ignition and cool flames, but were considered too slow to contribute to atmospheric chemistry. Recent theoretical studies, however, have proposed a set of alkylperoxy H-migration reactions, predicted to be competitive with traditional RO₂ sinks in the atmosphere. Such H-migrations occur in oxygenated and/or unsaturated alkylperoxy radicals, where the H-migration rate is enhanced by the availability of more weakly bonded hydrogen, e.g. an aldehydic H, an α -OH-substituted hydrogen, or an allylic H. To be effective in the atmosphere, the proposed reactions also need to form hydroperoxide products that do not readily back-migrate the hydrogen, either by have a sizable reverse barrier, or by undergoing facile subsequent rearrangements. The formation of hydroperoxide-substituted compounds through these H-migrations is implied in the regeneration of OH radicals in the VOC oxidation, isoprene in particular, in unpolluted conditions. A particular example of such an OH regeneration mechanism is the Leuven Isoprene Mechanism (1) found in models to yield high quantities of OH, in good agreement with field measurements. The identification of OH-generation reactions in the RO₂ chemistry has been largely driven by theoretical investigations, with very little experimental data available as yet on H-migration in RO₂ radicals in atmospheric conditions. Furthermore, the available experimental data sets seem not always consistent, with theoretical calculations able to reproduce some but not all observations (2). Given the dearth of experimental data, high accuracy of the theoretical predictions is critical.

We describe the impact of the level of quantum chemical theory used in the characterizations of the potential energy surface, and on the predictions of quantum chemical tunneling essential in the description of this reaction class. Furthermore, we work towards the development of a Structure-Activity Relationship for this reaction class, designed specifically for atmospheric conditions and addressing relevant substitutions and H-migration spans. Over 60 H-migrations are examined, covering 1,4- through 1,8-H-migration of primary, secondary and tertiary H-atoms, with oxo-, hydroxy- and unsaturated functionalities at various positions relative to the peroxy group and migrating H-atom. The systematic trends obtained thus are incorporated in a SAR predicting rate coefficients for H-migration.

References

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- (2) Taraborrelli, D.; Lawrence, M.G.; Dillon, T.J.; Gromov, S.; Groß, C.B.M.; Vereecken, L.; Lelieveld, J. *Nature Geosci.* **2012**, 5, 190-193.