RJ05

3:33 – 3:48

CRIEGEE INTERMEDIATES REACTIONS WITH FORMIC ACID PROBED BY FTMW SPECTROSCOPY

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Gas-phase ozonolysis is a major degradation mechanism of alkenes in the Earth's atmosphere and forms Criegee intermediates (CIs), carbonyl oxides, as reactive intermediates. The chemistry of CIs plays a central role in controlling the budgets of many tropospheric species including OH, organic acids, and secondary organic aerosols (SOA). The reaction of CIs with organic acids can provide a pathway in which alkenes are converted to low-volatility compounds and thus contribute to the formation of SOA. Here we report spectroscopic investigation, through pure rotational spectroscopy, of the reaction between the simplest Criegee intermediate, CH₂OO, and the simplest organic acid, the formic acid, HCOOH. In this experiment, CH₂OO molecules have been generated in the discharged plasma of a CH₂I₂/O₂ mixture, which containing a small amount of HCOOH enough to react with CH₂OO. The resulting products (including CH₂OO) were characterized by Fourier-transform microwave (FTMW) spectroscopy. Rotational transitions in the 6-40 GHz frequency range were observed by FTMW spectroscopy together with MW-mmW and MW-MW double-resonance techniques. Preliminary results for the reaction of both conformers of the methyl-substituted Criegee intermediate, CH₃CHOO, with formic acid are also presented.

RJ06

3:51 – 4:06

FTMW SPECTROSCOPY OF THE METHYL-VINYL CRIEGEE INTERMEDIATE

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Pure rotational transitions of the methyl-vinyl Criegee intermediate have been observed by FTMW spectroscopy. The species was produced by discharging a mixture, 1,3-diiodo-but-2-en and O₂ diluted in Ar. Among four possible isomers for this species with energy less than 3 kcal/mol, only the lowest energy isomer, the *syn-trans* isomer was detected. Thirty rotational transitions with internal rotation splitting for the methyl top were observed. The observed frequencies were analyzed by the XIAM program,¹ yielding the rotational constants, which agree very well for the lowest energy isomer, giving definite assignment of the isomer observed. Furthermore, the internal rotation barrier was determined to be 702.8(28) cm⁻¹, which also reasonably agrees with that of an *ab initio* calculation 680 cm⁻¹ at CCSD(T)/cc-pVTZ.

1. H. Hartwig and H. Dreizler, Z. Naturforsch. A 51, 923 (1996).

RJ07

4:09 – 4:24

THE REACTION OF CH₂OO WITH HNO₃ INVESTIGATED WITH A STEP-SCAN FTIR SPECTROMETER

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Carbonyl oxides, which are known as Criegee intermediates, are important intermediates produced in ozonolysis of unsaturated hydrocarbons.^a Criegee intermediates react readily with other atmospheric species such as HNO₃, SO₂, (H₂O)₂ and HCOOH, leading to production of OH, aerosols and organic acids in the atmosphere. The reaction coefficient between CH₂OO and HNO₃ was reported to be 5.4×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 298 K.^b Theoretical calculations also predict a similar rate coefficient for CH₂OO + HNO₃, the reaction goes through a barrierless path to form nitrooxymethyl hydroperoxide (NMHP, NO₃CH₂OOH). Besides, due to large exothermicity(-184.9 kJ mol⁻¹), internally excited NMHP might decompose further to CH₂ONO₃ and OH.^c

In this work, we utilized a step-scan FTIR coupled with a multipass White cell to record time-resolved IR absorption spectra of the reactants and products during the reaction of CH₂OO with HNO₃ in a flow system with total pressure about 10 Torr. CH₂OO was produced from the reaction of CH₂I + O₂; CH₂I was produced from photolysis of CH₂I₂ at 308 nm.^d The IR absorption spectra were recorded at instrumental resolution 0.3 cm⁻¹. Newly observed bands at 825, 967, 1053, 1294, 1348, 1424, 1686 and 3587 cm⁻¹ can be assigned to NMHP. The observed wavenumbers and relative intensities agree with the anharmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. In addition, we also observed several bands with clear rotational structure, which can be assigned to the absorption of NO₂, H₂CO and HO₂. Observation of these species indicates that another decomposition route for excited NMHP might exist. Furthermore, absorption bands of internally excited HNO₃ was also observed at low pressure, indicating that decomposition of pre-reaction complex can excite HNO₃. By probing the formation of NMHP and NO₂, the rate coefficient of this reaction was determined to be (5.3±0.8)×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.

^aR. Criegee, Angew. Chem. Int. Edit. 14, 745 (1975).

^bE. S. Foreman, K. M. Kapnas and C. Murray, Angew. Chem. Int. Edit. 55, 10419 (2016).

^cP. Raghunath, Y. P. Lee and M. C. Lin, J. Phys. Chem. A 121, 3871 (2017).

^dO. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross and C. A. Taatjes, Science 335, 204 (2012).

RJ08

4:27 – 4:42

INELASTIC COLLISION DYNAMICS OF O₃+Ar

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Collisional energy transfer between a metastable ozone molecule and an inert collider such as an argon atom is a key step in the formation process of ozone. Understanding these collisional cooling dynamics may provide insight into the “ozone isotopic anomaly”, which is the observation of larger than expected concentrations of certain heavy ozone isotopologues in the atmosphere. Although many explanations to understand this phenomenon have been put forward previously, quantitative prediction/understanding is still lacking. One of the major reasons is the lack of an accurate potential energy surface (PES) for the system. We have recently constructed a new and accurate 3D PES of O₃+Ar and computed bound states of the complex within the rigid rotor approximation.^a In this work, we now present the dynamics of collisions between this triatomic asymmetric top molecule and a heavy atom: O₃-Ar. The MultiConfiguration Time Dependent Hartree (MCTDH) method was used to study the scattering between the O₃ molecule and Ar atom. The state-to-state probabilities from the 0₀₀ rotational state to low lying excited rotational states as well as the state-to-state cross sections are determined for the system. The rate coefficients obtained for ¹⁶O¹⁶O¹⁶O-Ar, are compared with the rate coefficients obtained for the ¹⁶O¹⁶O¹⁸O-Ar isotopologue. The lowered symmetry in ¹⁶O¹⁶O¹⁸O-Ar results in roughly double the density of allowed states due to nuclear spin statistics for bosons, which impacts the scattering dynamics.

^a S. Sur, E. Quintas-Sánchez, S. A. Ndengué, R. Dawes "Development of a potential energy surface for the O₃-Ar system: Rovibrational states of the complex", Submitted, PCCP (2019)