

The Role of Chemical Activation in the OH-initiated Oxidation of Isoprene in the Troposphere

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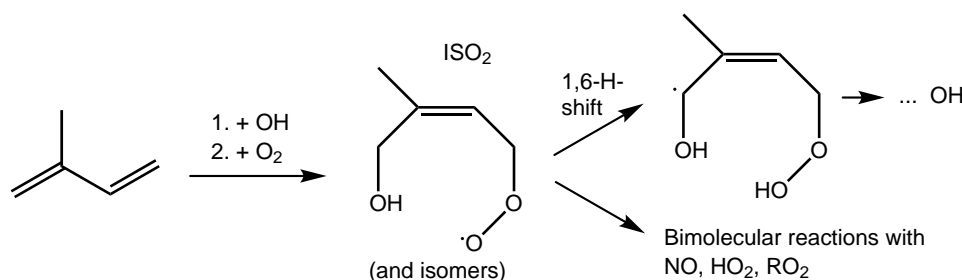
Isoprene is one of the most abundant biogenic hydrocarbons in the atmosphere. Its degradation, initiated by reactive species such as the hydroxyl radical, has been analyzed in numerous studies. While for high NO_x levels the oxidation mechanism is fairly well understood, there are discrepancies for unpolluted environments, where current models underpredict OH concentrations [1]. A reason could be that there are missing OH-regenerating pathways, which compete with the bimolecular sink reactions involving NO. In this context, unimolecular reactions of the hydroxyperoxy intermediates leading finally to OH were proposed in recent theoretical studies by Nguyen et al.[2] and da Silva et al.[3]. These comprise 1,5-H-shifts of the β-OH-O₂-adducts and 1,6-H-shifts of the δ-OH-O₂-adducts. In Scheme 1, an example for the latter reaction type is given.

It has remained an open question to which degree chemical activation from the exothermic addition steps of OH and O₂ can enhance these unimolecular reaction pathways. Therefore, we studied their kinetics, using master equations with specific rate coefficients from RRKM theory and a simplified statistical adiabatic channel model. Energy profiles were taken from Ref. [2]. One-dimensional tunnelling corrections were applied where necessary, and torsional modes were treated in a one-dimensional hindered rotator approach [4].

In order to account for multiple chemical activation processes, three master equations were coupled [5]. The energy distribution of the OH-isoprene adduct obtained by solving a first master equation was used as input distribution for two further master equations, which describe the unimolecular reactions of the relevant intermediates formed by addition of O₂. As a result, we found no noticeable enhancement of OH-regenerating pathways by chemical activation under atmospheric conditions. Obviously additional pathways have to be considered.

References

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Scheme 1. Reaction pathways of the (Z)-δ-OH-O₂-adduct radical formed after subsequent reaction of isoprene with OH and O₂.