

FREE RADICAL CHEMICAL CONVERSIONS WITHIN TROPOSPHERIC AQUEOUS AEROSOLS

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KEYWORDS

Aerosol Chemistry, Free Radicals, Oxidants, Ionic Strengths Effects, Models

Laser-based time-resolved techniques have been applied to study reactions of free radicals and radical anions such as NO_3^- , SO_4^- , Cl_2^- , Br_2^- and CO_3^- which are of interest for tropospheric aerosol and cloud chemistry which, from a chemical point of view, are often addressed as the 'atmospheric aqueous phase' (Herrmann et al. (1995), Huie 1995, Zellner und Herrmann 1995). Experimental studies have been performed with bulk aqueous phase chemical techniques. The results obtained, however, are used as input parameters for modelling chemical conversions involving the atmospheric aqueous aerosol when heterogeneous reaction sequences are treated by a sequence of phase transfer from the gas phase followed by condensed-phase reaction for a given species.

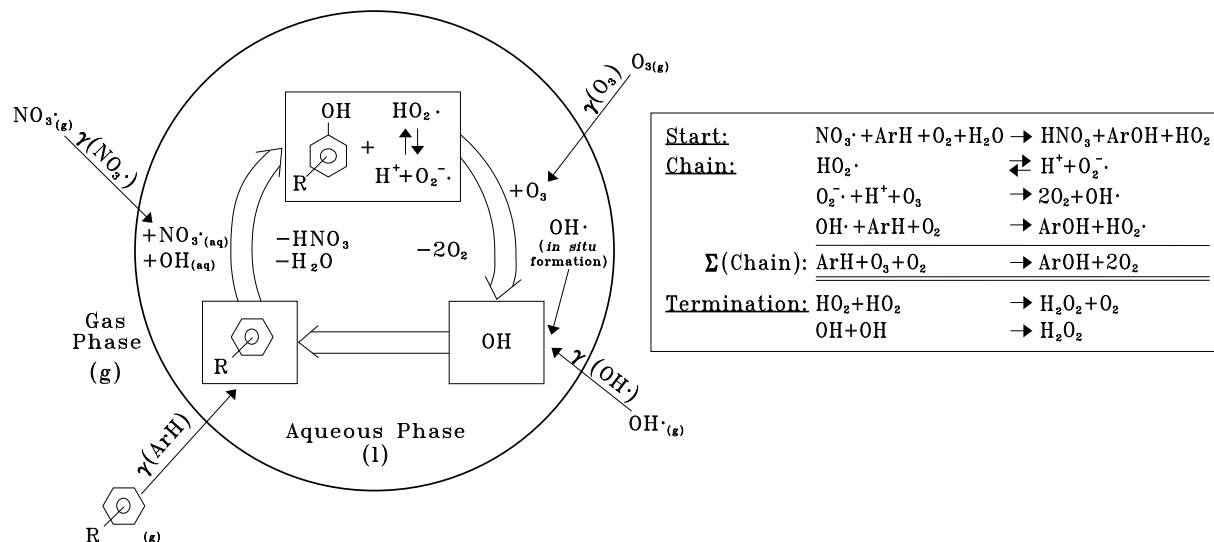


Fig. 1. Possible aqueous particle phase conversions of free radicals and aromatic compounds.

The results which are reported refer to free radical reactions with aqueous phase organic constituents from different substance groups such as aromatics, sulfur-containing compounds, aldehydes and acids. It will be shown that in some cases as in the reactions of HO_x/NO_y with polar aromatics in aerosol particles, chain reaction sequences may form leading to effective conversion of compounds at the tropospheric aqueous aerosol. A schematic for such a possible sequence is given in Figure 1.

Special emphasis was laid on the study of free radical reaction in the regime of high ionic strength as it is often observed in tropospheric aqueous aerosols. Field measurements within the framework of ACE-2 applying size-resolved chemical analysis and hygroscopicity measurements lead to detailed information of ionic strength regimes and compositions encountered within aqueous aerosols which will be presented.

With regards to the laboratory studies different model systems will be discussed where reaction rate constants have been determined over a wide range of ionic strength. Such systems have been studied in reactions of $\text{NO}_3\cdot$ (reactions with chloride, formate), $\text{Cl}_2\cdot^-$ (methanol, formate) and others. A simple model will be presented allowing the description of radical reaction rate constants by a simple kinetic scheme over a wide range of ionic strength in good agreement with the experimentally determined data.

Based on available laboratory kinetic data as discussed before an extensive chemical mechanism for use in modelling of tropospheric cloud and aerosol chemistry has been developed. Results from different case studies will be presented and the main effects of aerosol chemical conversions, which here include cloud droplet chemistry, will be discussed.

ACKNOWLEDGEMENTS

The work described here has substantially been supported by the EC-funded Projects RINOXA 2 (ENV4-CT95-0175) and MODAC (ENV4-CT97-0388). Aerosol chemical modelling is supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie under contract 07AF212 within the Schwerpunkt 'Aerosolforschung (AFS)'.

REFERENCES

H. Herrmann, M. Exner, H.-W. Jacobi, G. Raabe, A. Reese and R. Zellner (1995), Laboratory Studies of Atmospheric Aqueous Phase Free Radical Chemistry: Kinetic and Spectroscopic Studies of Reactions of NO_3 and SO_4^- Radicals with Aromatic Compounds, *Faraday Discuss.* **100**, 129-153.

R.E. Huie, Free Radical Chemistry of the Atmospheric Aqueous Phase, in *Progress and Problems in Atmospheric Chemistry*, Ed. J.R. Barker, pp. 375-419, World Scientific, Singapur 1995.

R. Zellner and H. Herrmann (1995), Free Radical Chemistry of the Aqueous Atmospheric Phase, in *Advances in Spectroscopy*, Vol. 24, Spectroscopy in Environmental Science, Eds. R.J.H. Clark and R.E. Hester, pp. 381 - 451, Wiley, London.