Criegee intermediate

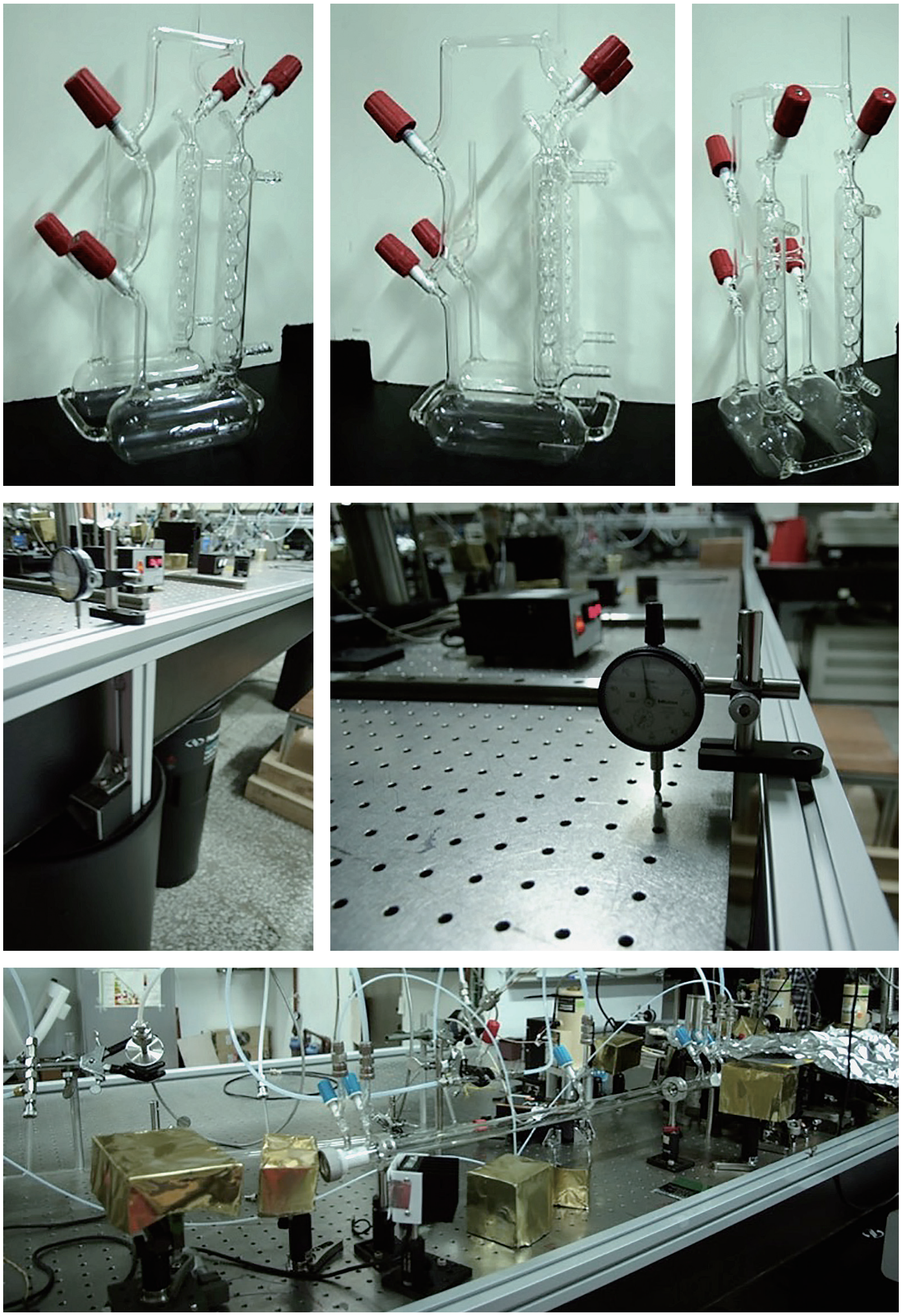
The ghost in the air

The simplest Criegee intermediate can react very rapidly with water vapor, and the reaction kinetics demonstrates a quadratic rate dependence on the concentration of water molecules, which indicates that two water molecules are required to react with one Criegee intermediate. This research result demystified the reaction kinetics between Criegee intermediate and water vapor, and thereupon has calmed academic disputes and caught the attention of international community in atmospheric chemistry. "Our result is different from previous knowledge and views, and I think this should be made known to all." Prof. Jim Jr-Min Lin said confidently. Prof. Lin's team has published this research on Science, the issue of January, 2015.

The formation of sulfuric acid in the atmosphere involves oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3). This process has always been an important research project because sulfuric acid, with a very low vapor pressure, is prone to transform into liquid particulates (one of the components of PM 2.5) which heavily affect the atmosphere. However, the reason why sulfur dioxide can be rapidly oxidized into sulfur trioxide still remains unclear. Since the monitored SO_2 oxidation rate is higher than the estimated value in the atmospheric chemistry model, scientists therefore assume the existence of other oxidizing reactions. Some had put forward the possibility that the strong oxidant, Criegee intermediate, played an important role in the SO_2 oxidation process, and an article published in Nature in 2012 discussed this assumption. But Prof. Lin holds the view that these studies had not made one very basic thing clear: whether water vapor reacts with Criegee intermediate. Because the water vapor content in the atmosphere is over a million times those of atmospheric pollutants like SO_2, and if most Criegee intermediates react with water, there cannot be considerable amount of Criegee intermediates to react with sulfur dioxide.

