# MODULE 3.3

Organic Air Pollutants

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A variety of organic compounds are emitted into the atmosphere by natural and human activities. They are so diverse that it is difficult to classify them neatly. However they can be divided into two categories namely primary pollutants and secondary pollutants. The primary pollutants are those that are emitted directly from the sources. Typical example of an organic pollutant in this category is vinyl chloride which can cause cancer. The secondary pollutants are those that are formed in the atmosphere by chemical interactions among the primary pollutants and normal atmospheric constituents. Secondary pollutants are formed from chemical and photochemical reactions in the atmosphere. An example of this category in the formation of photochemical smog due to the interaction between terpene hydrocarbons from conifer trees and nitrogen oxides from automobiles.

Natural source of hydrocarbons:

Most of the organic compounds in the atmosphere (85%) originate from the natural source from vegetation. Among them the methane is of concern since it is the most important greenhouse gas after carbondioxide. Methane is produced by the bacterial action, when dead organic matter is subjected to an oxygen-depleted highly reducing aqueous or terrestrial environment as per the following equation.

$$2\{CH_2O\} \text{ (bacterial action)} \rightarrow CO_2 \text{ (g)} + CH_4 \text{(g)}$$
(biomass) $\qquad ....(1)$

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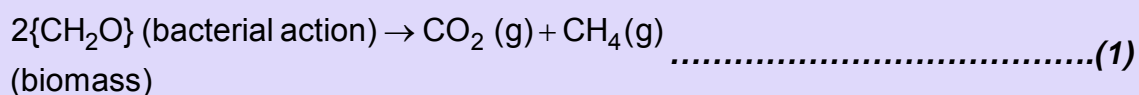
The present tropospheric concentration of methane is about 1.77 ppm and it is increasing at the rate of 0.5% every year. Methane undergoes photochemical dissociation in the stratosphere to give water vapour. But in the troposphere it undergoes photochemical reaction to give CO and O_3.

Ethylene, C_2H_4, is released to the atmosphere by a variety of plants. Most of the hydrocarbons emitted predominantly by trees are terpenes. Others are α - pinene, limonene, β - pinene; mycene; ocimene; α - terpinene and isoprene. These compounds contain olifinic bonds and hence are the most reactive compounds in the atmosphere. Terpenes react rapidly with hydroxyl radical, HO• and with other oxidizing agents in the atmosphere, particularly ozone, O_3. Such reactions form aerosols, which cause much of blue haze in the atmosphere above some heavy growths of vegetation. The compounds emitted by plants mostly consist of esters such as coniferyl benzoate. But the quantities emitted by them are small and have little influence in atmospheric chemistry. The principal sink for methane decomposition is oxidation via hydroxyl radicals in the troposphere.

$$CH_4 + OH \rightarrow •CH_3 + H_2O \textit{...(2)}$$

As discussed earlier this reaction is only the first step of a sequence which transforms methane ultimately to CO and then CO_2. The other sinks for methane gas are the reaction with soil and loss to the stratosphere.

Hydrocarbons:

The gaseous and volatile liquid hydrocarbons are of particular interest as air pollutants. Hydrocarbons can be saturated or unsaturated , branched or straight-chain, or can have a ring structure as in the case of aromatics or other

cyclic compounds. In the saturated class, methane is by far the most abundant hydrocarbon constituting about 40 to 80 percent of total hydrocarbons present in the urban atmosphere. Hydrocarbons prodominate among the atmospheric pollutants because of their widespread use in fuels. They enter the atmosphere either directly from the fuel or as by-products of partial combustion of other hydrocarbons, which tend to be unsaturated and relatively reactive. Several alkenes including ethylene, propylene, butadiene and styrene are among the top 50 chemicals produced each year and are released to the atmosphere during their production and use similarly aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene and cumene are among the top 50 chemicals produced each year and these are also released into the atmosphere during their production and use.
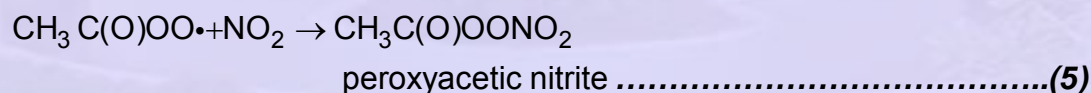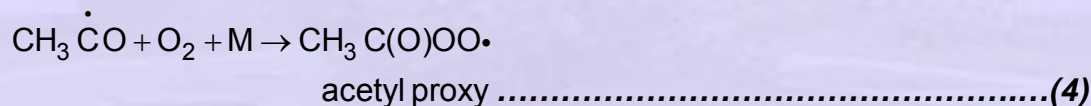
Polycyclic aromatic hydrocarbons (PAHs) commonly occur in urban atmospheres up to about 20µg m^{-3} level. Elevated levels of PAHs are observed in polluted urban atmospheres, in the vicinity of forest fires and burning of coal. Terpenes are a particular class of volatile hydrocarbons emitted largely by natural sources. These are cyclic non-aromatic hydrocarbons found in pine tar and in other wood sources as mentioned earlier.

