Assignment I (CE558)

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Ans 1 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 (HOX) and nitrogen oxides (NOX) to produce ozone and aldehyde byproduct. The overall reaction involving propene, HOX, and NOX to form ozone and aldehyde byproduct is as follows.

1. Initiation:- HOX : HO• (Hydroxyl radical)
   NOX : NO• (Nitric oxide radical)

2. Propene reacts with hydroxyl radical:

$$CH_2=CH-CH_3 + \cdot OH \rightarrow CH_2=CH-CH_2^{\cdot} + H_2O$$

Following a sequence of interactions with NO•, 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.

$$CH_2=CH-CH_2^{\cdot} + NO^{\cdot} \rightarrow \underset{\text{Acrolein}}{CH_2=CH-CH=O} + NO_2$$

Therefore one of potential aldehydes that could be formed as byproduct in this chemical pathway for creation of tropospheric ozone is acrolein ($CH_2=CH-CH=O$)

Ans 2 Given

$$dQ = dU + dW$$
$$dU = C_v dT$$
$$dW = PdV$$

Now $$dQ = C_v dT + PdV$$

amount of heat added to gas.

$$dQ = C_p dT$$

$$C_p dT = C_v dT + PdV \quad -①$$

Acc. to gas law $PV = nRT \Rightarrow PdV = nRdT$ ②

(at const. P)

Substituting ② in ①

$$\cancel{C_p dT = C_v dT + nRdT}$$
$$C_p dT = C_v dT + nRdT$$
$$(C_p - C_v) dT = nRdT$$
$$\boxed{C_p - C_v = nR}$$ Hence proved.

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Ans 3 The 'Black Summer' Australian fires of 2019-2020 injected unprecedented amount of organic gases and particles into stratosphere. These particles, primarly 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:-

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

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 195K). Organic aerosols have different chemical properties compared to typical stratosphere aerosols, and they were able to facilitate heterogenous Cl activation at warmer temperature (around 220k during austral autumn) in both midaltitude and polar region. This facilitated the reaction between HCl and $ClONO_2$, leading to formation of Cl_2 and HNO_3, 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:

$$HOCl + HCl \longrightarrow Cl_2 + H_2O$$

This reaction contribute to production of molecular chlorine (Cl_2), 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 $ClONO_2$) and consequently disturbances in stratospheric ozone level in 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.

Referances:-

"Stratosphere chlorine processing after the 2020 Australian wildfires derived from satellite data
Author:- Peidong Wang, Susan Soloman, Kane Stone"

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Ans 4. The phenomenon of significant and rapid reduction in tropospheric O_3 (ozone) observed in the atmosphere boundary layer in polar regions, especially during ozone depletion events, is a complex process ~~influen~~ 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 1ppb 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 ~~intimate~~ 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.

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$$Br + O_3 \rightarrow BrO + O_2$$
$$2BrO \rightarrow 2Br + O_2$$
$$Br_2 + h\nu \rightarrow 2Br$$

★ Role of Nitrogen oxides (NO_x):-
Nitrogen oxides, primarily NO and NO_2, also play a crucial role in ozone depletion events. They are involved in various reactions that both promote and inhibit ozone depletion.

→ NOx Reactions

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 \xrightarrow{M} O_3$$

→ Impact of NOx

* Low NO_x (<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.

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* High NOx (>55ppt): Beyond a critical threshold (around 55 ppt), higher initial NOx level delay ozone depletion. NOx 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.

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3. <u>Geographical and anthropogenic influences</u> :-
The sources of nitrogen oxides in polar regions are different, influenced by factors like snow photochemistry, lost-distance transport, and human activities. Changes in anthropogenic emissions due to activities like oil exploitation and shipping affect the NOx level, influencing Ozone depleting events intensity.

* <u>Comparision ~~of~~ with Non-polar Regions (Dead Sea)</u>
Studies in non-polar regions like dead sea area show a similar dependence on NOx levels. Anthropogenic NOx emissions can enhance bromine activity under low nitrogen conditions. However, above a certain NO_2 threshold, further increase in NO_2 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 depleting events. Comparable phenomena ~~of~~ in non-polar region, 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 environment

Reference:-

(1) ~~Zhou~~ "Influence of the Background nitrogen oxides on the tropospheric ozone depletion events in the artic during springtime, by jiashu Zhou, Le Cao, Simeng Li'