



Nighttime production of peroxy radicals at a semi-rural location

M. J. Jacob (1,3), P. S. Monks (1), A. C. Lewis (2), J. F. Hamilton (2), J. R. Hopkins (2)

(1) Department of Chemistry, University of Leicester, UK, (2) Department of Chemistry, University of York, UK, (3) Now at the Interdisciplinary Environmental Research Centre, TU Bergakademie, Freiberg, Germany (mark.jacob@ioez.tu-freiberg.de / Fax: 00 49 3731 394060 / Phone: 00 49 3731 392328)

The sum of organic peroxy radicals and HO₂, subsequently referred to as RO₂, was measured with a peroxy radical chemical amplifier (PERCA) during the Tropospheric ORganic CHEMistry experiment (TORCH) in August 2003 at a ground-based site 40 km northeast of London. Measurements were performed continuously over a five week period in the Summer of 2004. A notable result was the significant mixing ratios of peroxy radicals measured during the night. Secondary nighttime maxima in [RO₂] occurred on a number of occasions.

It is now well established that free radical formation can be initiated at night, ie non-photolytically, *via* ozonolysis of alkenes and NO₃ radical reactions with volatile organic compounds, VOCs. In order to investigate the contributions to peroxy radical production of these two sources, NO₃ concentrations were calculated assuming a steady state NO₃ concentration:

$$[\text{NO}_3]_{\text{ss}} = k_{\text{O}_3+\text{NO}_3}[\text{O}_3][\text{NO}_2]/$$

$$(k_{\text{NO}_3+\text{NO}}[\text{NO}]+k_{\text{NO}_3+\text{VOC}}[\text{VOC}]+k_{\text{NO}_3+\text{RO}_2}[\text{RO}_2]+k_{\text{NO}_3+\text{DMS}}[\text{DMS}])$$

where DMS (Dimethylsulphide) and VOCs were measured by GC FID.

NO₃ also reacts with NO₂ to form N₂O₅ which can be lost *via* heterogeneous reaction with water and this was included in the calculations. [NO₃]_{ss} ranged from 0 to 13 pptv

over the whole campaign with an average of 1.4 pptv. This range is consistent with measurements of NO_3 made at other locations. On a number of occasions $[\text{NO}_3]_{\text{ss}}$ was negatively correlated with $[\text{DMS}]$ and on many nights was positively correlated with $[\text{RO}_2]$.

The significance of these observations and the relative importance of the two nocturnal peroxy radical production pathways will be discussed in this work and compared with results of previous studies.