Subject	Chemistry
Paper No and Title	4, Environmental Chemistry
Module No and Title	19, Photochemical reaction in atmosphere and smog formation
Module Tag	CHE_P4_M19

Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		**Dr Vimal Rarh** Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Dr S K Garg **Principal** Deen Dayal Upadhyaya College University of Delhi	**Dr Bani Roy** **Associate Professor** Department of Chemistry Miranda House University of Delhi	**Dr. G S Sodhi** **Associate Professor** Department of Chemistry SGTB Khalsa College

Anchor Institute : SGTB Khalsa College, University of Delhi

TABLE OF CONTENTS

1. Learning outcomes-:

After studying this module you will know about:

- Photochemical reactions in the atmosphere.
- Sources and effects of photochemical reactions.
- Gases involved in photochemical reactions.
- Smog and its formation.
- Types of smog, i.e., Industrial and Photochemical and differences between them.
- Factors affecting smog formation.
- Mitigation measures for photochemical reaction.

2. Introduction-:

You are already familiar with the composition of the atmosphere. Nitrogen and oxygen are the major atmospheric gases and other gases such as argon and carbon dioxide are in minor amounts. Water vapour is also present in the atmosphere in wet air. Apart from the major and minor gaseous components, the atmosphere also contains some species which locally alters the chemical composition of air. In this module we will discuss reactions of these species in detail. As we know, according to the kinetic molecular theory of gases, the molecules present in the atmosphere are moving and colliding together continuously. In the day time, solar radiations are continuously delivered to the atmosphere. As a result, the molecules present in the atmosphere absorb the light energy and photochemical reactions take place, which would not occur under normal atmospheric temperatures, without light. To determine the nature of chemical species (including pollutant species) in the atmosphere, photochemical reactions play a crucial role. We will discuss this in detail.

3. Chemical and photochemical reaction in the atmosphere-:

Nitrogen dioxide, NO_2, present in air is known to be photochemically active due to the presence of an unpaired electron. NO_2 molecule reaches a higher level of energy when it absorbs a photon of light with energy hν, which converts the ground state molecule to electronically excited state molecule (designated here by an asterisk *).

$$NO_2 + h\nu \longrightarrow NO_2^*$$

The excited molecule, NO_2^* may quickly re-emit a photon of light, exhibiting *luminescence*:

$$NO_2^* \longrightarrow NO_2 + h\nu$$

Almost instantaneous re-emission of light is *fluorescence* and a significant delay in light emission is *phosphorescence*.

Alternatively, *photodissociation* may occur, i.e., when energy results in breaking of N – O bond and produces a nitrogen monoxide (NO) molecule and an oxygen atom (O).

$$NO_2 + h\nu \longrightarrow NO + O$$

Both of them are free radicals, as they contain unpaired electrons. Photodissociation of molecular oxygen results in two oxygen atoms.

$$O_2 \longrightarrow O + O$$

Free radicals, such as an oxygen atom, immediately react with another atom or molecule. Most of the radicals present in the atmosphere are highly reactive and exist for a short time but NO_2 molecule is not so reactive therefore it can exist in the atmosphere for a longer time.
Chemical species in the atmosphere excited due to absorption of light may also undergo *photoionization* through loss of an electron:

$$N_2^* \longrightarrow N_2^+ + e^-$$

An excited species may also react directly with another species:

$$O_2^* + O_3 \longrightarrow 2O_2 + O$$

Other phenomena undergone by excited chemical species may be *intermolecular energy transfer* or *intramolecular energy transfer*:

$$N_2^* + O_2 \longrightarrow N_2^+ + O_2^*$$

$$XY^* \longrightarrow XY^{\S}$$

Here, $XY^{\S}$ is another excited state of the same molecule.

4. Smog-:

Let us now discuss about the air pollution phenomenon, **smog.** The term smog is formed by the combination of two words, smoke and fog. Smog is basically of two types: *industrial smog* (or London smog) and *photochemical smog* (or Los Angeles smog). The Industrial Revolution has been the main reason for the increase in atmospheric pollutants over the last three centuries. Since the late 1700s, London, the place of origin of the Industrial Revolution, experienced occurrences of smog. The incidents of smog increased in frequency throughout the nineteenth century and the first half of the twentieth century. In the worst reported smog incident – which occurred in 1952, around four thousand people were killed. Smog in London is also known as sulphurous smog. Smog formed by smoke from coal fires contains a high percentage of particulates.These particles bind with the fine water droplets in fog to create a dirty mist. Its main toxic chemical constituent is sulphur dioxide.

