DISSOCIATIVE RECOMBINATION OF MOLECULAR IONS

S. Datz

Dissociative recombination (DR) of molecular ions with electrons leads to neutral fragments, e.g.,

$$\begin{aligned} ABC^+ + e &\rightarrow AB + C \\ &\rightarrow AC + B \\ &\rightarrow A + B + C, \text{ etc.} \end{aligned}$$

The process is importantly involved in the chemical dynamics of cold plasmas such as found in our photosphere, plasma deposition technology, and planetary ionospheres. Moreover, it is often the source of highly reactive free radicals in high temperature flames and in the plasmas formed in combustion energies, e.g., oxygen atoms and formed from $O_2^+ + e \rightarrow 2\ O$.

The use of heavy-ion storage rings for DR was initiated by the author while in Stockholm, Sweden, in 1992, and experiments are now being carried out in facilities in Stockholm, Heidelberg, Aarhus, and Tokyo. The advantages obtained include an enormous increase in luminosity, the relaxation of vibrational excitation, and the ability to track branching in both projectile exit channels and energy distributions.

Research continued this year on the simple molecules HD^+, H_2^+, $^3HeD^+$, and $^4HeH^+$. In these cases, in addition to total cross sections, final state distributions were determined by measuring the distance and hence the recoil kinetic energy of the two fragments obtained in the DR process. Knowing the total energy then yields the internal energy of the fragments. In the case of the $^3HeH^+$ and $^4HeD^+$, we demonstrated last year that at "zero kinetic energy" the product was exclusively $He(1s^2) + H(n=2)$. This result was reproduced by the Heidelberg group who also showed when the collision energy was increased to 0.6 eV, the product was exclusively H(n=3). Our work at Stockholm, in the "direct excitation" region (11–15 eV) gave complex spectra with evidence for anisotropic distributions in the center of mass ($\cos^2$-like) as well as isotropic distribution yielding excited He $^3S(1s,2s)$ states. In the case of hydrogen, low-collision energies (<3 eV), single H atoms are formed preferentially in highly excited states (n>2) at higher electron energies (>12 eV), where "direct" mechanisms dominate both fragments exit electronically excited.

Two methane hydrocarbons were investigated this year: CH_5^+ and CH_2^+. CH_5^+ is formed by the radiative association process $CH_3^+ + H_2 \rightarrow CH_5^+ + n$. DR of CH_5^+ can occur by as many as nine paths but, below 0.2-eV collision energy, only five are energetically possible. These results are contrary to the theoretical expectations of both Bates (1991) and of Kim and Fox (1994).

Branching Path	Branching Fraction Experiment	Bates 1991 Theory	Kim and Fox 1994 Theory
$CH_5^+ + e \rightarrow CH_4 + H$	0.05	0.82	
$\rightarrow CH_3 + H_2$	0.05		
$\rightarrow CH_3 + 2H$	0.70	0.18	0.20
$\rightarrow CH_2 + H_2 + H$	0.17		0.80
$\rightarrow CH + 2H_2$	0.03		

For CH_2, the three-body channel is again dominant at "zero" relative energy (± ~5 meV) the branching fractions are

$CH_2 + e \rightarrow$	$C + H_2$	0.12
$\rightarrow$	$CH + H$	0.25
$\rightarrow$	$C + H + H$	0.63

again in contradiction with theoretical expectations.

Plans for future work in this area include ions such as NeH^+, a molecular ion planned for use in cooling the plasma at the divertor region of ITER and the nitrogen hydride ions NH^+, NH_2, and NH_3^+. This work will include a new aspect: the dynamics of the breakup, e.g. In the dominant three-body breakup of CH_2, is there correlation between the H fragment momenta leaving a spectator C atom? Or, is there a sequential breakup to give $CH^* + H$ which then dissociates to C + H + H? Preliminary experiments on this reaction have been carried out.