The hydrocarbon in air by themselves alone cause no harmful effects. They are of concern because the hydrocarbons undergo chemical reactions in the presence of sunlight and nitrogen oxides forming photochemical oxidants of which the predominant one is ozone.
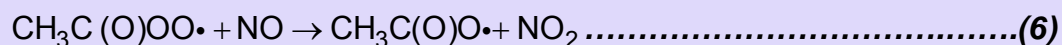
Oxygen-Containing Organic Compounds:
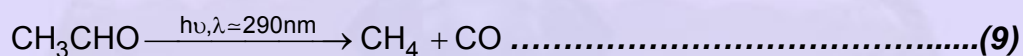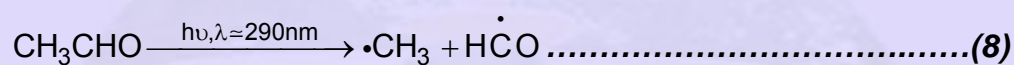
Aldehydes and ketones:

The aldehydes and ketones enter the atmosphere from a large number of sources and processes. These include direct emission from internal combustion engine exhausts, incinerator emission, spray painting, polymer manufacture, printing, printing, and lacquer manufacture. Formaldehyde and acetaldehyde are produced by microorganisms and acetaldehyde is emitted by some kind of vegetation. They are also produced from hydrocarbons.by the photochemical oxidation in the atmosphere. These aldehydes and ketones are somewhat stable species, but they undergo reactions of their own as shown below.

$$CH_3CHO + \cdot OH \rightarrow CH_3 \overset{\bullet}{C}O + H_2O \quad ....(3)$$

$$CH_3 \overset{\bullet}{C}O + O_2 + M \rightarrow CH_3 C(O)OO\bullet$$
$$\text{acetyl proxy} \quad ....(4)$$

$$CH_3 C(O)OO\bullet + NO_2 \rightarrow CH_3C(O)OONO_2$$
$$\text{peroxyacetic nitrite} \quad ....(5)$$

There is yet another reaction initiated by hydroxyl radicals followed by the addition of dioxygen and then reaction with nitrogen dioxide to form a member of PAN family of compounds. A second possibility also starts with reactions as explained in 3,4 &5. The acetyl peroxy radical then gives up an oxygen to nitric oxide followed by cleavage of the C-C bond to form a methyl radical and carbon dioxide.

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$$CH_3C\,(O)OO\bullet + NO \rightarrow CH_3C(O)O\bullet + NO_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\textbf{(6)}$$

$$CH_3C(O)O\bullet \rightarrow \bullet CH_3 + CO_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\textbf{(7)}$$

A third important route for decomposition is by photolysis. Aldehydes are capable of absorbing UV radiation longer than 290 nm and this leads to photochemical degradation. For acetaldehyde the observed photolytic reactions are

$$CH_3CHO \xrightarrow{h\upsilon,\lambda \simeq 290nm} \bullet CH_3 + H\overset{\bullet}{C}O \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\textbf{(8)}$$

$$CH_3CHO \xrightarrow{h\upsilon,\lambda \simeq 290nm} CH_4 + CO \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\textbf{(9)}$$

The alkenyl aldehydes because of the presence of both double bonds and carbonyl groups are especially reactive in the atmosphere. Acrolein is the most common of these found in the atmosphere which is used as an industrial chemical. The life time of aldehydes in the atmosphere is in the range of 24 hours.

Organohalide Compounds:

Organohalide compounds contain atleast one atom of F,Cl, Br or I. They may be saturated or unsaturated and exhibit different physical and chemical properties. Chlorofluro carbons (CFCs) are used in wide variety of industrial applications including aerosol propellents, refrigerants, and foam blowing. The CFC's which have attracted most attention in ozone depletion are $CFCl_3$, CF_2Cl_2 . The lifetime of $CFCl_3$ is about 77 years, while that for CF_2Cl_2 is 139 years. Hence any reduction in CFC release will have little effect in the immediate future. The most abundant organochlorine compounds in the atmosphere are CCl_2F_2, CCl_3F, CH_3Cl, CCl_4 and CH_3CCl_3 . It has been reported that trace amounts of bromine

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might efficiently catalyse the ozone reduction. The predominant anthroprogenic source is CH_3Br and CF_3Br. Sometimes sources such as CF_2BrCl and $C_2H_4Br_2$ are entirely man made. CH_3Br is used as a soil fumigant and other compounds of bromine as fire retardants and fuel additives.