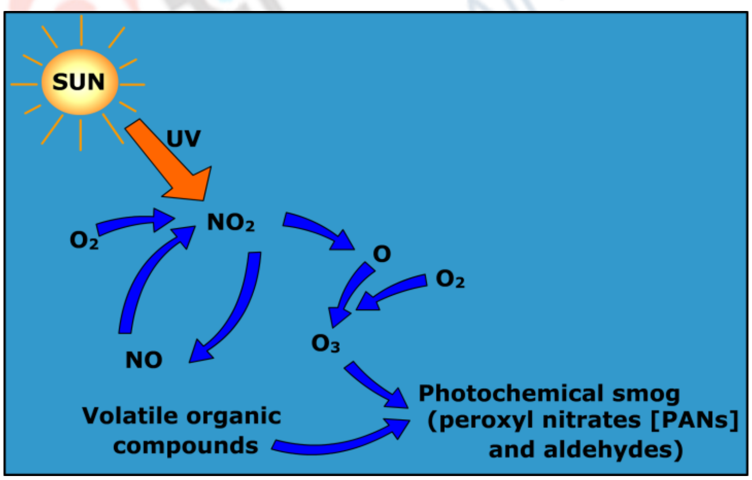
Photochemical smog is driven by the radiant energy from the sun. The primary chemical constituent of photochemical smog is nitrogen dioxide which is formed by the combination of nitric oxide with oxygen. The brownish tinge characteristic of Los Angeles air is because of nitrogen dioxide present in the atmosphere. In the presence of sunlight, ozone and peroxy compounds are formed which are corrosive in nature.

Industrial and photochemical smog can be differentiated on the bases of weather conditions, content and source as you can see in the table below.

Name	Industrial smog	Photochemical smog
Weather	Cool, damp	Sunny
Content	Particulates, sulphur oxides	NO_x, ozone, hydrocarbons
Chief Source	Coal combustion	Gasoline combustion

4.1 Formation of photochemical smog

Nitrogen oxides (the mixture of NO and NO_2 together referred to as NO_x) and volatile organic compounds (VOCs) are primary air pollutants, released in the atmosphere by automobiles and industrial processes. Nitrogen dioxide absorbs ultraviolet light and formation of nitric oxide and atomic oxygen takes place. Ozone is generated by the reaction of oxygen gas with this atomic oxygen. Ozone, aldehydes and peroxyacetyl nitrate so formed are thus secondary air pollutants. Photochemical smog is a mixture of primary and secondary air pollutants.



Motor vehicles are responsible for production of exhaust gases rich in oxides of nitrogen which include nitrogen dioxide (NO_2) and nitric oxide (NO). At the high temperatures in a car's combustion chamber (cylinder), nitrogen and oxygen from the air react to give nitric oxide:

$$N_2 + O_2 \longrightarrow 2NO$$

Some of the amount of NO so formed then reacts with oxygen and NO_2 is formed

$$2NO + O_2 \longrightarrow 2NO_2$$

In the presence of sunlight, nitrogen dioxide molecule present in high concentration breaks up and gives oxygen atom

$$NO_2 + h\nu \longrightarrow NO + O$$

This atomic oxygen (O) reacts with oxygen molecules present in the atmosphere and ozone (O_3) is formed:

$$O + O_2 \longrightarrow O_3$$

Ozone so formed then reacts with NO to form NO_2 and O_2:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

The reaction in which ozone forms is dominant when the ratio of NO_2 to NO is more than 3. If the ratio is less than 0.3, however, the nitric oxide so formed results in destruction of ozone at the same rate as that of its formation and results in lowering the concentration of ozone to less harmful levels. The reactions of hydrocarbons (from unburned petrol) with nitric oxide and oxygen in the presence of sunlight generate aldehydes, ketones and peroxy compounds.

