Low Temperature Measurements of Electron Attachment to POCl₃

<u>G.Saidani^{1*}</u>, S. Carles¹, C.Berteloite¹, J.L. LeGarrec¹, J.B.A. Mitchell¹, A.A. Viggiano²

¹ Institut de Physique de Rennes UMR 6251 CNRS

² Air Force Research Laboratory, Space Vehicles Directorate, Hanscom Air Force Base, Bedford, Massachusetts 01731-3010, USA.

* Corresponding author: saidanighassen@gmail.com

The solution phase chemistry of phosphorous trichloride (POCl₃) is well characterized as this molecule is used in a number of industrial processes including the synthesis of important organophorous compounds [1], such as flame retardants, plasticizers, insecticides and fuel additives. However, the gas phase chemistry of POCl₃, including the ion-molecule and electron-molecule reactions, has not been well studied especially at low temperatures despite the fact that the pure substance have relatively high vapor pressure. In the present work, we have investigated the reactivity of POCl₃ with thermal electrons and have measured their attachment rate constants at different temperatures in a low density plasma (~10⁹ cm⁻³) using the CRESU technique. This reaction displays at low temperature (39K-170K), a high rate constant of ~ 10⁻⁷ cm³ molecule⁻¹s⁻¹ and is a relatively temperature dependent in our temperature range [2]. Electron attachment to POCl₃ is a rich process in which a non-dissociative channel (POCl₃⁻) competes with a dissociative one (POCl₂⁻) [3]. We have shown that the main product at low temperature (\leq 170K) is POCl₃⁻, which is the non dissociative channel, where the reaction is governed by termolecular collisions. At higher temperature it is rather the dissociative one which prevails confirming others studies at higher temperatures [3-6].

References

- 1. Sanderson, R.T., Simple Inorganic Substances: A New Approach (Drieger, Malabar, FL, 1989), pp. 336–343.
- 2. Shuman, N.S., et al., *Electron attachment to POCl₃*. *II. Dependence of the attachment rate coefficients on gas and electron temperature*. International Journal of Mass Spectrometry. **306** p. 123-128.
- 3. Shuman, N.S., et al., *Electron attachment to POCl₃. III. Measurement and kinetic modeling of branching fractions.* The Journal of Chemical Physics. **134**(9): p. 094310-10.
- 4. Miller, T.M., et al., *Electron attachment to PCl₃ and POCl₃, 296--552 K.* The Journal of Chemical Physics, 1998. **109**(2): p. 578-584.
- 5. Van Doren, J.M., et al., *Electron attachment to POCl₃: Measurement and theoretical analysis of rate constants and branching ratios as a function of gas pressure and temperature, electron temperature, and electron energy.* The Journal of Chemical Physics, 2006. **124**(12): p. 124322-9.
- 6. Williamson, D.H., et al., *Effect of pressure and temperature on the competition between nondissociative and dissociative electron attachment to POCl₃.* The Journal of Chemical Physics, 2000. **113**(24): p. 11035-11043.