ATMOSPHERIC CHEMISTRY

Just add water dimers

Fast reaction with water dimers may limit the impact of the simplest Criegee intermediate on atmospheric chemistry

By Mitchio Okumura

Alkenes constitute a large fraction of the natural and human-made volatile organic compounds (VOCs) that are emitted into the troposphere. Their oxidation products degrade air quality and contribute to climate warming. Alkene oxidation is thought to involve Criegee intermediates (CIs), highly reactive molecules that form when ozone reacts with alkenes. However, the impact of CIs may be limited if they react rapidly with water. Modellers have found it difficult to quantify the effect of CIs on atmospheric composition, because laboratory data on CI reactions with water have been contradictory. On page 751 of this issue, Chao et al. (1) show that the simplest CI, formaldehyde oxide (CH$_2$OO), reacts rapidly with the water dimer, (H$_2$O)$_2$. Similar results are reported by Lewis et al. (2).

Alkene ozonolysis is a common reaction in organic chemistry (see the figure) (3). Alkenes colliding with ozone initially form a primary ozonide, which rapidly dissociates to produce a stable ketone or aldehyde and a carbonyl oxide: the Criegee intermediate. This highly unusual molecule is both very reactive and highly polar. During ozonolysis, some CIs are formed hot and decay or react immediately, but a sizable fraction becomes stabilized. Scientists have long sought to determine the yields of stabilized CIs as well as their reactivity (4, 5), but the measurements were hampered by an inability to directly detect the elusive intermediate in the gas phase.

In 2008, Taatjes et al. reported the successful detection of a CI—formaldehyde oxide, CH$_2$OO—in the gas phase with photoionization spectroscopy using vacuum ultraviolet synchrotron radiation (6). In 2012, they showed that relatively high concentrations of CIs could be generated in a short pulse by photolyzing diiodomethane, CH$_2$I$_2$, to form CH$_2$I, which reacts with O$_3$ to form CH$_2$OO in a gentle, nearly thermoneutral reaction (7). These two discoveries led to a rapidly growing literature that includes detection of larger CIs, discovery of a strong ultraviolet absorption band, and determination of a number of reaction rate coefficients (8, 9).

Experiments that directly observed CIs found far higher reaction rates with atmospheric species such as NO$_2$, SO$_2$, and organic acids than did earlier studies. The fast reaction with SO$_2$, which oxidizes very slowly in the atmosphere, led modellers to propose that CIs contribute substantially to sulfate aerosol formation in the troposphere (10).

The evidence for the reaction of CIs with water has been contradictory. End-product studies done over a decade ago concluded that CIs are lost with high yields at high relative humidities in environmental chambers. These experiments led atmospheric chemists to assume that CIs are rapidly lost at moderate to high relative humidities. However, more recent laboratory experiments found that CIs react slowly, if at all, with water molecules (7, 11, 12).

In 2004, Ryzhkov and Ariya proposed that CIs react not with isolated water molecules but rather with water dimers (13). On the basis of quantum chemistry and statistical rate calculations, they predicted that the water dimer would react 3.5 $\times$ 10$^7$ times as quickly as with the monomer. The enhancement stems from the cooperativity of cyclic hydrogen-bonded structures, which preferentially stabilize polar transition states (see the figure), an effect well known from water cluster studies.

Experimental support for enhanced reactivity of the water dimer with CIs comes from experiments reported in 2014. Berndt et al. used a relative rate approach to show that CH$_2$OO reacts with water dimers at a fast rate that depends quadratically on relative humidity (14). However, their rates exceeded upper bounds set in two experiments that used CH$_2$I chemistry (11, 12).

Chao et al. and Lewis et al. have now succeeded in measuring the reaction rate of the simplest CI, CH$_2$OO, with water vapor over a wide range of relative humidities. Both groups use the CH$_2$I chemistry and take advantage of the strong UV absorption spectrum discovered by Beames et al. (9) to follow the decay of CH$_2$OO in real time at much higher pressures and larger relative humidities than is possible with photoionization detection. Both groups find that the decay rate depends quadratically on the water vapor concentration—evidence that the CIs are reacting with the water dimer. By using the known equilibrium constant for the water dimer, they arrive at similar rate coefficients for the bimolecular reaction of CH$_2$OO with (H$_2$O)$_2$. Chao et al. recorded more precise data over a wider range of relative humidity.
ORGANIC CHEMISTRY

Harnessing weak interactions for enantioselective catalysis

The traditional tools of physical organic chemistry benefit from modern data analysis techniques

By Tongxiang Lu and Steven E. Wheeler

Lucidating catalytic reaction mechanisms is often a challenge, and these difficulties are compounded in the case of enantioselective catalysts. The ability of a catalyst to preferentially form one enantiomer over the other often hinges on the balance of many attractive and repulsive nonbonded interactions that occur in competing transition states. On page 737 of this issue, Milo et al. (1) combine physical organic and computational quantum chemistry with modern data analysis techniques to identify these interactions. Their predictive mathematical models elucidate the underlying reaction mechanism and the role of nonbonded interactions in these enantioselective reactions, facilitating the rational design of more effective catalysts.

Enantioselectivity typically arises from a difference in free energy between competing transition states that lead to two possible enantiomeric products. Traditionally, such free-energy differences were rationalized by the destabilization of the pathway leading to the undesired product by repulsive steric interactions. However, there has been recent emphasis on the role of favorable noncovalent interactions in enantioselective reactions (2), and more effective catalysts can be designed by preferentially stabilizing one pathway over other, un-

References

3. Catalytic design cycle. Screening of an initial catalyst library yields extensive data sets, which are then distilled into predictive mathematical models through multivariate regressions. These models yield new mechanistic insights and lead to improved catalyst designs. Abbreviations: Pr, isopropyl; Ph, phenyl.