

### SNAM1-3

#### Can the Night-Time Atmospheric Oxidant $\text{NO}_3^\bullet$ Damage Aromatic Amino Acids?

Uta Wille, Duanne Sigmund

*The University of Melbourne, Melbourne, VIC, Australia*

Adverse health effects of ambient air pollutants have been addressed by numerous epidemiological studies. In particular, an association between increased concentrations of ozone and nitrogen oxides, and increases in respiratory morbidity and hospital admissions for asthma in both adults and children has been proposed, but the underlying mechanism is not clear. It has been suggested that  $\text{O}_3$  and  $\text{NO}_2^\bullet$  may modulate airway diseases, such as asthma, by increasing the release of inflammatory mediators from bronchial epithelial cells and that the cells of asthmatic patients may be more susceptible to the adverse effects of these pollutants. Quite remarkably, to our knowledge, neither of these studies considered that in the atmosphere  $\text{NO}_2^\bullet$  and  $\text{O}_3$  form highly reactive nitrate radicals,  $\text{NO}_3^\bullet$ .

$\text{NO}_3^\bullet$  is rapidly photolyzed during the daytime, but after sunset tropospheric concentrations of  $\text{NO}_3^\bullet$  rise to ppt levels, and this radical is responsible for the initiation of atmospheric transformations at night. Although during the past decades the role of  $\text{NO}_3^\bullet$  in atmospheric chemistry was addressed by many studies, virtually no link between this oxidant and oxidative damage in biomolecules exposed to the atmosphere has been made. A recent investigation by a German research group showed that birch pollen proteins are efficiently nitrated in polluted air, suggesting that protein nitration may play a central role in the promotion of allergies by air pollutants and a direct involvement of  $\text{NO}_3^\bullet$  in this process. Although the atmospheric concentration of  $\text{NO}_3^\bullet$  is less than that of  $\text{NO}_2^\bullet$  or  $\text{O}_3$ ,  $\text{NO}_3^\bullet$  is many orders of magnitude more reactive, and this reactivity can outweigh its lower abundance.

In our effort to obtain fundamental insight into the  $\text{NO}_3^\bullet$  induced oxidative damage of proteins, we studied the products formed in the reaction of photochemically generated  $\text{NO}_3^\bullet$  with selected aromatic amino acids using mass spectrometry. Rapid oxidation was observed at both the aromatic ring and in  $\beta$ -position, leading to nitro-aromatic compounds and  $\beta$ -nitrate esters and their subsequent oxidation products. Our results suggest that  $\text{NO}_3^\bullet$  may be the real culprit in some pollution-derived diseases.