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Chemical Education

Harries Ozonolysis

Vitthalrao B. Khyade

Research Group, A.D.T. And Shardabai Pawar Mahila Mahavidyalaya, Shardanagar, Malegaon
(Dr. APIS) (Baramati) Dist. Pune – 413115, **INDIA**

Email: vitthalrao.khyade@gmail.com

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ABSTRACT

Research contribution of Carl Dietrich Harries (5 August 1866 – 3 November 1923) served a lot to investigate polymers and rubber and to establish experimental procedures for ozonolysis. Carl Dietrich Harries demonstrated the generality of the chemical reaction of unsaturated compounds with ozone. This leads to conclude the possibility of use of ozone for the synthesis of a variety of compounds. Ozone is used for fragmentation of alkenes into any of the alcohols, aldehydes, ketones or carboxylic acids. Acid anhydride or diketone products are released through the ozonolysis of alkynes. The method of ozonolysis was famous for the confirmation of the structural repeat unit in natural rubber as isoprene.

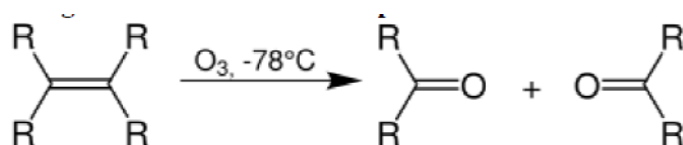
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INTRODUCTION

The highest levels of ozone in the atmosphere are in the stratosphere, in a region also known as the ozone layer between about 10 km and 50 km above the surface (or between about 6 and 31 miles). However, even in this layer, the ozone concentrations are only two to eight parts per million, so most of the oxygen there remains of the dioxygen type. Ozone in the stratosphere is mostly produced from short-wave ultraviolet rays (in the UVC band) but it can be also produced from x-rays reacting with oxygen.

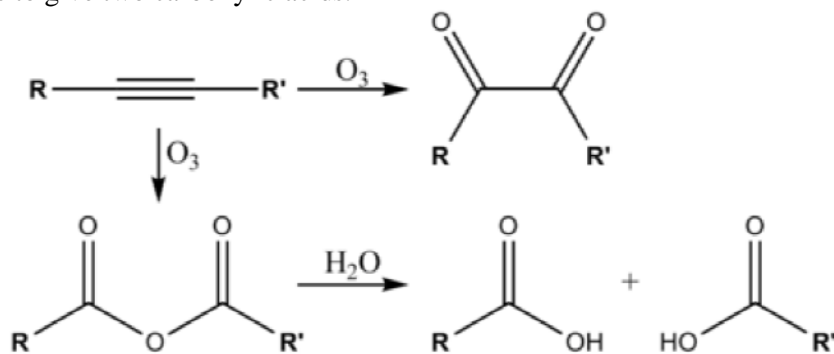
Ozone in the ozone layer filters out sunlight wavelengths from about 200 nm UV rays to 315 nm, with ozone peak absorption at about 250 nm.[2] This ozone UV absorption is important to life, since it extends the absorption of UV by ordinary oxygen and nitrogen in air (which absorb all wavelengths < 200 nm) through the lower UV-C (200–280 nm) and the entire UV-B band (280–315 nm). The small unabsorbed part that remains of UV-B after passage through ozone causes sunburn in humans, and direct DNA damage in living tissues in both plants and animals. Ozone's effect on mid-range UV-B rays is illustrated by its effect on UV-B at 290 nm, which has radiation intensity 350 million times as powerful at the top of the atmosphere as at the surface. Nevertheless, enough of UV-B radiation at similar frequency reaches the ground to cause some sunburn, and these same wavelengths are also among those responsible for the production of vitamin D in humans. Ozonolysis is the cleavage of an alkene or alkyne with ozone to form organic compounds in which the multiple carbon–carbon bonds have been replaced by a double bond to

oxygen [1-4]. The outcome of the reaction depends on the type of multiple bonds being oxidized and experimental conditions.



History of Ozonolysis: Ozonolysis was invented by Christian Friedrich Schönbein in 1840. Before the advent of modern spectroscopic techniques, it was an important method for determining the structure of organic molecules. Chemists ozonize an unknown alkene to yield smaller and more readily identifiable fragments. The ozonolysis of alkenes is sometimes referred to as: "Harries Ozonolysis," because some attribute this reaction to Carl Dietrich Harries.

Ozonolysis of Alkynes: Ozonolysis of alkynes generally gives an acid anhydride or diketone product [14], not complete fragmentation as for alkenes. A reducing agent is not needed for these reactions. The exact mechanism is not completely known [15]. If the reaction is performed in the presence of water, the anhydride hydrolyzes to give two carboxylic acids.



