SO_2 addition to alkenes: a new formation mechanism of organosulfates in the atmosphere

M. Passananti[1], J. Shang[2], Y. Dupart[1], S. Perrier[1], C. George[1]

[1] Université de Lyon 1, Lyon, F-69626, France; CNRS, UMR5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, F-69626, France[2]State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, People's Republic of China
Keywords: organosulfates, sulphur dioxide, alkenes, interface reactions.
Presenting author email: monica.passananti@ircelyon.univ-lyon1.fr

Secondary organic aerosol (SOA) formation and composition have received increasing attention in the last years due to their impact on climate, air quality and human health. Organosulfates have been increasingly and widely detected in tropospheric particles and has been suggested to arise as side products from SOA production (Tolocka, 2012). Therefore, they have also been identified as SOA tracers (Zhang, 2012). Originally, the production of organosulfates was explained by the esterification reaction of alcohols, but this reaction in atmosphere is kinetically negligible. Other formation pathways have been suggested such as hydrolysis of peroxides and reaction of organic matter with sulfite and sulfate radical anions ($SO_3^{-\bullet}$, $SO_4^{-\bullet}$) (Nozière, 2010), but it remains unclear if these can completely explain atmospheric organo-sulfur aerosol loading.

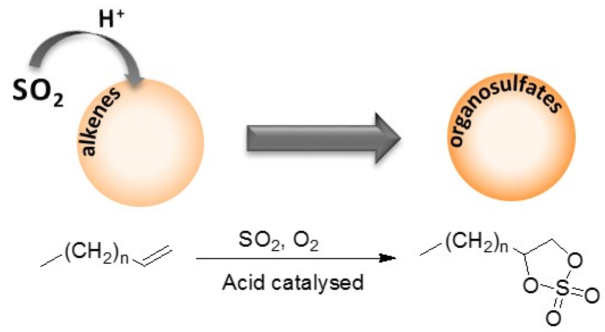

Figure 1. A possible formation pathway of organosulfates in atmosphere.

We have investigated a new formation pathway of organo-sulfur compounds: the addition of SO_2 to alkenes (Figure 1). The sulphur dioxide addition to double bond can occur with different mechanisms (photoreaction, ene-reaction, cycloaddition) (Jones, 1974; Vogel, 2007; Lan, 2011). Differently to ozone, sulphur dioxide is a 1,3-dipole with a strong zwitterion character and the most favourable cycloaddition to double bond is a 2+2 addition. On the other hand, O_3 adds to alkenes by a well-known 3+2 cycloaddition (Lan, 2011). In order to better understand this reaction and its environmental impact we have studied the reactivity of SO_2 with respect to different alkenes (cis/trans, terminal/internal alkenes). The experiments were carried out at the solid (or liquid)-gas interface. A custom built coated-wall flow tube reactor was developed to control relativity humidity, SO_2 concentration, temperature and gas flow rate. The uptake coefficients of SO_2 on organic films were calculated and resulting products were identified using liquid chromatography coupled with an orbitrap mass spectrometer (LC-HR-MS).

The results show that surprisingly SO_2 reacts efficiently with alkenes to form organulfates. For examples, the experiments carried out on 1-dodecene highlighted a rapid SO_2 uptake and the efficient formation of $C_{12}H_{24}O_4S$, which could be a cyclic organosulfate (Figure 1). Moreover, we have observed that the reaction is acid-catalysed, a faster uptake of SO_2 is observed in presence of an acid function. Indeed, it was observed that unsaturated acids (oleic acid) are very sensitive to SO_2 addition. These preliminary results tend to elucidate the role of organo-sulfates interfacial chemistry, as a significant pathway for understanding of atmospheric SOA formation.

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