Atmospheric pressure plasmas as radical sources for atmospheric chemistry investigations: measurement of Cl atom reactivity in a proxy air sample

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Abstract: An atmospheric pressure radio-frequency driven plasma source is used to generate atomic chlorine which is detected indirectly using a volatile organic compound marker and proton transfer reaction mass spectrometry. A mixture of argon and chlorine is used as the working gas mixture in a 40.68 MHz driven capacitively coupled plasma source, the effluent of which enters a reaction vessel, where the chosen reference compound is mixed in radially.
Keywords: chlorine, argon, atmospheric pressure, radio frequency, reactivity

1. Introduction

The lifetime of short-lived reactive species such as atomic chlorine (Cl) and hydroxyl radicals (OH) in the atmosphere is strongly determined by the reactivity of the ambient air to those species. The reactivity of a sample of air to Cl can be written as:

$$R_{air}(s^{-1}) = \sum k_{Cl+x}[x] \qquad (1)$$

Where k_{Cl+x} is the reaction rate of compound x with Cl and $[x]$ is the concentration of x in the sample of air. With a reactor vessel and correct choice of reference compound the reactivity of a sample of air to Cl can be directly measured using a technique similar to V. Sinha's 'Comparative reactivity method' (CRM) [1]. To use this technique, a reliable source of atomic chlorine is needed. The equation

$$R(s^{-1}) = \frac{C_3-C_2}{C_1-C_3} \times k_{ref}C_1 \qquad (2)$$

is used to measure the reactivity of Cl in a given sample of air. k_{ref} is the reaction rate of Cl with the chosen reference compound x_{ref} and concentrations C_1, C_2 and C_3 correspond to the concentrations shown in figure 1. Figure 1 shows the procedural outline of the CRM, starting with a baseline measurement of the reference compound in zero air, giving C_1. Atomic chlorine is then added to the reactor vessel and depletes the reference compound resulting in concentration C_2. The zero air is then replaced with the air to be sampled, which results in Cl also reacting with the components of the sample air, giving concentration C_3.

The production of short-lived reactive species in the atmospheric chemistry community is usually through the use of pulsed lasers, photolysis lamps or microwave cavities. The restrictions on these techniques include low conversion rates, absence of suitable radical precursors, interference from secondary reactions, excited-state chemistry and difficulty in measuring absolute radical concentrations.

To mitigate some of these issues an atmospheric pressure plasma is used to generate atomic chlorine.
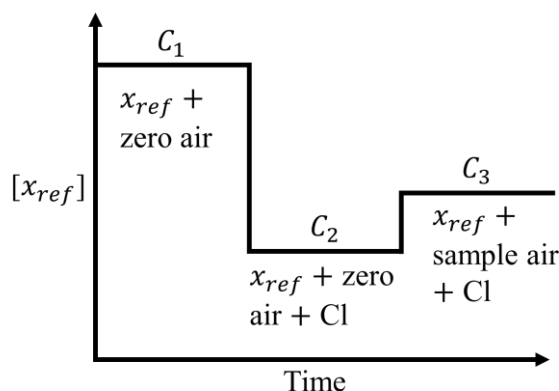

Fig. 1. CRM procedural overview. Zero air is synthetic air containing less than 0.1 ppm hydrocarbons and 5 ppm moisture.

2. Experimental

The design of the plasma source is based on the 'COST reference microplasma jet' [2]. The plasma source (fig 2.) consists of two planar copper electrodes 50 mm x 5 mm in length and width respectively, clamped to either side of a 0.5 mm x 5 mm ID rectangular borosilicate glass capillary. The top electrode is powered using an Advanced Energy Cesar 403 40.68 MHz power supply connected through a Coaxial Power Systems MMN 150 L-type manual matching network, while the bottom electrode is connected to earth. Typical flow rate is 0.5 slm and a mixing ratio of 0.11% chlorine/argon.

The outlet of the plasma source is connected using a glass ball and socket joint to a cylindrical glass reactor vessel (fig 2.) of dimensions 20 mm x 90 mm diameter and length respectively. The reference compound is mixed with nitrogen at approximately 100 ppb and is introduced through three radial internal ports with a typical flow rate of 0.3 slm.

An IONICON proton transfer reaction quadrupole mass spectrometer (PTR-QMS) is attached to the outflow of the reactor to detect changes in the concentration of the

reference compound as a function of different operating conditions.

