

MAKING HYDROGEN BONDS: REACTION KINETICS OF HETERODIMER FORMATION

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The determination of the structures of hydrogen bonded complexes has been a major field of research in gas-phase chemistry. By contrast, the characterization of the process of complex formation has barely been addressed, despite its importance. Complex formation is a key step in homogeneous nucleation and particle formation, for example in cloud formation in planetary atmospheres and dust particle inception in circumstellar shells. Moreover, under the appropriate conditions, low temperatures and/or high degrees of supersaturation, the formation of the first complex, the dimer, is the-rate limiting step of nucleation, which can become a barrierless process.

A few previous studies have been performed on the kinetics of formation of homodimers. These studies used the CRESU (reaction kinetics in uniform supersonic flow) technique mainly coupled with mass spectrometric detection and high-level quantum calculations and models. Here we use a completely new detection scheme, chirped-pulse FTMW spectroscopy, to study the kinetics of heterodimer formation. This innovative technique combines the ability to generate continuous cold uniform supersonic flows with the high selectivity and general applicability of MW spectroscopy, allowing the simultaneous following of both reactant and products. Moreover, the high sensitivity achieved allows us to employ pseudo-first-order conditions to obtain absolute rate constants. Quantum chemistry calculations have been performed in order to model and better understand the reaction paths of the complexation process. We report the measurements of rate constants for the formation of formic acid-CO₂ heterodimer in a range of different pressures and temperatures. All of these characterize for the first time the kinetics of heterodimer formation.

Keywords

Gas-phase. Strong Hydrogen Bond. Reaction kinetics. Complexation.

This abstract is submitted for....

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