A part of the ozone formed above reacts with volatile organic compounds (VOC) such as hydrocarbons, especially olefins, also released from automobile exhaust giving carboxyl free radicals ($RCO_2^{\cdot}$):

$$O_3 + RH \longrightarrow RCO_2^{\cdot} + RCHO + R_2CO$$

The free oxygen atoms formed react with hydrocarbons to produce alkyl/aryl free radicals ($R^{\cdot}$) as well as acyl free radicals ($RCO^{\cdot}$):

$$O + RH \longrightarrow R^{\cdot} + RCO^{\cdot}$$

Similarly, some of these acyl free radicals react with atmospheric oxygen giving acylperoxy radicals ($RCO_3^{\cdot}$):

$$RCO^{\cdot} + O_2 \longrightarrow RCO_3^{\cdot}$$

Acylperoxy radicals may also be formed by the reaction of carboxyl radicals and oxygen atoms:

$$RCO_2^{\cdot} + O \longrightarrow RCO_3^{\cdot}$$

Any acetylperoxy radicals formed further react with nitrogen dioxide giving peroxyacetyl nitrate (PAN):

$$R\dot{C}O_3 + NO_2 \longrightarrow RCO_3NO_2$$

Example:

$$H_3C-CO_3^{\cdot} + NO_2 \longrightarrow \underset{(PAN)}{H_3C-CO_3NO_2}$$

If the peroxy radical reacting with nitrogen dioxide has an aromatic ring as substituent, peroxybenzoyl nitrate (PBzN) is formed:

$$C_6H_5-CO_3^{\cdot} + NO_2 \longrightarrow \underset{(PBzN)}{C_6H_5-CO_3NO_2}$$

4.2 Effects of Photochemical Smog-:

Let us now examine the effects of photochemical smog. All the major constituents of photochemical smog are detrimental to human health and the environment. Being a cocktail of chemical oxidants such as ozone, nitrogen dioxide and peroxy compounds, it is often termed as oxidising smog.

- The brown nitrogen dioxide in smog affects visibility.
- Nitrogen dioxide, ozone, VOCs and peroxyacetyl nitrates, all result in eye irritation and respiratory problems.
- Prolonged exposure to NO_2 lowers resistance towards respiratory infections.

Chemical species	Anthropogenic Sources	Enviromental and Health Effects	Comments
Nitrogen Oxides (NO and NO_2)	• Combustion of gasoline in automobile engines • Gasoline, coal, gas in industry	• Decreased visibility due to yellowish colour of NO_2 • High levels of NO_2 exposure give rise to cough and shortness of breath • Eye irritation • May increase the cases of cancer • NO_2 is responsible for supressing growth of plants • Nitrogen dioxide when exposed in high concentration increases respiratory infection. • NO_2 reacts in the atmosphere to form acid rain, which can harm plants and animals.	Only 5% of the total concentration of nitrogen dioxide is results from combustion and most is formed from reactions invoving NO from lightning, bacterial action in soil and volcanic activity.

- Apart from being irritants to the eyes and respiratory tract, some VOCs are also believed to be carcinogenic.

Volatile Organic Compounds (VOCs)	• Evaporation of solvents • Evaporation of fuels • Incomplete combustion of fossil fuels	• Eye irritation • Respiratory irritation • Some are carcinogenic • Decreased visibility due to blue-brown haze	VOCs in the atmosphere include naturally occurring compounds such as terpenes from vegetation

- Ozone has a harsh odour and causes coughing, wheezing and eye irritation.
- Ozone causes oxidative damage to plant and animal tissue.

Ozone (O_3)	• **Formed from photolysis of NO_2**	• **Harsh odour** • **Bronchial constriction** • **Coughing, wheezing** • **Respiratory irritation** • **Breaks down rubber** • **Damage plastics** • **Retards plant growth** • **Decreased yields of crop** • **Eye irritation**	**People with asthma and respiratory problems are mostly affected by it. Its 0.1 parts per million concentrations can reduce half of the total photosynthesis.**

- PAN causes irritation in eye and respiratory problems. It is considered to be more toxic than ozone for plants. Let us discuss about sources and environmental effects of the various constituents of photochemical smog.