Vinyl chloride which is an unsaturated halide is used primarily in the production of polyvinylchloride resins. It is known to cause cancer. Methylchloride is used in the manufacture of silicones.Trichloroethylene is a solvent that was quite commonly used as a cleaning agent and it is a suspected carcinogen. 1,2-dichloroethane is a metal degreaser and used in the manufacture of number of products such as varnish removers, fumigants and soap compounds. High level exposure of this solvent is known to cause injury to the central nervous system, liver and kidneys.

The organochlorine compounds such as methyl chloride, methyl chloroform and carbon tetrachloride have tropospheric concentrations ranging from ten to several tenths of ppm. Methyl chloroform is relatively persistent in the atmosphere with residence time of several years. Therefore they may pose the threat to ozone layer as CFCs. Another class of organohalides are polychlorinated biphenyls (PCBs). They are made by chlorinating the aromatic compound biphenyl. A complex mixture results with variable numbers of chlorine atoms substituted at various positions of the rings. They were mainly used as the coolant in the power transformers and capacitors because they are excellent insulators, are chemically stable, and have low flammability and vapour pressure. In later years they were also used as heat transfer fluids in other machinery and as plasticisers for polyvinylchloride and other polymers; they found additional uses in carbonless copy paper, as de-linking agents for recycled newsprint and as weathering agents. As a result of industrial discharges and the disposal of all

these products, PCBs were spread widely in the environment. These PCBs can be transported with atmospheric particles.

## Chlorofluoro Carbons And Depletion Of Ozone Layer:

Chlorinated fluorocarbons (CFCs) are a class of compounds initially developed in 1930s; they have properties that make them particularly useful in a number of applications. As mentioned in the previous paragraph under organo-halide compounds, these CFCs have desirable properties such as low viscosity, low surface tension, low boiling point, and chemical and biological inertness. The last property accounts for their being non-toxic and non-flammable. Because of these advantageous properties, these compounds were used as refregerants, solvents for cleaning electronic and other components, and blowing agents for polymer foams.

One of the important environmental properties of these CFCs is the ozone depletion potential (ODP). It is defined as the ratio of the impact on ozone from a specific chemical to the impact from an equivalent mass of CFC-11 ($CFCl_3$), the standard by which all others are calculated. The ODP values takes into account the reactivity of the species, its atmospheric lifetime, and its molar mass. The The amount of chlorine in the chemical species is also important. Most of the CFCs have ODP values between 0.1 and 1.0, while hydrofluorocarbons (HCFCs) have ODP values which are about ten times lower (0.01-0.1). Hydrofluorocarbons, which contain no chlorine, have a zero ODP value.
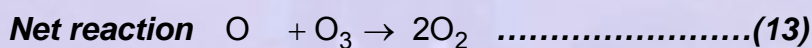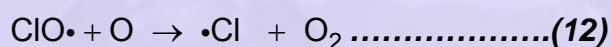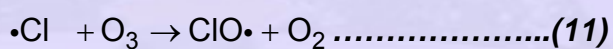
Another important property of the CFCs is that they are almost completely inert both biologically and chemically in the earth's environment, in the troposphere. Because they do not react, they circulate through the troposphere

until they escape into the stratosphere. While unreactive in the troposphere, at higher altitudes they are able to undergo ultraviolet photolytic decomposition, as a consequence of being exposed to intense flux of energetic ultraviolet radiation.

$$CFCl_3 + h\upsilon \ (\lambda < 290 \ nm) \rightarrow \bullet CFCl_2 + \bullet Cl \ \dots\dots\dots\dots\dots\dots\dots\dots\dots(10)$$
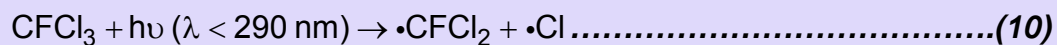
The released chlorine radical is now able to take part in the catalytic cycles shown in reactions 11,12 & 13.

