



Spectroscopic and Kinetic Investigations of OH-Radical Reactions in Aqueous Solution

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The high reactivity and the ubiquity of OH radical make it one of the most important sink for volatile organic compounds both in the gas and aqueous tropospheric phases. A semi-direct method was developed and applied for the study of the reactivity of OH radical towards organic compounds in aqueous phase. Spectroscopic and kinetic investigations were carried out using a laser flash photolysis long path laser absorption (LFP-LPLA) setup by means of which the reactions of OH with: (1) 2-propanol, (2) 1-butanol, (3) 2-butanol, (4) propionaldehyde, (5) butyraldehyde, (6) acetone, (7) 2-hydroxy-3-butanone, (8) D,L- malic acid, (9) D,L-maleate dianion, (10) glutaric acid, (11) D,L-glutarate dianion, (12) adipic acid, (13) adipate dianion, (14) pimelic acid, (15) pimelate dianion, (16) suberic acid and (17) suberate dianion were studied at 298 K. The following second order rate constants were obtained: $k_1 = (2.1 \pm 0.2) \cdot 10^9$, $k_2 = (4.1 \pm 0.8) \cdot 10^9$, $k_3 = (3.5 \pm 0.4) \cdot 10^9$, $k_4 = (2.8 \pm 0.3) \cdot 10^9$, $k_5 = (3.9 \pm 1.0) \cdot 10^9$, $k_6 = (1.3 \pm 0.1) \cdot 10^8$, $k_7 = (2.9 \pm 1.0) \cdot 10^9$, $k_8 = (7.1 \pm 1.3) \cdot 10^8$, $k_9 = (8.4 \pm 1.0) \cdot 10^8$, $k_{10} = (6.0 \pm 2.0) \cdot 10^8$, $k_{11} = (1.0 \pm 0.2) \cdot 10^9$, $k_{12} = (1.7 \pm 0.3) \cdot 10^9$, $k_{13} = (2.4 \pm 0.2) \cdot 10^9$, $k_{14} = (2.4 \pm 0.7) \cdot 10^9$, $k_{15} = (2.9 \pm 0.8) \cdot 10^9$, $k_{16} = (5.0 \pm 0.4) \cdot 10^9$, $k_{17} = (5.8 \pm 0.3) \cdot 10^9$. All the rate constants are expressed in $l \text{ mol}^{-1} \text{ s}^{-1}$. In some cases the temperature dependences of the rate constant were studied and the following Arrhenius expressions were obtained: $k_1(T) = (6.1 \pm 0.3) \cdot 10^{10} \cdot \exp[(-1000 \pm 300) \text{ K/T}] l \text{ mol}^{-1} \text{ s}^{-1}$, $k_2(T) = (1.0 \pm 0.1) \cdot 10^{11} \cdot \exp[(-1000 \pm 100) \text{ K/T}] l \text{ mol}^{-1} \text{ s}^{-1}$, $k_3(T) = (7.4 \pm 0.3) \cdot 10^{10} \cdot \exp[(-910 \pm 330) \text{ K/T}] l \text{ mol}^{-1} \text{ s}^{-1}$; $k_4(T) = (2.6 \pm 0.1) \cdot 10^{11} \cdot \exp[(-1300 \pm 300) \text{ K/T}] l \text{ mol}^{-1} \text{ s}^{-1}$, $k_5(T) = (8.1 \pm 0.3) \cdot 10^{10} \cdot \exp[(-900 \pm 300) \text{ K/T}] l \text{ mol}^{-1} \text{ s}^{-1}$, $k_6(T) = (8.4 \pm 0.4) \cdot 10^{10} \cdot$

$\exp[(-1900 \pm 330) \text{ K/T}] \text{ l mol}^{-1} \text{ s}^{-1}$, $k_7(\text{T}) = (2.9 \pm 0.1) \cdot 10^{11} \cdot \exp[(-1400 \pm 300) \text{ K/T}] \text{ l mol}^{-1} \text{ s}^{-1}$. In the case of (1) 2-propanol and (3) 2-butanol the influence of the ionic strength on the reaction constant was also investigated. The obtained kinetic data represent input parameters for recently developed aqueous phase tropospheric model such as CAPRAM 3.0.