Rate constants, product distributions, and electron catalysis of mutual neutralization

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Of the four elementary plasma chemistry processes, the literature data on ion-ion mutual neutralization is far and away the sparsest. We have recently developed a novel technique, Variable Electron and Neutral Density Attachment Mass Spectromtetry (VENDAMS), using a traditional flowing afterglow-Langmuir probe (FALP) apparatus capable of measuring kinetics and neutral product distributions of a range of negative ions with monatomic positive ions. The technique involves varying the plasma density from well below to well above an electron attaching neutral density, allowing for a data to be extracted by modeling the multi-order kinetics. Mutual neutralization kinetics are determined by measuring the relative decay of an anion of interest to that of a monatomic anion similarly produced in the flow tube, taking advantage of the fact that two monatomic species neutralize at a negligible rate. The accuracy of the technique is improved over previous FALP studies of mutual neutralization in that it does not rely on quantification of ion densities using the Langmuir probe. Rate constants for mutual neutralization reactions are measured to 10-25% uncertainties. Systems including a polyatomic species neutralize with rate constants of 4-6 $x10^{-8}$ cm^3 s^{-1}, about 10-20% slower than previous data. Reactions of a diatomic anion and a monatomic cation are significantly slower, with rate constants of 3 $x10^{-8}$ cm^3 s^{-1}. An upper limit for rate constants of neutralization of two monatomic species of $5x10^{-9}cm^3$ s^{-1} is in agreement with prior data. The first neutral product distributions for mutual neutralization reactions are reported for SF_6^-, SF_5^-, and SF_4^- with Ar^+, Kr^+, and Xe^+ over the temperature range 300 K – 500 K. A large amount of product dissociation is observed, with more dissociated product for the more exothermic neutralizations; no temperature dependences in the product branching are observed. Finally by going to electron densities approaching $5x10^{10}$ cm^3 s^{-1}, we have found that mutual neutralization is catalyzed by e^-, a process we have dubbed electron catalyzed mutual neutralization (ECMN). ECMN rate constants vary between 10^{-19} and 10^{-17} cm^6 s^{-1} at 300 K and display a steep negative temperature dependence of around T^{-3}. We postulate a mechanism for ECMN in which interaction with the third-body electron facilitates the deposition of kinetic energy of the system into the internal modes of the polyatomic anion.

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