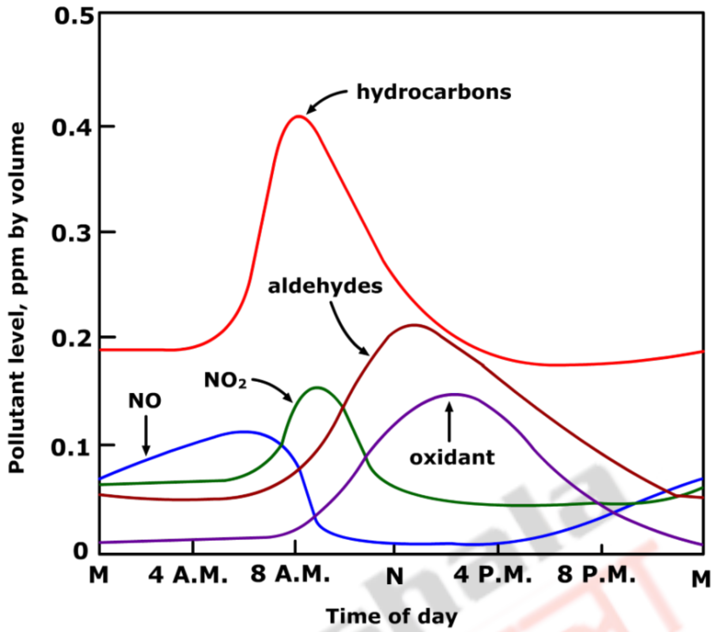
Peroxy acetyl nitrate (PAN) and related compounds	➤ **Formed by the reaction of NO_2 with VOCs**	➤ **Eye and respiratory irritation** ➤ **Affect plants** ➤ **Cause damage to proteins**	**Was not detected until recognized in smog; higher toxicity to plants than ozone**

4.3 Factors Affecting the Formation of Photochemical Smog-:

There are several factors that affect the formation of photochemical smog:

- High concentrations of nitrogen oxides and volatile organic compounds are associated with automobile exhausts and emissions from industry where this combination of substances arises due to fossil fuel combustion.

- The concentration of photochemical smog present in atmosphere varies with "the time of day". The graph below shows the daily variation in the composition of photochemical smog.



The graph suggests that as the traffic in early morning increases, the concentrations of nitrogen oxides and VOCs also increase. But as the traffic decreases later in the morning, the reaction between nitrogen oxides and volatile organic compounds takes place and nitrogen dioxide is formed which results in increase in its concentration. Around noon, the intensity of sunlight is high and it results in breakdown of nitrogen dioxide and formation of ozone. At the same time, some of the nitrogen dioxide can react with the volatile organic compounds to form PAN and other toxic chemicals. Ozone and the peroxy compounds are together depicted as oxidants in the graph. As the sun goes down, the production of ozone and PAN ceases. There are several reactions which result in consumption of the ozone and other oxidants present in the atmosphere.

- There are many meteorological factors affecting the formation of photochemical smog. Rain can dissipate photochemical smog as the pollutants are rinsed out of the atmosphere with rainfall. Photochemical smog can be blown away by wind and resulting in replacement by fresh air. However, temperature inversion can cause increase in the impact of photochemical smog. Normally, during the day, air which is near the earth's surface is warmed and rises up, carrying pollutants with it. However, a temperature inversion traps pollutants near the surface of the earth. A temperature inversion is a phenomenon in which the normal tropospheric decrease in temperature with height changes to increase in temperature with increasing height. A temperature inversion thus traps a layer of cold air beneath warm air, reducing mixing of the atmosphere due to convection. Dispersion of pollutants, therefore, decreases. Inversions can remain in place for some days which may stretch to several weeks.

- Topography also affects a smog event. Towns located in valleys are more affected by photochemical smog because the surrounding hills and mountains reduce air flow, allowing the amounts of pollutants to rise. Valleys are also sensitive to photochemical smog because there is a stronger tendency for temperature inversion to take place in valleys.

4.4 Mitigation Measures for Photochemical Smog

The Great Smog of 1952 led to the Clean Air Acts of 1956 and 1968 in Great Britain which resulted in banning of black smoke emitted by industries and conversions to smokeless fuels. Since then, things have started improving and the extreme smog formation episodes have not been repeated in London. Control regulations for automobiles emissions and stress on clean energy in California have resulted in improved quality of air in Los Angeles, according to a 2013 study sponsored by the National Oceanic and Atmospheric Administration. According to the study, levels of chemicals which initiate smog formation have decreased along with levels of ozone and peroxyacetyl nitrate.

Many other cities in the world have the problem of photochemical smog. These include New York, Chicago, Vancouver and Delhi. There are some general mitigation measures which could be applied globally, the foremost being catalytic converters for automobile engines. Let us discuss this in detail.

