Angewandte Highlights

Criegee Intermediates

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Carbonyl Oxides—Rising Stars in Tropospheric Chemistry

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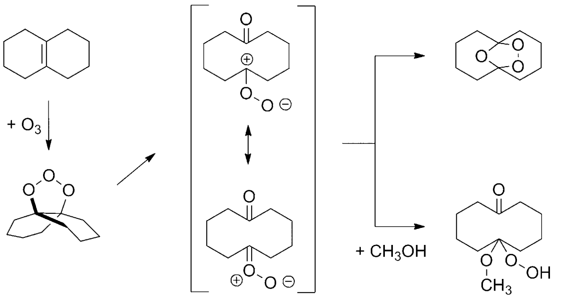
carbonyl oxide · gas-phase reactions · IR spectroscopy · reaction kinetics · troposphere

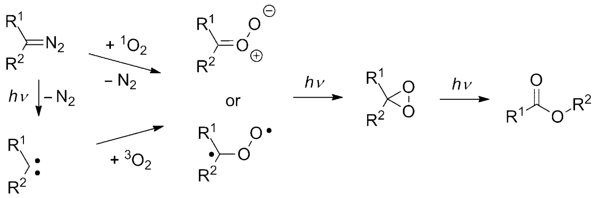
When Rudolf Criegee described the mechanism of the ozonolysis of $\Delta^{9,10}$-octalin in 1949, he postulated a reactive carbonyl *O*-oxide as the key intermediate to explain the formation of all observed reaction products.[1] He found that this intermediate can be trapped by alcohols or acetic acid to form hydroperoxides, and thus must be polar (zwitterionic) and have a finite lifetime in solution. Criegee's important discovery was that not the "ozonides" (1,2,4-trioxolanes) but rather the carbonyl oxides are the common intermediates in product formation (Scheme 1). This type of reactive intermediate, now commonly known as a "Criegee intermediate",[2] is not only well known to the organic chemistry community, but was recently the subject of much discussion in the field of tropospheric chemistry.



Scheme 1. Mechanism of the ozonolysis of $\Delta^{9,10}$-octalin as described by Criegee in 1949.

Criegee's work on ozonolysis triggered a large number of mechanistic studies, and the reaction sequence with two consecutive 1,3-dipolar cycloaddition reactions (Huisgen cycloadditions) is now a textbook example for these type of reactions. Although they are generally accepted as intermediates, the elusive carbonyl oxides escaped detection in ozonolysis reactions for decades. Only in 2009 did Ault and Hoops succeed in directly observing a carbonyl oxide as an intermediate in the reaction between olefins and ozone.[3] By co-deposition of ozone and olefins with a large excess of argon on a cold spectroscopic window, direct spectroscopic evidence was obtained for the formation of carbonyl oxides in the ozonolysis reaction.

Alternative methods for the generation of carbonyl oxides as transient species in solution[4] and in matrix-isolation studies[5] include the reactions of carbenes with molecular (triplet) oxygen and reactions of diazo compounds with singlet oxygen (Scheme 2). After some ups and downs, misinterpretations and corrections, the experimental and computational studies conducted in the 1980s and 1990s provided extensive spectrosopic and kinetic data for carbonyl oxides, and a detailed picture of the electronic structure of these species. The most characteristic spectroscopic features are the strong O−O stretching vibration between 900 and 1000 cm^{-1} and the very intense absorption in the visible region around 420 nm, which makes carbonyl oxide intensely yellow-to-red colored and extremely sensitive towards photolysis.[5f] The electronic structure of carbonyl oxides is described best as a highly polar singlet diradical. Although carbonyl oxides are generally short lived in solution (lifetimes on the order of µs at room temperature), the highly sterically hindered dimesitylketone *O*-oxide is stable enough at dry-ice temperature to be characterized by ^{13}C NMR spectroscopy.[4e]



Scheme 2. Synthesis and photochemistry of carbonyl oxides produced by oxidation of diazo compounds. Basically all carbenes with triplet ground states (e.g. R = Ph) and a few singlet-ground-state carbenes (e.g. R^1 = Ph, R^2 = Cl) react with molecular oxygen according to this scheme.