$$\bullet Cl \ + O_3 \rightarrow ClO\bullet + O_2 \ \dots\dots\dots\dots\dots(11)$$

$$ClO\bullet + O \rightarrow \bullet Cl \ + \ O_2 \ \dots\dots\dots\dots(12)$$

_____

Net reaction $\ O \ + O_3 \rightarrow \ 2O_2 \ \dots\dots\dots\dots\dots(13)$

A second and possibly third chlorine radical could also be produced by further decomposition of the remnant. $\bullet CFCl_2$ radical, generating additional potential for ozone depletion.
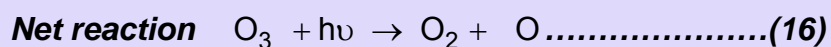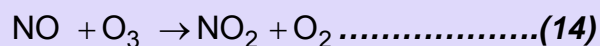
CFC substitutes:

Current research is centered on modifying the relative amounts of fluorine, chlorine and hydrogen in new compounds. A common approach has been to incorporate hydrogen in the structure which is then called as hydroflurocarbons (HCFCs) or replace chlorine altogether and produce what are known as hydrofluorocarbons (HFCs). Increasing the hydrogen content reduces the inertness, in this way making the tropospheric lifetime shorter. The presence of hydrogen increases the reactivity and flammability of the compound and higher reactivity is a disadvantage in some applications. Increasing the proportion of fluorine at the expense of chlorine tends to to produce a highly stable compound.

However such compounds are excellent and persistent green house gases. For compounds containing no chlorine, obviously no chlorine atoms can be released, so that there is no potential to deplete ozone.

From the combined industrial-environmental perspective, one of the more promising new compounds is HFC-134a (CF_3CH_2F). This HFC has intermediate stability; it is oxidised by the hydroxyl radical in the troposphere, and has a residence time of 18Y. It is not very flammable. Since it does not contain any chlorine, it will have no ozone depletion potential. Unfortunately it is expensive to manufacture. Another CFC replacement is HCFC-123 (CF_3CHCl_2) , which contains chlorine but has only about one-tenth the ozone depletion potential of CFC-11, largely because of its relatively short tropospheric lifetime.

It is important to mention here that there are other processes that occur in the stratosphere which are in competition with the catalytic cycles. Their relative importance further complicates our ability to make predictions about the extent of ozone destruction that may occur under various conditions. Null and holding cycles are two other types of reaction sequences that prevent the species from taking part in the catalytic processes.
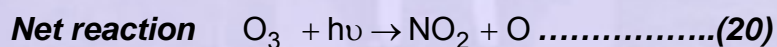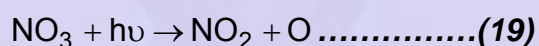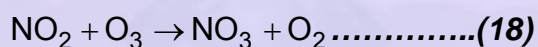
Null (do nothing) cycles interconvert the species X and XO while effecting no net odd oxygen removal. Null cycles involving nitrogen oxides are shown below.

$$NO + O_3 \rightarrow NO_2 + O_2 \ldots\ldots\ldots\ldots.(14)$$

$$NO_2 + h\upsilon \rightarrow NO + O \ldots\ldots\ldots\ldots\ldots(15)$$

Net reaction $$O_3 + h\upsilon \rightarrow O_2 + O \ldots\ldots\ldots\ldots\ldots(16)$$

This sequence competes with catalytic cycle and is important only during daytime as it requires radiation in the near-ultraviolet region. While the net effect is ozone photolysis, ozone is rapidly and stoichiometrically synthesised by reaction (17).

$$O + O_2 + M \rightarrow O_3 + M \ldots\ldots\ldots\ldots\ldots\ldots(17)$$
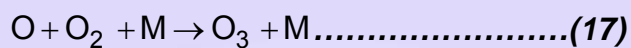
Another example of a null cycle is the reaction involving NO_2 which results in the production of NO_3 and the establishement of a cycle.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \ldots\ldots\ldots..(18)$$
$$NO_3 + h\upsilon \rightarrow NO_2 + O \ldots\ldots\ldots\ldots(19)$$

Net reaction $O_3 + h\upsilon \rightarrow NO_2 + O \ldots\ldots\ldots..(20)$

Some of the NO_3 reacts in a three-body process to produce N_2O_5.

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M \ldots\ldots\ldots\ldots...(21)$$
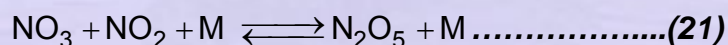
The N_2O_5 is a relatively stable species and therefore it behaves as an unreactive reservoir of NO_x. N_2O_5 is not permanently stable as it ultimately decomposes back to NO_2 and NO_3. Reaction (21) therefore acts as a holding cycle, temporarily preventing the catalytic decompostition of ozone.

