

Assignment 1

(CE55 8)

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Ans:

Aldehydes can be formed as byproducts in some of the photochemical reactions that can lead to creation of tropospheric ozone (O_3) in atmosphere. It is process in which propene ($CH_2=CH-CH_3$) reacts with hydroxyl radical ($HO\cdot$) and nitrogen oxides ($NO\cdot$) to produce ozone and aldehyde byproduct. The overall reaction involving propene, $HO\cdot$, and $NO\cdot$ to form ozone and aldehyde byproduct is as follows.

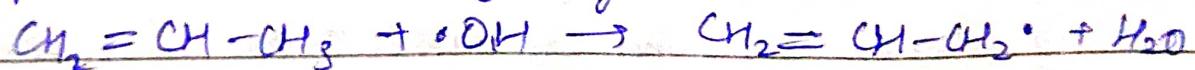
1.

Initiation:- $HO\cdot$ (Hydroxyl radical)

$NO\cdot$ (Nitric oxide radical)

2.

Propene reacts with hydroxyl radical:



Following a sequence of interactions with $NO\cdot$,

the resultant $CH_2=CH-CH_2\cdot$ can produce

nitrogen dioxide (NO_2) and other compounds.

An aldehyde may be produced as a result of one of processes.



Acrolein

Therefore, one of potential aldehydes that could be formed as byproduct in this chemical pathway for creation of tropospheric ozone is acrolein ($\text{CH}_2=\text{CH}-\text{CH}=\text{O}$)

Ans 2

Given

$$dQ = \delta U + dW$$

$$\delta U = CvdT$$

$$dW = PdV$$

Now

$$dQ = CvdT + PdV$$

amount of heat added to gas.

$$dQ = CpdT$$

$$CpdT = CvdT + PdV \quad \text{--- (1)}$$

$$\text{Acc to gas law } PV = nRT \Rightarrow PdV = nRdT \quad \text{--- (2)}$$

(at const. P)

Substituting (2) in (1)

$$CpdT = CvdT + nRdT$$

$$CpdT = CvdT + nRdT$$

$$(C_p - C_v)dT = nRdT$$

$$\boxed{C_p - C_v = nR}$$

Hence proved.

Ans 3

The 'Black Summer' Australian fires of 2019-2020 injected unprecedented amount of organic gases and particles into stratosphere. These particles, primarily organic aerosols, had significant impact on chemistry of stratosphere, particularly regarding levels of chlorine (Cl) species and their reactions, leading to disturbances in stratospheric ozone (O_3) levels.

One of the key reactions in stratosphere ozone depletion is heterogeneous reaction between hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$) on the surface of aerosol particles. This reaction which occurs at cold temperatures, lead to the formation of molecular chlorine (Cl_2) and nitric acid (HNO_3). Cl_2 is highly reactive and can participate in ozone-depleting reactions in the stratosphere.

The relevant reaction can be represented as follows:-



In the context of the Australian wildfires, the presence of organic aerosols in stratosphere created a unique environment for these reaction to occur at higher temperature than previously observed (above 198K). Organic aerosols have different chemical properties compared to typical stratosphere aerosols, and they were able to facilitate heterogeneous Cl activation at warmer temperature (around 220K during austral autumn) in both midlatitude and polar region. This facilitated the reaction between HCl and ClONO₂, leading to formation of Cl₂ and HNO₃, which can contribute to ozone depletion.

Furthermore, the reaction involving hypochlorous acid (HOCl) and hydrogen-chloride (HCl) can also occur on the surface of organic aerosols at warmer temperatures:



This reaction contribute to production of molecular chlorine (Cl₂), which, as mentioned earlier, can participate in ozone-depleting reactions.

The injection of these organic aerosols and the subsequent chemical reactions occurring on their surface led to significant changes in levels of Cl species (such as HCl and ClONO₂) and consequently disturbances in stratospheric ozone level at the affected regions. The reactions and their rates can be influenced by various factors, such as composition of organic aerosols, environmental conditions, particle size and surface area, presence of other atmospheric compounds and, localized and regional variations.