- **Catalytic converters-:**

Smog formation could be reduced if the amounts of oxides of nitrogen and hydrocarbons released in the atmosphere decrease. This is done by installing efficient catalytic converters in automobiles. A two-way catalytic converter, consisting of a mixture of platinum and palladium supported on a ceramic or metal honeycomb bed, removes hydrocarbons and carbon monoxide from the exhaust. It is an oxidation catalyst which converts CO to CO_2 and hydrocarbons to CO_2 and water when the exhaust gases are forced through it.

$$2CO + O_2 \xrightarrow{\text{catalyst}} 2CO_2$$

$$RH\ (\text{hydrocarbons}) + O_2 \xrightarrow{\text{catalyst}} CO_2 + H_2O$$

A three-way catalytic converter consisting of a mixture of platinum, palladium and rhodium deposited on a high surface area ceramic and metal honeycomb or alumina pellets removes hydrocarbons, carbon monoxide and nitrogen oxides from the exhaust. The converter contains an oxidation-reduction catalyst mixture. Hydrocarbons and carbon monoxide are oxidised while nitrogen oxides are reduced. In the exhaust system the nitric oxide reacts with carbon monoxide to give nitrogen and carbon dioxide:

$$2NO + 2CO \xrightarrow{\text{catalyst}} N_2 + 2CO_2$$

If NO is only partially reduced to N_2O, the converter would still work because N_2O is easily decomposed:

$$2N_2O \xrightarrow{\text{catalyst}} 2N_2 + O_2$$

NO_x and hydrocarbons interact to give nitrogen, carbon dioxide and water:

$$NO_x + RH \xrightarrow{\text{catalyst}} N_2 + CO_2 + H_2O$$

A three-way converter operating under the stoichiometric conditions of air: fuel ratio 14.6:1 and at temperatures of 400 to 600^{o}C can achieve almost 90% efficiency in removing all three offending emissions from auto exhaust:

- **Free radical traps-:**
  Certain compounds can act as free radical traps i.e. when sprayed in the atmosphere, they result in production of free radicals that readily combine with free radical initiators of photochemical smog (such as O., R., RO., H. etc.). The introduction of such compounds will slow down the conversion of NO to NO_2 from the usual 2-6 hours to 6-12 hours. Thus the conversion will take place around the time of sunset and photochemical decomposition of nitrogen dioxide, which is the smog initiation step, would be inhibited. The compound diethyl hydroxylamine, $(C_2H_5)_2NOH$ has been found to be effective in inhibiting smog in lab tests. Though it is cheaper than catalytic converters, its unpleasant odour at > 0.5 ppm concentration is a disadvantage.

- **Petrol reformulation-:**

Summer petrol used in some European countries is a reformulated gasoline in which 1/10 of the aromatic hydrocarbons have been replaced by oxygenated fuel such as includes methyl tertiary butyl ether. These additives allow more complete and efficient combustion, thus suppressing the emission of volatile organic compounds. The emission of nitrogen oxides is reduced since petrol containing oxygenates burns at a lower temperature. Decreased emission of VOCs and nitrogen oxides suppresses smog formation.

- **Alternative energy sources-:**

Hybrid cars, hydrogen fuelled cars and cars run on different types of biodiesel may be viable methods of cutting down on vehicular exhaust emissions in the near future.

5. Summary-:

Let us now summarize what we have learnt.

We learnt about photochemical reactions occurring in the atmosphere in the presence of sunlight. These type of reactions proceeds by excitement of molecules and emission of energy by the excited species in accordance with different mechanisms. Under normal conditions, the atmosphere is affected by many photochemical reactions taking place simultaneously. In a polluted environment, there are chemicals present in large amounts. Therefore, many more types of photochemical reactions can occur.

We have discussed about nature and effects of atmospheric photochemical reactions. We have also talked about harmful effects of some photochemical reaction and mitigation measures for such reactions.

We have discussed the phenomenon of smog and types of smog, i.e., industrial and photochemical and differences between them. Photochemical smog is driven by the radiant energy from the sun. The chemicals comprising photochemical smog are nitrogen dioxide which is obtained by combining nitric oxide with oxygen, as well as ozone, aldehydes ketones and peroxy compounds. We have also discussed the factors that affecting the formation of photochemical smog, the effects of such smog and its mitigation measures.

So now you are familiar with the photochemical reactions occurring in the atmosphere and know how these reactions alter the chemical composition of the atmosphere.