



Research paper

Degradation mechanism of *trans*-2-hexenal in the atmosphere

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ABSTRACT

The tropospheric decomposition mechanism of *trans*-2-hexenal with oxidants (i) $\bullet\text{NO}_3$, (ii) $\bullet\text{OH}$, (iii) Cl, and (iv) O_3 present in the atmosphere is discussed employing density functional theory. We found that reaction with Cl atom has the lowest barrier amongst all oxidants. Also, preference for aldehydic H abstraction over α - or β -addition and allylic H abstraction pathways is noticed for reactions with $\bullet\text{OH}$ and $\bullet\text{NO}_3$. Lower barriers are seen for O_3 addition when a water molecule assists the reaction. Understanding the decomposition mechanism of such VOCs is important since degradation products participate in secondary organic aerosol (SOA) formation in the atmosphere.

1. Introduction

Exploration of atmospheric degradation mechanisms and the kinetics of volatile organic compounds (VOC) are significant toward atmospheric modelling as well as understanding the effects of organic aerosols in the environment. VOCs are believed to be the essential nucleation precursors leading to the formation and subsequent growth of secondary organic aerosols (SOA), which has been an area of intense recent interest [1,2]. VOCs that get released continuously from biogenic and anthropogenic sources [3,4] interact with each other as well as with other species present in the atmosphere, leading to the formation tropospheric ozone, smog and aerosols, causing adverse environmental impacts [5–7].

VOCs originate mainly from the terrestrial biosphere (biogenic volatile organic compounds - BVOCs), with a minor contribution from anthropogenic sources [2,8]. Mono and sesqui-terpenes as well as green leaf volatiles (GLVs) are important members of BVOCs and are efficient precursors of SOA [9–11]. GLVs consist of carbonyl compounds, especially C_6 aldehydes, alcohols and esters [12–13]. Oxygenated BVOCs have broad implications on the ecosystem due to their reactivity and toxicological properties [14]. *Cis*-3-hexenylacetate, *cis*-3-hexen-1-ol and *trans*-2-hexenal are important members of the GLVs [15,16]. Among these, *cis*-3-hexenol is reported to be a better precursor for SOA compared to *cis*-3-hexenyl acetate due to the high oligomerisation capabilities of its oxidation products [12]. The present work focuses on the tropospheric reactivity of *trans*-2-hexenal, a bifunctional molecule, where the presence of a double bond is expected to enhance aerosol formation.

Once released into the atmosphere, photodegradation as well as reaction with $\bullet\text{OH}$, Cl, O_3 , or $\bullet\text{NO}_3$ are the major elimination pathways of *trans*-2-hexenal [14,17–19]. Among these, the reaction with NO_3 and OH contributes toward removal mechanisms during the night and the day, respectively [17–19]. Ozone also plays a vital role in the oxidation of atmospheric species during both the day and the night [20–22]. Free radicals and small molecules generated by the action of the radicals/reagents mentioned above can cause further fragmentation and functionalisation, thereby leading to the formation of aerosols [23]. Herein, we discuss the mechanistic details of tropospheric decomposition pathways of *trans*-2-hexenal by atmospheric oxidants viz. $\bullet\text{NO}_3$, $\bullet\text{OH}$, Cl, and O_3 by using computational tools. For each oxidant except ozone, three possible routes were considered: addition of oxidants to the double-bonded carbon atoms at the α and β , positions of C(H)O group, and the abstraction of the H atom from the C(H)O group and γ (allylic) position of hexenal [17,18]. The study details the mechanistic routes by which *trans*-2-hexenal degraded, the nature of degradation products and their influence in secondary aerosol formation.

2. Computational methods

Geometry optimization of intermediates, transition states, and products have been carried out at the BHANDHLYP/6-31G*(B1) level of theory, using the Gaussian09 suite of a quantum chemical program [24–26]. All stationary points on the respective potential energy surfaces were characterised at the same level of theory by evaluating corresponding Hessian indices. Careful verification of the unique imaginary frequencies for transition states was carried out to check whether the

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