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Kinetics of transient species with cations and electrons[1]

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Weakly ionized plasma will generally contain some concentrations of transient species, e.g. small fluorocarbon radicals in a discharge through CF_4. Experimental measurements of the kinetics of these species with electrons and with ions are scarce in the literature, in part due to the difficulty in producing and quantifying transient species. We have developed a technique, termed variable electron and neutral density attachment mass spectrometry (VENDAMS), employing a flowing afterglow-Langmuir probe apparatus that provides access to the kinetics of a wide range of radical or otherwise unstable species reacting with electrons or with cations. The kinetics of electron attachment to small fluorocarbon and hydrofluorocarbon radicals have been measured at thermal conditions from 300 – 1000 K. The results are interpreted using a kinetic modeling approach rooted in statistical theory, which allows extrapolation of the results to conditions not accessible by the experiment, including to extreme temperatures, pressures, or non-thermal conditions. The ion-molecule kinetics of small hydrocarbon, fluorocarbon, and hydrofluorocarbon radicals with a number of cations were also studied under thermal conditions. Surprisingly, the radical species react less efficiently and with a lower likelihood of long-range charge transfer than similar reactions of stable, closed-shell species with the same cations. The VENDAMS technique is also used to study ion-ion mutual neutralization processes. The rate coefficients of mutual neutralization in systems involving greater than 3 atoms vary by no more than about a factor of 5. On the other hand, the rate coefficients of mutual neutralization of two atomic species can vary widely. In some systems the rate coefficients are of similar magnitude to those for polyatomic species, but in other cases at least 2 orders of magnitude smaller. A large number of measurements are distilled down to a simple parametrization to predict the rate coefficients of unstudied systems.

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