Ozonolysis of Alkenes: Alkenes can be oxidized with ozone to form alcohols, aldehydes or ketones, or carboxylic acids. In a typical procedure, ozone is bubbled through a solution of the alkene in methanol at -78°C until the solution turns to a characteristic blue color, which is due to unreacted ozone. This indicates complete consumption of the alkene. Alternatively, various other chemicals can be used as indicators of this endpoint to detect the presence of ozone. If ozonolysis is performed by bubbling a stream of ozone-enriched oxygen through the reaction mixture, the gas that bubbles out can be directed through a potassium iodide solution. When the solution has stopped absorbing ozone, the ozone in the bubbles oxidizes the iodide to iodine, observed by its violet color [5]. For closer control of the reaction itself, an indicator such as Sudan Red III also functions well. Ozone reacts with this indicator more slowly than with the intended.

Ozonolysis Target: The ozonolysis of the indicator, which causes a noticeable color change, only occurs once the desired target has been consumed. If the substrate has two alkenes that react with ozone at different rates, one can choose an indicator whose own oxidation rate is intermediate between them, and therefore stop the reaction when only the most susceptible alkene in the substrate has reacted [6]. Otherwise, the presence of unreacted ozone in solution (with its blue color) or in the bubbles (via iodide detection) only indicates when all alkene has reacted. After completing the addition, a reagent is added to convert the intermediate ozonide to a carbonyl derivative. Reductive work-up conditions are far more commonly used than oxidative conditions. The use of triphenylphosphine, thiourea, zinc dust, or dimethyl sulfide produces aldehydes or ketones while the use of sodium borohydride produces alcohols. The use of hydrogen peroxide produces carboxylic acids. Recently, the use of amine N-oxides has been reported to

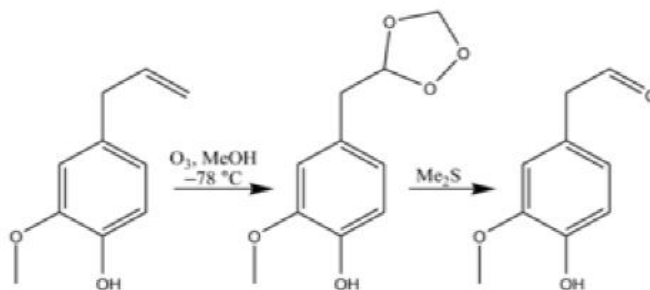
produce aldehydes directly [7]. Other functional groups, such as benzyl ethers, can also be oxidized by ozone. It has been proposed that small amounts of acid may be generated during the reaction from oxidation of the solvent, so pyridine is sometimes used to buffer the reaction. Dichloromethane is often used as a 1:1 co solvent to facilitate timely cleavage of the ozonide. Azelaic acid and pelargonic acids are produced from ozonolysis of oleic acid on an industrial scale.



A widely used alternative method [1] for the ozonolysis of symmetrical alkenes allows differentially terminated hydrocarbons to be generated:

- ▶ $O_3/MeOH/CH_2Cl_2$; TsOH; sodium bicarbonate ($NaHCO_3$); dimethyl sulfide (DMS), aldehyde and dimethyl acetyl termini
- ▶ $O_3/MeOH/CH_2Cl_2$; acetic anhydride (Ac_2O), triethylamine (Et_3N), methyl esters and aldehyde termini.
- ▶ $O_3/MeOH/CH_2Cl_2$; TsOH; Ac_2O , Et_3N , methyl ester and dimethyl acetyl termini.

An example is the ozonolysis of eugenol converting the terminal alkene to an aldehyde [8].

