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Aqueous OH kinetics and activation parameters of aliphatic esters

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Hydroxyl radicals (OH) play a key role in atmospheric and environmental chemistry due to their high reactivity toward organic compounds. [1] Water-soluble organic compounds (WSOCs), including aliphatic esters, are widespread in the environment and may undergo degradation through reaction with OH in atmospheric waters and water treatment systems. [2] Oxidation of WSOCs contributes to the formation of secondary organic aerosols (SOAs) and influences the atmospheric lifetimes of various organics. [3-4] Despite their environmental relevance, kinetic data describing aqueous-phase reactions of aliphatic esters with OH remain limited.

In this work, the aqueous-phase bimolecular rate coefficients ($k_{OH_{aq}}$, $M^{-1}\ s^{-1}$) for the reactions of selected aliphatic esters with OH were measured in the temperature range 278-318 K using the relative rate technique. OH were generated by photolysis of hydrogen peroxide in a temperature-controlled aqueous photoreactor. The investigated esters included formates, acetates, propanoates, butyrates, valerates, and hexanoates. Concentrations of analytes were monitored using headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry (SPME-GC/MS). Relative kinetic and Arrhenius plots showed good linearity, confirming the reliability of the experimental approach.

The measured $k_{OH_{aq}}$ values at 298 K ranged from $3.59 \times 10^{8}\ M^{-1}\ s^{-1}$ to $4.05 \times 10^{9}\ M^{-1}\ s^{-1}$. In general, the reactivity of esters toward OH radicals increased with increasing carbon number and temperature.

The obtained kinetic data expand the currently available database for aqueous OH with WSOCs and contribute to a better understanding of aqueous atmospheric oxidation processes occurring in clouds, fogs, and atmospheric aerosols.

Literature:

[1] Gligorovski S., Strekowski R., Barbati S., Vione D., Chem. Rev. 2015, 115, 13051–13092.
[2] Zepp R. G., Faust B. C., Hoigné J., Environ. Sci. Technol. 1992, 26, 313–319.
[3] Volkamer R., Jimenez J. L., San Martini F., Dzepina K., Zhang Q., Salcedo D., Molina M. J., Geophys. Res. Lett. 2006, 33, L17811.
[4] Kurylo M. J., Orkin V. L., Chem. Rev. 2003, 103, 5049–5076.