

# Kinetic Studies of Imidazoles in Tropospheric Aqueous-Phase Chemistry: Photochemistry of Imidazole-2-carboxaldehyde and Oxidation Reaction of Imidazoles with Hydroxyl Radicals

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## Abstract

The formation of imidazoles in atmospheric particles occurs via the reaction of dicarbonyls with nitrogen containing compounds. A current study has been shown that imidazole-2-carboxaldehyde (IC), one of the products formed by this reaction, can efficiently photo-induce the growth of aerosols. [1] This compound thus acts as a potential photosensitizer [2] possibly initiating secondary organic aerosol (SOA) growth. Therefore, the presence of photosensitizers in atmospheric particles is an important new field of research of increasing activity. A recent field study quantified and qualified imidazoles in ambient aerosol samples from Europe and China. [3] However, kinetic data and mechanisms of particle-phase reactions involving imidazoles are still scarce.

The reactivity of the excited triplet state of imidazole-2-carboxaldehyde (IC) in the presence of bromide anion, oxygen, formic acid, and isopropanol has been studied by laser flash photolysis-laser long path absorption (LFP-LLPA). IC is more efficiently quenched by oxygen ( $k_q = (2.5 \pm 0.07) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ), and formic acid ( $k_q = (8.8 \pm 0.5) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ) than by bromide anion ( $k_q = (1.6 \pm 0.3) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ ). The quenching reaction of IC with isopropanol is investigated and compared to the reaction with formic acid to propose a preliminary mechanism of photosensitized reactions of IC with organic compounds. It is suggested that an electron transfer occurs, as it is the case for inorganics. [2] The determination of a quenching rate constant of IC with isopropanol is not possible because the reaction proceeds either slowly or not at all.

Furthermore, rate constants of hydroxyl (OH) radical oxidation reactions with different imidazole compounds were determined. Following rate constants are obtained at a temperature of 298 K:  $k(\text{imidazole-2-carboxaldehyde}) = (3.3 \pm 1.3) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k(1\text{-methylimidazolium hydrogen sulfate}) = (2.7 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k(2\text{-methylimidazole}) = (5.4 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k(4(5)\text{-methylimidazole}) = (5.1 \pm 0.3) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k(1\text{-ethylimidazole}) = (3.0 \pm 0.3) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k(2\text{-ethylimidazole}) = (5.0 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . The OH radical reaction rate constants of imidazoles are in the same range as for non-heteroaromatic compounds. Therefore, imidazoles can be expected to exist just for a limited time in the atmosphere ( $\tau = 16 - 29$  hours) after their formation. The received kinetic data will be added into model studies to evaluate the importance of aqueous-phase chemistry of imidazoles for atmospheric processes as well as the impact of photosensitized reactions on atmospheric particles possibly contributing to SOA formation.

## References

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