

# Laser-based Studies of OH with Oxygenated Organics in Aqueous Solutions

A contribution to the subproject CMD-APP

Saso Gligorovski and Hartmut Herrmann

*Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig, Germany  
saso@tropos.de; herrmann@tropos.de*

Free radicals play an important role in the chemistry of the tropospheric aqueous phase. The OH radical is the most important oxidant both in the tropospheric gas and aqueous phase. Organic solvents are used in a large number of industrial processes including cleaning and degreasing applications, paints, pharmaceutical process synthesis, polymer disposal agents and adhesives. Due to their volatility, in many of these processes they are emitted either directly or indirectly into the atmosphere. A number of organic compounds employed as solvents at the present time have been shown to have adverse health effects i.e., carcinogenic, mutagenic and reprotoxic properties.

In the present study the rate constants of the OH radical reactions with such organic compounds have been investigated at different conditions for T and I i.e. temperatures and ionic strengths. These investigations were performed using a laser photolysis long path absorption apparatus (LFP-LPLA) and applying competition kinetics (reference substance: SCN<sup>-</sup>).

For the reactions of OH with (1) acetone, (2) methyl ethyl ketone, (3) acetylacetone, (4) isobutyraldehyde, (5) ethyl formate, the following Arrhenius expressions were obtained:

- (1)  $k(T) = (2.8 \pm 0.4) \cdot 10^{11} \exp((-2200 \pm 1300)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (18 \pm 11) \text{ kJ/mol}$
- (2)  $k(T) = (1.2 \pm 0.1) \cdot 10^{13} \exp((-3000 \pm 1100)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (23 \pm 9) \text{ kJ/mol}$
- (3)  $k(T) = (5.1 \pm 0.1) \cdot 10^{11} \exp((-1900 \pm 1000)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (16 \pm 8) \text{ kJ/mol}$
- (4)  $k(T) = (3.0 \pm 0.2) \cdot 10^{10} \exp((-720 \pm 360)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (6 \pm 3) \text{ kJ/mol}$
- (5)  $k(T) = (1.8 \pm 0.1) \cdot 10^{10} \exp((-1200 \pm 500)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (10 \pm 4) \text{ kJ/mol}$

No T-dependent data are currently available in the literature.

The kinetic investigations contribute to fill the existing gaps with regard to OH radical reaction kinetics in aqueous solution and will be implemented into the chemical aqueous phase mechanism CAPRAM 2.4 (MODAC mechanism) in an extended version..