

Dark reaction of NO₂ with conjugated alkenes

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Nowadays, it is well established that alkenes react preferentially with ozone, OH and NO₃ radicals in the atmosphere (1). However, environmental chamber experiments have shown that NO₂ could contribute significantly to the consumption of some alkenes when using high concentrations of reactants (at ppm level). Previous kinetic measurements showed that the reaction of monoalkenes or non-conjugated alkenes (i.e., α -pinene, 1,4-cyclohexadiene) react slowly with NO₂ in contrast to conjugated alkenes (i.e., α -terpinene, α -phellandrene) (2,3). However, although the reactivity of these compounds through reaction with NO₂ has been demonstrated, the degradation mechanism in gas phase is still poorly defined.

In order to gain further knowledge about the NO₂ chemistry with alkenes, a series of smog chamber experiments have been conducted at ~ 298 K and 760 Torr under dry conditions (RH < 5%). In this study, four alkenes have been selected: isoprene, myrcene, ocimene and 1,3-cyclohexadiene. These species have been chosen according to their emission rates into the atmosphere and their apparent reactivities with NO₂. Reactants (alkenes and NO₂) and oxidation products have been measured by FT-IR spectroscopy. Rate coefficients of NO₂ reaction with the selected alkenes have been determined and found to be as follows (in cm³ molecule⁻¹ s⁻¹): $k(\text{isoprene} + \text{NO}_2) = (1.12 \pm 0.09) \times 10^{-19}$; $k(\text{myrcene} + \text{NO}_2) = (2.5 \pm 0.1) \times 10^{-19}$; $k(\text{ocimene} + \text{NO}_2) = (8.4 \pm 0.6) \times 10^{-19}$ and $k(1,3\text{-cyclohexadiene} + \text{NO}_2) = (1.5 \pm 0.1) \times 10^{-18}$. In addition, FT-IR examination of the gas phase mixtures showed that selected alkenes can be divided in two groups: ocimene and myrcene have shown to produce acetone as major identified products whereas isoprene and 1,3-cyclohexadiene lead preferentially to nitrogen-containing products where major IR bands have been assigned to -NO₂ and -O₂-NO₂ functional groups.

The reactivity of NO₂ with alkenes will be discussed and tentatively linked to the chemical structure of the studied alkene. The gas phase mechanism leading to the identified oxidation products will be presented and discussed.

References

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