Investigation of key reaction pathways in air-plasma-induced chemistry with experimentally validated chemical kinetic model

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Abstract: In this contribution, we report the latest understanding of air-plasma-induced reaction chemistry, led by a comparison of quantification results of reactive oxygen and nitrogen species in the gas and liquid phases and calculation results using chemical kinetic modelling. This will contribute to facilitating air plasma applications with the controlled delivery of reactive species.

1. Introduction

Atmospheric-pressure plasmas (APPs) have been of great interest and are widely used in medical, agricultural, and environmental applications. In particular, air APP can convert nitrogen (N_2), oxygen (O_2), and water (H_2O) molecules on-site into gaseous reactive species $H_xN_yO_z$ [for example, ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2), and hydroxyl radical (OH)]. Air APP directly or remotely interacting with liquids can also activate reactive oxygen and nitrogen species (RONS) chemistry in the liquid phase. These gas- and liquid-phase species can play key roles in various applications. However, understanding the generation pathways and control of these species remains challenging.

For nearly 10 years, our consistent intention has been to understand and control air plasma-induced chemistry, especially focusing on effective utilization in the agricultural field [1]. Recent important studies include the selective generation of N_2O_{5gas} [2], high-density generation of NO_{3gas}, and generation of droplets containing lifetime-controlled O_{3aq} [3] and $HOONO_{aq}$ [1]. These technologies are based on understanding chemical reactions with experimental measurements and chemical kinetic modelling, which will be comprehensively introduced in this presentation.

2. Methods

The gas-phase RONS were quantified using Fourier transform infrared (FTIR) absorption spectroscopy, and the liquid-phase RONS were quantified using absorption and fluorescence spectroscopy, electron spin resonance (ESR) spectroscopy, and liquid chromatography.

The temporal evolution of the RONS densities in the gas and liquid phases was implicitly solved based on the Newton-Raphson method using MATLAB with a variable time-step method. The elementary reactions in the gas phase were carefully selected by reviewing the NIST Chemical Kinetics Database [2]. Also, Elementary reactions in the liquid phase were carefully selected by reviewing NIST Solution Kinetics Database and some papers based on our previous experimental results as shown in the review paper [1].

3. Results and Discussion

Figure 1 shows the key reaction pathway in air-plasma-induced liquid phase chemistry. Under typical conditions (*e.g.*, pH = 3–7, low species concentration) of air plasma-treated water chemistry, the main components are likely

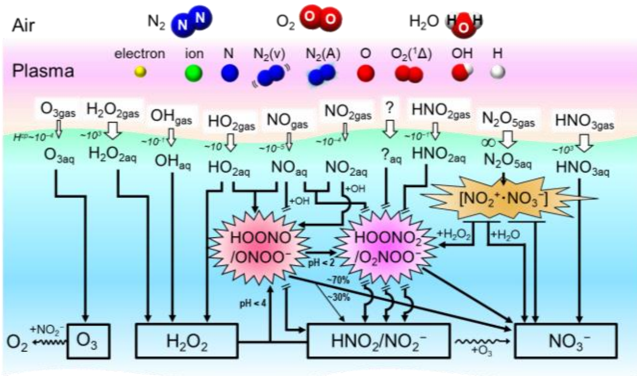

Fig. 1 Key reaction pathway in air-plasma-induced liquid phase chemistry.

H_2O_{2aq}, $NO_2^-{}_{aq}$, $NO_3^-{}_{aq}$, and possibly O_{3aq}. However, some precursor species, which are temporally generated before leading to the main species or are continuously generated under the coexistence of the main species, can exert dominant effects. Understanding the time constants of precursor species generation and the main species loss is very important for the effective use of air-plasma-induced chemistry. Notably, the short-lived species are $HOONO_{aq}$ and $HOONO_{2aq}$, and the associated reactions are very sensitive to solution pH and temperature. Notable loss mechanisms of the main species are the H^+-catalyzed reaction loss of H_2O_{2aq} and $NO_2^-{}_{aq}$, reaction loss of O_{3aq} by dissolved $NO_2^-{}_{aq}$, and volatilization loss of O_{3aq}. For practical lifetime design, it is very important to predict these time characteristics using experimental conditions and known parameters such as reaction rate constants and diffusion constants. In this presentation, practical examples will be introduced along with specific parameters.

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References

[1] T. Kaneko, K. Takashima, and S. Sasaki, Plasma Chem. Plasma Process., **44**, 1165-1201 (2024).

[2] S. Sasaki, K. Takashima, and T. Kaneko, Ind. Eng. Chem. Res., **60**, 798-801 (2021).

[3] K. Takashima, Y. Hu, T. Goto, S. Sasaki, and T. Kaneko, J. Phys. D. Appl. Phys., **53**, 354004 (2020).