3. Results

To validate the experimental setup, a proxy air standard of isoprene and toluene in zero air at 161 ppb and 23 ppb respectively, was used. From the known concentration and reaction rate with Cl of the two volatile organic compounds used in the proxy air sample, using equation 1, the reactivity of the sample to Cl is known. To test whether its Cl reactivity could be measured using the apparatus, different dilutions of the proxy air sample were used. In figure 3, the concentration of diethyl ether leaving the reactor vessel is measured by the PTR-QMS as a function of time. At t=0 to t=35 mins, a working plasma gas mixture of 0.5 slm 0.11% Cl_2 in argon was used, with a constant flow of 0.3 slm of the reference compound (approx. 400 ppb diethyl ether) in dry nitrogen into the reactor vessel through the wheel mixing port. During the times signified as A, B, C and D in figure 3, the proxy air sample was added to the flow of the reference compound in increasing amounts, causing more of the reference compound to survive in the reactor vessel.

Fig. 3. Measured concentration of the reference compound (diethyl ether) with increasing amounts of a proxy polluted air sample (areas A, B, C, D).

In figure 4, the reactivity calculated using equation 2 is plotted against the reactivity calculated using equation 1, which should be the same. Each point is labelled with the corresponding measurement from figure 3. The linear fit shown in figure 4 shows that there is an overestimation of the measured reactivity.
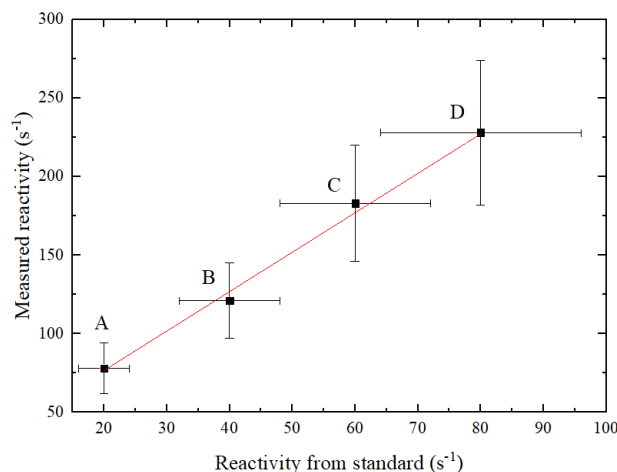
Fig. 4. Measured against predicted reactivity. The gradient and y-intercept of the linear fit is 2.5±0.1 and 26±5 respectively.

4. Conclusion

Plasma generated atomic chlorine has been used for high contrast reactivity measurements of toluene and isoprene. Due to the discrepancy between the predicted and measured reactivity, further tests with different proxy air mixtures are planned.

5. References

[1] V Sinha, et al, Atmos. Chem. Phys. **8**, 2213-2227 (2008).
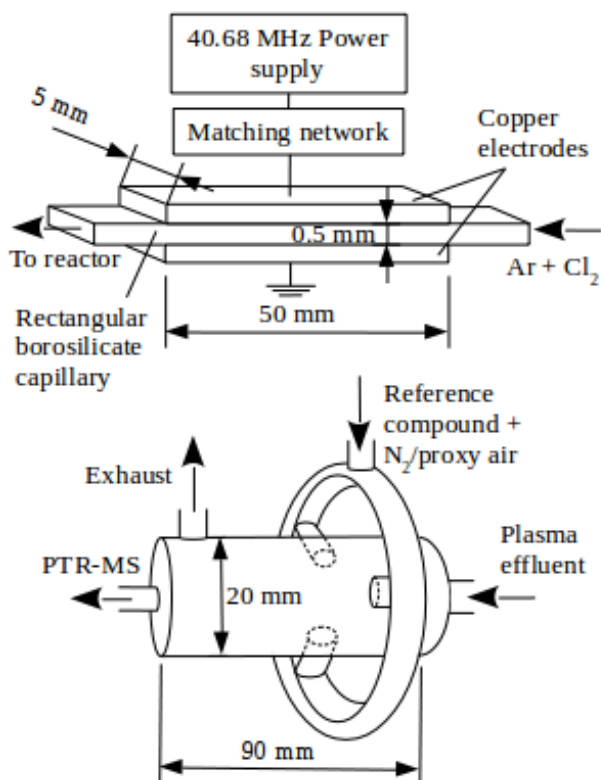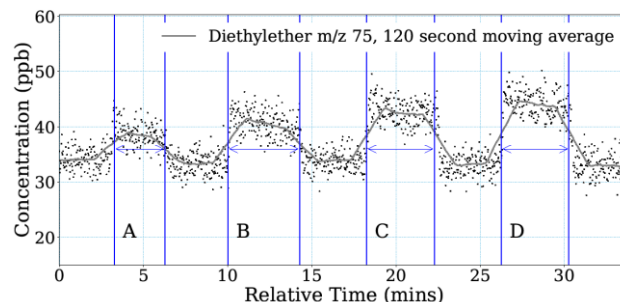[2] J Golda, et al, J. Phys. D **49**, 084003 (2016).

Fig. 2. Experimental schematic showing dimensions of the plasma source (top) and reactor vessel. The distance between the plasma source and reactor is approximately 120 mm.