Direct, Time-Resolved Kinetic Experiments to Understand Chemistry of Unimolecular and Bimolecular Reactions of Criegee Intermediates

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Recently, we introduced a new time-resolved, broadband cavity-enhanced absorption spectrometer (TR-BB-CEAS) apparatus operating in the UV-range, which we have desinged, constructed, and utilized to measure uni- and bimolecular kinetics of stabilized Criegee Intermediates (sCIs) over wide range of temperature and pressure conditions [1]. In our first experiments we utilizsed a new method for the smallest sCI production, that is, 213 nm photolysis of CH_2IBr to produce CH_2I, which reaction with O_2 then led to formaldehyde oxide, CH_2OO. We showed that this new method is more resistant to secondary reaction chemistry that may be a problem, especially, in unimolecular reaction kinetic measurements of sCIs. Indeed, significant differences in unimolecular reaction kinetics of CH_2OO were observed between the results of our new measurements and the results of a previous investigation using 266 nm photolysis of CH_2I_2 to produce CH_2I. On the other hand, results of CH_2OO + HCOOH were the same within experimental uncertainty with both photolytic precursors.

In our more recent study [2], we have investigated unimolecular reaction kinetics of acetone oxide $(CH_3)_2COO$ using the same method (i.e. R_1R_2CIBr + 213 nm), that is, in this case 213 nm photolysis of $(CH_3)_2CIBr$ to produce $(CH_3)_2CI$ radical that in presence of O_2 produces $(CH_3)_2COO$. Very interestingly, our new direct measurements using the new method to produce $(CH_3)_2COO$ are in excellent agreement with a previous indirect measurement, but not with a previous direct measurement where 248 nm photolysis of $(CH_3)_2CI_2$ was used to produce $(CH_3)_2COO$. Also, our new measurements strongly suggest that unimolecular decomposition is much more important main atmospheric loss process of $(CH_3)_2COO$ than was previously suggested.

Very recently we have also started unimolecular reaction kinetics measurements of $(CH_3CH_2)_2COO$ using the same R_1R_2CIBr + 213 nm method and the new results are slightly faster then those of $(CH_3)_2COO$ under the same conditions, which is in agreement with calculations [3].

We have also used 193 nm photolysis of CH_2ICl to produce CH_2I and subsequently formaldehyde oxide in kinetic measurements of CH_2OO + RCN (R = H, CH_3, C_2H_5).

In addition to above atmospherically-relevant results of sCIs kinetics, we will also discuss our most recent measurements using laser photolysis – photoionization mass-spectrometry apparatus to understand a potential secondary reaction chemistry problem associated with $R_1R_2CI_2$ gem-diiodide photolytic precursors.

[1] J. Peltola, et al., *Phys. Chem. Chem. Phys.* **22**, 11797 (2020).
[2] J. Peltola, et al., *Phys. Chem. Chem. Phys.* **24**, 5211 (2022).
[3] L. Vereecken, et al., *Phys. Chem. Chem. Phys.* **19**, 31599 (2017).