A T-dependent Study of the Reaction of the Superoxide Radical Anion (O_2^-) with Ozone in aqueous Solution

A contribution to subproject CMD

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The kinetics of the reaction of O_2^- with ozone and the following decay of the O_3^- radical anion have been investigated with a laser photolysis-long path absorption apparatus (LP/LPA). O_2^- was generated at pH = 10.0 by laser photolysis of sodium acetate according to:

$$CH_3COO^- + h\nu\ (\lambda = 193\ nm) \rightarrow e^- + CH_3COO\cdot \quad (1)$$

$$e^- + O_2 \rightarrow O_2^- \quad (2)$$

The superoxide radical anion formed in this reaction reacts with added ozone to form the ozonide radical anion (O_3^-):

$$O_2^- + O_3 \rightarrow O_2 + O_3^- \quad (3)$$

$$O_3^- \rightarrow O_2 + O^- \quad (4)$$

For the kinetic investigations O_3^- has been monitored by using the output of a high power halogen lamp at 430 nm recorded with a monochromator/photomultiplier combination. To increase the sensitivity of the experiment the light beam was reflected eight times through the reaction cell by the use of two aluminium coated mirrors in White configuration. In this study the rate coefficients of the formation (3) and the decay of O_3^- (4) were measured in the temperature interval between 278 and 318K. The following Arrhenius-expressions are derived

$$k_3\ (T) = (2.3 \pm 0.3)\cdot 10^{12}\cdot \exp\ [-(2200 \pm 1100)K/T]\ l\cdot(mol\cdot s)^{-1}$$

$$k_4\ (T) = (7 \pm 1)\cdot 10^{9}\cdot \exp\ [-(4500 \pm 1000)K/T]\ s^{-1}$$

corresponding to activation energies of E_A (3) = (18 ± 9) kJ·mol^{-1} and E_A (4) = (37 ± 9) kJ·mol^{-1}, respectively.

The obtained results are used in our multiphase modelling system (RACM + CAPRAM 2.4) to give a better understanding of tropospheric aqueous phase chemistry.