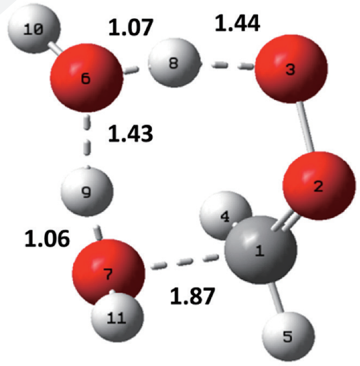
The breakthrough comes from a student from the Department of Chemistry of National Taiwan University, Wen Chao, a junior to be a senior. He was admitted to Prof. Lin's laboratory as a training student when he was a sophomore, and had successively taken part in the summer research project of the Institute of Atomic and Molecular Sciences, Academia Sinica, and junior college student research project of the Ministry of Science and Technology. Prof. Lin assigned him the research called "Whether Criegee Intermediate Reacts with Water" as his junior college research project. Wen Chao had to start his research from designing the experiment: the first difficulty of which was to have water vapor contained in an apparatus and keep it at a proper concentration, thus rendering the laboratory apparatus appropriate for monitoring Criegee intermediate. Only this procedure had taken him much time. First, in the glass apparatus there must be windows for the probe light to go through, but on which water vapor would meanwhile absorbed, so water vapor and the windows should be appropriately isolated, thus enabling the apparatus to be used in conditions of high water vapor concentration. As a result they applied nitrogen to isolate water vapor and the windows. The next question was how to keep a stable water vapor concentration. Since the evaporation of water is an endothermic process, if the water is not heated, it would become colder, and the pressure of water vapor consequently becomes lower. Through multiple experiments, they finally figure out how to have the apparatus properly heated and an appropriate amount of liquid water evaporated into vapor but not clogging the apparatus. Furthermore, the student and his workmates, Jun-Ting Hsieh, a sophomore at Stanford University and Chun-Hung Chang, a research assistant graduated from the Department of Physics at National Tsing Hua University, had to solve the vibration of the optical table, which affected the monitoring, and consistently improve the detection limit and lower the concentration of Criegee intermediate lest high concentration Criegee intermediate reacts between themselves or with other free radicals.

To everyone's surprise, the experiment result revealed that Criegee intermediate can react



The above figures are the Criegee intermediate experiment apparatuses

Water vapor gets into the reaction tube through the middle inlet and then is discharged near the two sides. At the ends of the tube there are windows which are isolated from the water vapor and sample gas by nitrogen purge. The advantage of this glass apparatus lies in that with a small caliber of the pipe, a smaller amount of the sample gas is needed, thus making reaching a high gas pressure possible. It is interesting that when Prof. Lin was designing this apparatus, he did not realize this advantage, just accommodating to the size of the parts already-have.



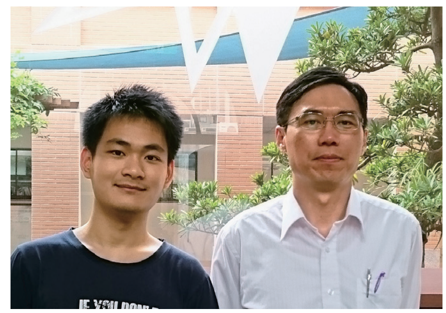
$CH_2OO+(H_2O)_2$ transition state geometry. The atom 1 is carbon; the red spheres represent oxygen atoms; the rest are hydrogen atoms. The bond lengths are in unit of Angstrom.

Citation: Liang-Chun Lin, Master thesis (2016), Department of Chemistry, National Taiwan University.

very rapidly with water, and the reaction rate demonstrates a quadratic dependence on the concentration of water molecules, which means that two water molecules are required to react with one Criegee intermediate. This reaction had been reported based on theoretical calculations in 2004, but observed in experiment for the first time. Prof. Lin then resolved to write an essay on this breakthrough and submitted it to Science. Reviewers at Science were deeply interested in this breakthrough, and offered many suggestions which surpassed the length of the essay itself. Thus it took a long time for the team to do additional experiments and reply. After some ups and downs, eventually, the paper, Direct Kinetic Measurement of the Reaction of the Simplest Criegee Intermediate with Water Vapor, had been published.

Prof. Lin and his team have published on international journals eight articles on Criegee intermediate, from the reaction kinetics of the simplest Criegee intermediate to those of the more complicated. Prof. Lin's research team finds that double-methyl substituted Criegee intermediate does not react with water (a substitution effect) or reacts very slowly with water, but reacts rapidly with sulfur dioxide, which reveals that Criegee intermediate might be a candidate for sulfur dioxide oxidation. In addition, the papers also discuss the reaction types and kinetics of Criegee intermediate of different structures, for example, the reaction with water molecule(s) (monomer or dimer), the thermal decomposition of Criegee intermediate, and the reaction with sulfur dioxide, etc. One of the biggest challenges in future research is "how to synthesize the precursors of Criegee intermediates of different substituent groups".

Prof. Jim Jr-Min Lin switches from his former research on basic molecular beam to the research on free radicals and has established his moderate reputation in atmospheric chemistry. "In the past, the story of how Criegee intermediate reacts was enveloped in mystery, but now half of it has been made clear and the other half remains to be further explored," Prof. Lin says. To Prof. Lin, Criegee intermediate is a new interesting free radical in atmospheric chemistry, and finally a good approach which can synthesize it efficiently, has come out for close investigations. No matter whether it can be put into practical use, its reactivity and molecular structure are special enough to deserve careful study, and the research results would probably find their place in textbooks in the future.



References

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2. The written record of the interview of Prof. Jim Jr-Min Lin on April 18th, 2016.
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