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Teaching an old dog new tricks: Using the Flowing Afterglow Langmuir Probe apparatus to measure electron attachment to radicals and ion-ion neutralization[1]

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Accurate kinetics of plasma processes are necessary for modeling of the chemistry occurring in the upper atmosphere, reentry, combustion, and discharges. While a great deal of data exists in the literature for many types of plasma processes, there remain gaps for reactions less amenable to traditional measurements due to the difficulty in preparing well-defined initial conditions. In particular ion-ion mutual neutralization reactions have received relatively little study, and essentially no detailed product branching fractions are known. Similarly, while hundreds of electron attachment rates to stable species have been reported, only one measurement of an electron attachment rate to an unstable radical species exists in the literature. We report several measurements of involving these classes of reactions using a novel flowing afterglow technique which we have called Variable Electron and Neutral Density Attachment Mass Spectrometry (VENDAMS). The technique takes advantage of these processes occurring as secondary and tertiary chemistry in high density plasmas, and uses excess electrons as chemical ionization agents to monitor neutral product concentrations. Systems starting with a variety of neutrals have been studied over a temperature range of 300 to 550 K, including SF_6, SF_5Cl, $SF_5C_6H_5$, SF_4, $PSCl_3$, and $POCl_3$. Electron attachment rate constants to the radical species SF_5, SF_3, SF_2, $PSCl_2$, and $POCl_2$, are reported; an unusual negative temperature dependence in the attachment rate constants for several of the species is seen. Product branching fractions in the mutual neutralization reactions of SF_6^- and SF_5^- are reported, showing little temperature dependence and a correlation between the fraction of dissociative product and the total energy available to the dissociation. Additionally, we present evidence of an electron catalyzed mutual neutralization process ($Ar^+ + M^- + e^- \diamondsuit$ neutrals $+ e^-$) not previously reported in or speculated on in the literature. Typical rate constants for the process are on the order of 10^{-18} cm^6 s^{-1}, meaning that the catalyzed process becomes competitive with two-body mutual neutralization at electron densities above 10^{10} cm^{-3}, and may be the dominant mechanism in plasmas containing monatomic cations at higher electron densities.

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