MODELLING ENTROPY IN UNIMOLECULAR DISSOCIATION REACTIONS

Paul M. Mayer,[1] Anne-Marie Boulanger,[1] Emma E. Rennie,[1] David M.P. Holland[2] and David A. Shaw[2]

[1]*Department of Chemistry, University of Ottawa, Ottawa, Canada, and* [2]*Daresbury Laboratory, Daresbury, UK*

The energy and entropy changes that occur as a reaction proceeds from reactant to transition state are fundamental to understanding the competitive processes that occur in ion dissociation reactions. The observed product ion ratios depend on the rate constants for their formation, which in turn depend on activation energy and entropy. Modern computational chemistry has made predicting the activation energies of reactions fairly routine. More difficult is predicting the entropies of these processes. For reactions involving discrete saddle points on the potential energy surface, it is a relatively straight forward task to obtain their vibrational frequencies and rotational constants and hence the entropies of activation. For bond cleavage reactions in which there are no saddle-points on the surface this information is more difficult to come by. One approach to this problem is the use of variational transition state theory to locate an appropriate dividing surface. It can be difficult, however, to assess the reliability of this approach.

We have employed variational RRKM theory to model the bond cleavage reactions in three methyl-substituted hydrazine ions. The change in energy over the course of each dissociation reaction was calculated at the B3-LYP/6-31+G(d) level of theory (which was assessed against other levels of theory to assure its reliability). The molecular configuration corresponding to the minimum sum-of-states was located and used as the transition state in the RRKM calculation of k(E). This theoretical k(E) was then used to model the threshold breakdown diagrams for each ion obtained from threshold photoelectron photoion coincidence spectroscopy as a way of assessing their reliability. To do this the k(E) data was convoluted with the internal energy distribution of the ion, the electron transmission function of the electron analyser and the monochromator band-pass width to simulate the experimental breakdown curves. The results indicate that there is a strong internal energy dependence for the entropy of activation of methyl radical loss in all cases. We have examined the source of this entropy change by examining the structure and vibrational frequencies of the dissociating complexes.