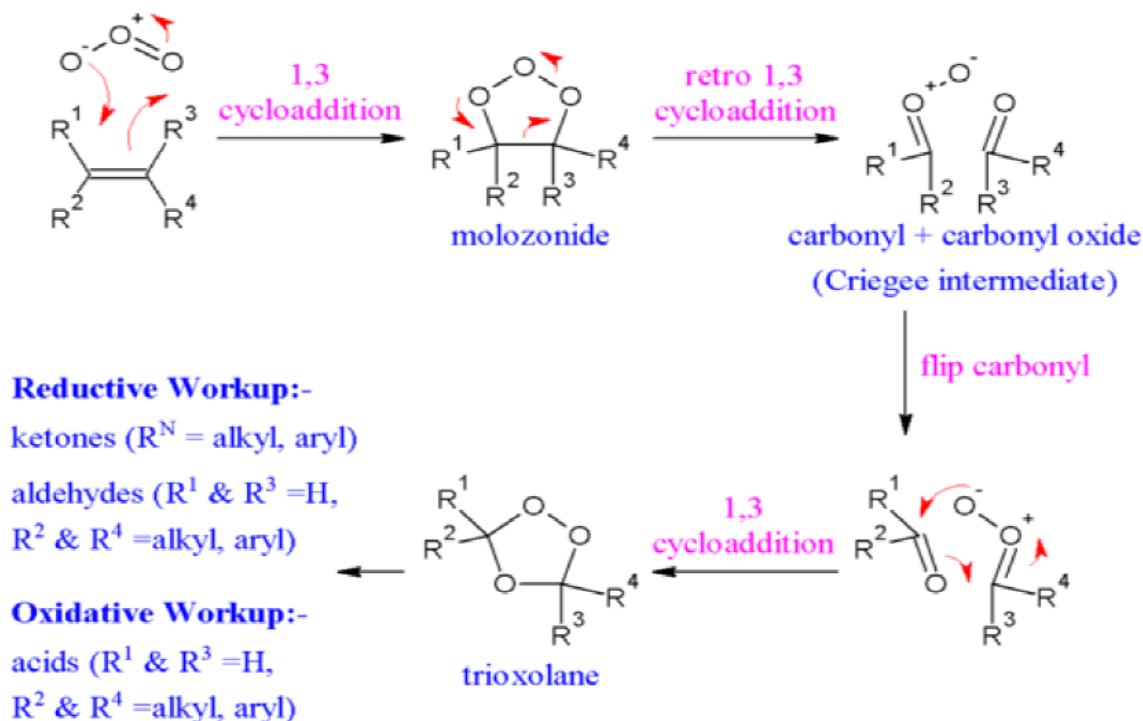


Reaction Mechanism: In 1953, Rudolf Criegee proposed mechanism [9-11] wherein the alkene and ozone form an intermediate molozonide in a 1,3-dipolar cycloaddition. Then, molozonide reverts to its corresponding carbonyl oxide (also called the Criegee intermediate or Criegee zwitterion) and aldehyde or ketone in a retro-1,3-dipolar cycloaddition. The oxide and aldehyde or ketone react again in a 1,3-dipolar cycloaddition or produce a relatively stable ozonide intermediate (a trioxolane) evidence for this mechanism is found in isotopic labeling.

When ^{17}O -labelled benzaldehyde reacts with carbonyl oxides, the label ends up exclusively in the ether linkage of the ozonide.[12] There is still dispute over whether the molozonide collapses via a concerted or radical process; this may also exhibit a substrate dependence.

Ozonolysis of Elastomers: The method was used to confirm the structural repeat unit in natural rubber as isoprene. It is also a serious problem, known as "ozone cracking" where traces of the gas in an atmosphere will cut double bonds in susceptible elastomers, including natural rubber, polybutadiene, styrene-butadiene and nitrile rubber. Ozone cracking is a form of stress corrosion cracking where active chemical species attack products of a susceptible material. Ozone cracking was once commonly seen in the sidewalls of tires but is now rare owing to the use of antiozonants. Other means of prevention include replacing susceptible rubbers with resistant elastomers such as polychloroprene, EPDM or Vinton. Ozone cracking creates small

cracks at right angles to the load in the surfaces exposed to the gas, the cracks growing steadily as attack continues. The rubber product must be under tension for crack growth to occur.



APPENDIX

Carl Dietrich Harries was a German Chemist born in Luckenwalde, Brandenburg, Prussia. He received his doctorate in 1892. In 1900, he married Hertha von Siemens, daughter of the electrical genius Werner von Siemens and the inventor of one of the earliest ozone generators. In 1904, he moved as full professor to the University of Kiel, where he remained until 1916. During that time he published many papers on ozonolysis. His major publication detailing ozonolysis was published in Liebigs Ann. Chem. 1905, 343, 311. Dissatisfied with academic life and having failed to obtain either of two positions at universities, he left academic career to become Director of Research at Siemens and Halske. He died on 3 November 1923 as a result of post-surgical complications for cancer. His great-grandfather was the German theologian Heinrich Harries. He investigated polymers, rubber and showed that rubber consisted of repeating units. He established experimental procedures for ozonolysis, demonstrated the generality of the reaction of unsaturated compounds with ozone.



Carl Dietrich Harries
5 August 1866 to 3 November 1923

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AUTHORS' ADDRESS

1. **Vitthalrao B. Khyade**
Research Group, A.D.T. And Shardabai Pawar Mahila Mahavidyalaya,
Shardanagar, Malegaon (Dr. APIS) (Baramati) Dist. Pune – 413115, INDIA
Email – vitthalrao.khyade@gmail.com