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Kinetics of OH-initiated oxidation of oxygenated organic compounds in the aqueous phase: new rate constants, structure–activity relationships and atmospheric implications

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Abstract

The kinetics of OH oxidation of several organic compounds of atmospheric relevance were measured in the aqueous phase. Relative kinetics were performed using various organic references and OH sources. After validation of the protocol, temperature-dependent rate constants for the reactions of OH radical with ethyl ter-butyl ether ($k_{297\,\mathrm{K}} = 1.5(\pm 1.7) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, $E_a/R = 580\ (\pm 560)\,\mathrm{K}$), *n*-butyl acetate ($k_{297\,\mathrm{K}} = 1.8\ (\pm 0.4) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, $E_a/R = 1000\ (\pm 200)\,\mathrm{K}$), acetone ($k_{298\,\mathrm{K}} = 0.11\ (\pm 0.05) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, $E_a/R = 1400\ (\pm 500)\,\mathrm{K}$), methyl ethyl ketone ($k_{298\,\mathrm{K}} = 0.81(\pm 0.18) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, $E_a/R = 1200\ (\pm 200)\,\mathrm{K}$), methyl iso-butyl ketone ($k_{298\,\mathrm{K}} = 2.1(\pm 0.5) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, $E_a/R = 1200\ (\pm 300)\,\mathrm{K}$) and methylglyoxal ($k_{298\,\mathrm{K}} = 0.53(\pm 0.04) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, $E_a/R = 1100\ (\pm 300)\,\mathrm{K}$) were determined. A non-Arrhenius behavior was found for phenol, in good agreement with the contribution of an OH addition to the mechanism, which also includes H-abstraction by OH radicals. Global rate constants of acetaldehyde, propionaldehyde, butyraldehyde and valeraldehyde were studied at 298 K only, as these compounds partly hydrate in the aqueous phase. All the obtained data (except those of phenol) complemented by literature data were used to investigate three methods to estimate rate constants for H-abstraction reactions of OH radicals in aqueous solutions when measured data were not available: Evans-Polanyi-type correlations, comparisons with gas-phase data, structure activity relationships (SAR). The results show that the SAR method is promising; however, the data set is currently too small to extend this method to temperatures other than 298 K. The atmospheric impact of aqueous phase OH oxidation of water-soluble organic compounds is discussed with the determination of their global atmospheric lifetimes, taking into account both gas- and aqueous-phase reactivities. The results show that atmospheric droplets can act as powerful photoreactors to eliminate soluble organic compounds from the atmosphere.

Keywords: Relative kinetics; Photo-oxidations; Structure–activity relationship; Tropospheric lifetime

1. Introduction

The atmosphere is a complex medium where numerous chemicals are released, dispersed by physical processes and oxidized by photochemical reactions initiated by solar radiations. One of the most efficient

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oxidants is the OH radical produced by complex photochemical processes (Atkinson, 2000).

In the past, tropospheric photochemistry of volatile organic compounds (VOCs) was studied only in the gaseous phase, although the atmosphere contains a significant amount of condensed matter. The inter-phase phenomena and multiphase interactions were neglected. It was only in the early 1980s that theoretical studies considered chemical interactions of organic compounds between gaseous and aqueous phases of clouds (Graedel and Weschler, 1981). It was then recognized that the aqueous-phase photochemistry of water-soluble organic compounds (WSOC) has an important impact on the gaseous concentrations of key species in the atmosphere such as OH, HO_2 and ozone (Jacob, 1986; Lelieveld and Crutzen, 1990; Monod and Carlier, 1999; Barth et al., 2003). More recently, the presence of WSOC in aerosols has been found to contribute to the aerosol hygroscopicity and to the ability of particles to act as condensation nuclei. In this manner, WSOC play a role on climate changes (Facchini et al., 2000; Fuzzi et al., 2002).

Cloud droplets contain numerous chemical species originating from both the gaseous phase and the condensation nuclei, providing a medium where complex chemistry and photochemistry occur. Several free radicals (e.g. OH, NO_3, Cl, Cl_2^-, SO_4^-) are formed, which can react with dissolved organic matter. Among these radicals, one of the most efficient oxidizing species is the OH radical (Ervens et al., 2003; Herrmann, 2003).

The study of OH-initiated oxidation of WSOC in the aqueous phase has been carried out in laboratory studies by numerous authors and has been compiled in reviews (Buxton et al., 1988; NIST, 2002). However, most of these studies have only been carried out at room temperature and deal with compounds that are not necessarily relevant to the atmosphere.

In the present work, we measured aqueous phase OH-initiated oxidation rate constants of several oxygenated organic compounds relevant to the atmosphere or chosen as test compounds (ethanol, *t*-butanol, 1-butanol, 2-propanol, 1-propanol, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, phenol, ethyl ter-butyl ether (ETBE), *n*-butyl acetate, acetone, methyl ethyl ketone (MEK), methyl iso-butyl ketone (MIBK), and methylglyoxal). We also measured the temperature dependence of the corresponding rate constants for most of these compounds. The obtained data, compiled together with previous data, were used to investigate various methods to estimate rate constants for H-abstraction reactions of OH radicals in aqueous solutions when measured data were not available. Finally, assuming Henry's law equilibrium for some compounds, we calculated their atmospheric lifetimes in both dry and cloudy atmospheric conditions in order to estimate the importance of aqueous chemistry in the atmosphere.

2. Experimental procedures

2.1. Continuous photolysis apparatus

The apparatus consisted of a Pyrex vessel of 450 cm^3 (Fig. 1). The irradiation source was a xenon arc lamp, 300 W. The lamp was fixed above the vessel, at a constant and reproducible distance from the surface of the water. The light beam entered the reactor through a quartz window. For highly photosensitive species, the quartz window was replaced by a pyrex window, which filters light below 300 nm. The aqueous solution was continuously stirred and maintained at a constant temperature (±0.2 K).

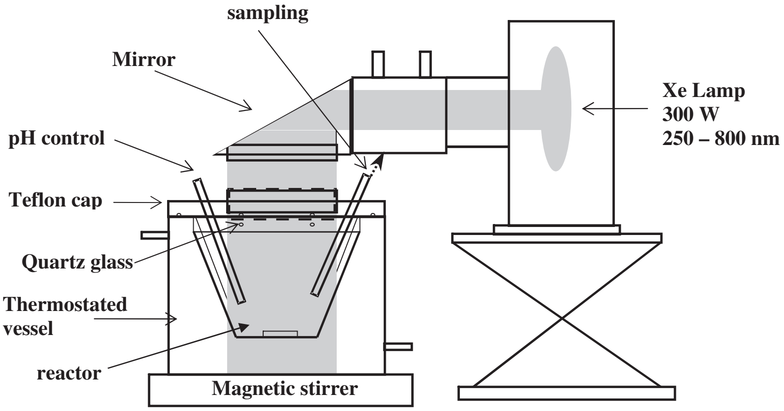

Fig. 1. Scheme of the static photoreactor.