

INTÉZETI SZEMINÁRIUM



Mike Pilling

University of Leeds

School of Chemistry

Large molecules at high temperatures - unusual kinetic behaviour

Many reactions occur on potential energy surfaces with several stable intermediates. Reaction involves both isomerisation and dissociation from one of more of the intermediates. The rates depend on both pressure and temperature and considerable advances have been made in recent years using both experimental and theoretical techniques. A master equation description of the reaction, based on electronic structure calculations, is central to any theoretical analysis and forms the basis of the interpretation of experimental results.

One master equation approach is based on matrix techniques. The calculation generates a set of negative eigenvalues (although one may be zero). The magnitudes of the eigenvalues are the reciprocal timescales of the reaction. The fast timescales relate to collisional relaxation and the eigenvalues are termed internal energy relaxation eigenvalues (IEREs). The smallest magnitude eigenvalues are termed the chemically significant eigenvalues, CSEs, and relate directly to chemical reaction. Generally, the CSEs are much smaller than the IEREs and well defined rate constants for the component chemical reactions can be unequivocally determined from them.

Large molecules, such as the polycyclic aromatic compounds involved in soot formation, can behave differently, especially at high temperatures. The large numbers of internal vibrational modes lead to molecular energy distributions that extend to high energies – well above the energies of transition states for dissociation and isomerisation. At these energies, the rate constants for crossing these transition states are very large and the rates of reaction can compete with, and even exceed, the rates of collisional relaxation. This leads to some novel and interesting behaviour, but it also presents problems in determining rate constants for overall reaction for incorporation in combustion models.

The behaviour will be exemplified by reference to calculations on reactions of the corannulene oxyradical.

2016. október 6. csütörtök, 15:00

Északi Tömb, 062-es terem