The renewed interest in carbonyl oxide chemistry in recent years is linked to one of the big mysteries of tropospheric chemistry. Of key importance to understanding the oxidation of hydrocarbons, SO$_2$, and other trace gases in the troposphere is the OH radical, which is formed by photolysis of ozone and subsequent reaction of the O(^{1}D) atoms with

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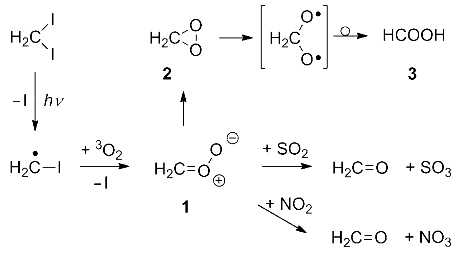
water. Thus, the concentration of OH depends on both the concentration of ozone and the intensity of the sunlight. While there is no doubt that ozone photolysis provides a major source of hydroxyl radicals, field measurements in a Finnish forest suggest that another oxidant, the “X factor”, contributes substantially to the oxidation of SO_2, in particular during the evenings and nights when ozone photolysis is inefficient.[6] These field experiments clearly indicate that monoterpenes emitted from trees play a role in the formation of the X factor, and it is tempting to designate this new oxidant as a carbonyl oxide. In matrix-isolation and solution experiments it was demonstrated that carbonyl oxides are strong oxidants able to generate O atoms and OH radicals under mild conditions.[5]

To verify this hypothesis, it was necessary to detect carbonyl oxides under simulated tropospheric conditions by direct spectrosopic methods, and to measure the kinetics of their bimolecular reactions with other constituents of the troposhere. For this purpose the ozonolysis reaction is not suitable, since other oxidants such as ozone and ozonides are involved which lead to complicated side reactions that obscure the reaction rates.

A clean source of formaldehyde oxide (**1**) in the gas phase that can be used for direct kinetic measurements is the recently discovered reaction of the iodomethyl radical CH_2I with O_2 (Scheme 3).[7] CH_2I is generated by photolysis of CH_2I_2 ($\lambda = 248$ nm) and it reacts rapidly with O_2 to produce CH_2O_2 and I atoms. Three CH_2O_2 isomers that could in principal be generated in these experiments were considered: the formaldehyde oxide (**1**), its cyclic isomer dioxirane (**2**), and formic acid (**3**), the lowest energy structure after rearrangement (Scheme 3). These three isomers are clearly distinguishable by their ionization potentials, and therefore mass-selected photoionization spectra were measured. Earlier experiments and calculations suggested that the ionization potential of formaldehyde oxide (**1**) should be about 1 eV lower than for the two other isomers, and this was nicely corroborated in the experiment. The lifetime of **1** was determined to be approximately 2 ms, long enough to measure pseudo-first-order kinetics for the fast reactions with small molecules relevant to tropospheric chemistry. Very fast reactions were observed for SO_2 and NO_2, whereas NO and H_2O react extremely slowly. These new measurements allowed Taatjes and co-workers to correct the rates used in current tropospheric models by factors between 50 and 10000![7a] The iodoalkyl radical oxidation is not limited to the synthesis of formaldehyde oxide, but very recently was also used to synthesize acetaldehyde oxide and to measure its conformer-dependent reactivity.[8]



Scheme 3. Synthesis and bimolecular reactions of formaldehyde oxide in the gas phase.

This research—the new exciting gas-phase and the older condensed-phase experiments—comes full circle with the recent publication of the first IR spectrum of formaldehyde oxide in the gas phase obtained by Lee et al.[9] Using again the reaction of CH_2I with O_2, they could detect formaldehyde oxide (**1**) in a flow reactor as a transient species with a lifetime of approximately 50 μs. The lifetime of **1** is limited by wall reactions and bimolecular reactions with various trace compounds (including **1** itself), and thus critically depends on concentrations and reaction conditions. It is therefore not surprising that the higher concentrations necessary to detect **1** by the less sensitive IR spectroscopy in Lee’s experiments results in a much shorter lifetime[9] than that observed in Taatjes’s[7b] experiments using mass spectrometry. The IR spectrum of **1** is dominated by two intense absorptions at 1286 and 908 cm^{-1}, assigned to the C–O and O–O stretching vibrations, respectively. It is interesting to note that the highly characteristic O–O stretching vibration is not much influenced by substitution: in benzaldehyde oxide, benzophenone oxide, and benzoylchloride oxide this vibration is found between 890 and 915 cm^{-1}, very close to the value for formaldehyde oxide (**1**).[5g]

The spectroscopic characterization of formaldehyde oxide (**1**, the parent “Criegee intermediate”) in the gas phase will open the door for the kinetic studies necessary to construct more accurate models of the complex oxidation chemistry of the troposphere. The goal is now to detect carbonyl oxides directly in the atmosphere and establish them as potent oxidants, the X factor, comparable only to OH radicals. After more than 60 years, “Criegee intermediates” are back at the forefront of modern research.

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[2] Please note that the entirely different intermediate in Bayer–Villiger oxidations is also called a “Criegee intermediate”. To avoid confusion across different chemical communities, I suggest staying with the chemical name carbonyl oxide.

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