References -

"Stratosphere chlorine processing after the 2020 Australian wildfires derived from satellite data
Author:- Ridong Wang, Susan solomon, kane stone'

Ans 4

The phenomenon of significant and rapid reduction in tropospheric O₃ (ozone) observed in the atmosphere boundary layer in polar regions, especially during ozone depletion events, is a complex process influenced by various chemical reactions and atmospheric conditions.

Ozone depleting events, characterized by rapid decrease in ozone levels from a background level to less than 1 ppb within a few days, are particularly prominent in polar regions during springtime. These events are triggered by presence of reactive bromine and chlorine species, which initiate a chain reaction leading to ozone depletion.



Chemical Reactions and Reactions

1.

Bromine Explosion Mechanism :-

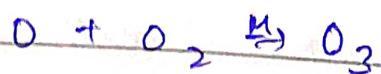
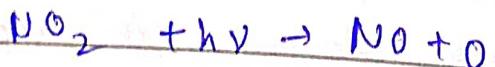
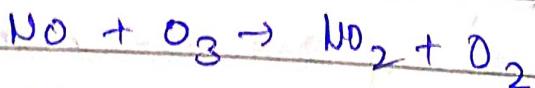
Bromine compounds (Br and BrO) are key players in destruction of ozone. The presence of bromine species results in series of reactions, especially the Bromine explosion mechanism, leading to rapid ozone depletion.



Role of Nitrogen oxides (NOx) :-

Nitrogen oxides, primarily NO and NO₂, also play a crucial role in ozone depletion events. They are involved in various reactions that both promote and inhibit ozone depletion.

→ NOx Reactions



→ Impact of NOx

* low NOx (< 88 ppt):- In this scenario, the increase in initial NOx concentration advances ozone depletion. The presence of NOx promotes the formation of HOBr, accelerating the bromine explosion mechanism.

* High NO_x ($> 85 \text{ ppt}$) : Beyond a critical threshold (around 50 ppt), higher initial NO_x levels delay ozone depletion. NO_x can terminate the halogen radical chain reaction, inhibiting ozone destruction, or lead to the formation of bromine explosion products, advancing ozone depleting events. The balance between these mechanisms determine the ozone depletion rate.

→ Factors influencing ozone depleting events :-

1. Temperature and stability → low temperatures and stable atmosphere conditions, such as strong temperature inversions, favour the occurrences of ozone depletion events. These conditions lead to accumulation of bromine species, intensifying ozone depletion.
2. Wind shear and meteorological factors → Wind shear, passage of lows, and downward diffusion of warm air caused by clouds can influence the termination of ozone depletion events. These factors contribute to the dynamics of ozone depletion events in polar regions.

3

Geographical and anthropogenic influences →

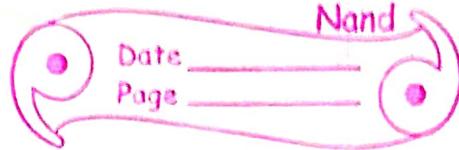
The sources of nitrogen oxides in polar regions are different, influenced by factors like snow photochemistry, long-distance transport, and human activities. Changes in anthropogenic emissions due to activities like oil exploration and shipping affect the NO_x level, influencing ozone depletion events intensity.

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Comparison w/ Non-polar Regions (Dead Sea)

Studies in non-polar regions like dead sea area show a similar dependence on NO_x levels. Anthropogenic NO_x emissions can enhance bromine activity under low nitrogen conditions. However, above a certain NO₂ threshold, further increase in NO_x concentrations decrease bromine levels, affecting ozone depletion.

The significant and rapid reduction in tropospheric ozone during ozone depletion events in polar region is result of intricate interactions between bromine and nitrogen oxide species, temperature, stability, and other meteorological factors.



The balance between promoting and inhibiting reactions involving bromine and nitrogen oxides, along with specific atmosphere conditions, determines the intensity and duration of ozone depletion events. Comparable phenomena in non-polar regions, like the Dead Sea area, exhibit similar NO_x -dependent ozone depletion patterns, emphasizing the importance of understanding these chemical processes for both polar and non-polar environments.

Reference:-

- (1) "Influence of the Background nitrogen oxides on the tropospheric ozone depletion events in the Arctic during springtime, by Joshua Zhou, Le Cao, Simeng Wu"