Nitric acid and hydrochloric acid are formed in the stratosphere and these reactions serve as reservoirs for ozone depleting nitric oxide and chlorine species.

$$\cdot NO_2 + \cdot OH + M \rightarrow HNO_3 + M \ldots\ldots\ldots\ldots\ldots\ldots(22)$$
$$\cdot Cl + CH_4 \rightarrow HCl + \cdot CH_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(23)$$

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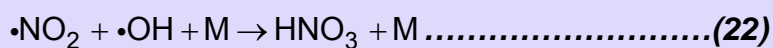
Almost 50% of NO_x is stored in nitric acid reservoir and 70% of chlorine is stored in hydrochloric acid reservoir.

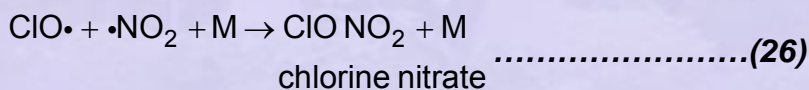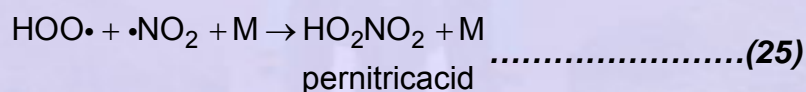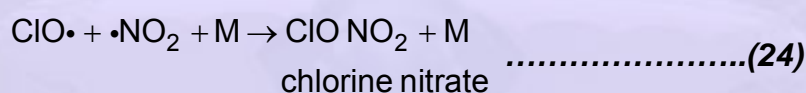The nitric acid undergoes photolysis in the day light , producing nitrogen dioxide in the reverse reaction of (22) and the hydrochloric acid releases chlorine and water after reaction with hydroxyl radical.

In addition several other species have been identified as reservoirs for NO_x and Cl in the stratosphere as indicated by the following equations.

$$ClO\bullet + \bullet NO_2 + M \rightarrow ClO\,NO_2 + M$$
$$\text{chlorine nitrate} \quad\ldots\ldots\ldots\ldots\ldots..(24)$$

$$HOO\bullet + \bullet NO_2 + M \rightarrow HO_2NO_2 + M$$
$$\text{pernitricacid} \quad\ldots\ldots\ldots\ldots\ldots(25)$$

$$ClO\bullet + \bullet NO_2 + M \rightarrow ClO\,NO_2 + M$$
$$\text{chlorine nitrate} \quad\ldots\ldots\ldots\ldots\ldots(26)$$

These compounds act as reservoirs for Cl and NO_x until they are released as active catalysts into the troposphere.

The appearence of Antartic and Arctic 'Ozone holes' is the consequence of the release of these as active catalysts.

Consequences Of Ozone Depletion:

Ozone depletion has a number of consequences for human health and agriculture. These include increased rate of skin cancer and eye cataracts, weakening of immune systems, damage to crops, reductions in primary produces (plankton) in the ocean and increasing air pollution.

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Photo Chemical Smog:

Photo chemical smog was first observed in Los Angeles, U.S.A in the mid 1940s and since then this phenomenon has been detected in most major metropolitan cities of the world. The conditions for the formation of photochemical smog are air stagnation, abundant sunlight, and high concentrations of hydrocarbon and nitrogen oxides in the atmosphere. Smog arises from the photochemical reactions in the lower atmosphere by the interaction of hydrocarbons and nitrogen oxide released by exhausts of automobiles and some stationary sources. This interaction results in a series of complex reactions producing secondary pollutants such as ozone, aldehydes, ketones, and peroxyacyl nitrates. The nature of the dynamic photochemical smog is illustrated in Fig.1.

The fig.1 illustrates the characteristic variation with time of the day in levels of NO, NO_2, hydrocarbons,aldehydes and oxidants under smoggy atmospheric conditions in a city with heavy vehicular traffic. From the figure it can be seen that shortly after sun rise, the level of NO in the atmosphere decreases markedly followed quickly by increase in NO_2. NO_2 reacts with sunlight leading to various chain reactions and ultimately to the production of ozone and other oxidants. During the midday when the concentration of NO has fallen to a very low level, the levels of aldehydes and oxidants become relatively high. The concentration of total hydrocarbon in the atmosphere reaches it maximum in the morning and then decreases during the remaining daylight hours. The typical smog episode occurs in hot, sunny weather under low humidity conditions. The characteristic symptoms are the brown haze in the atmosphere, reduced visibility, eye irritation, respiratory distress and plant damage.

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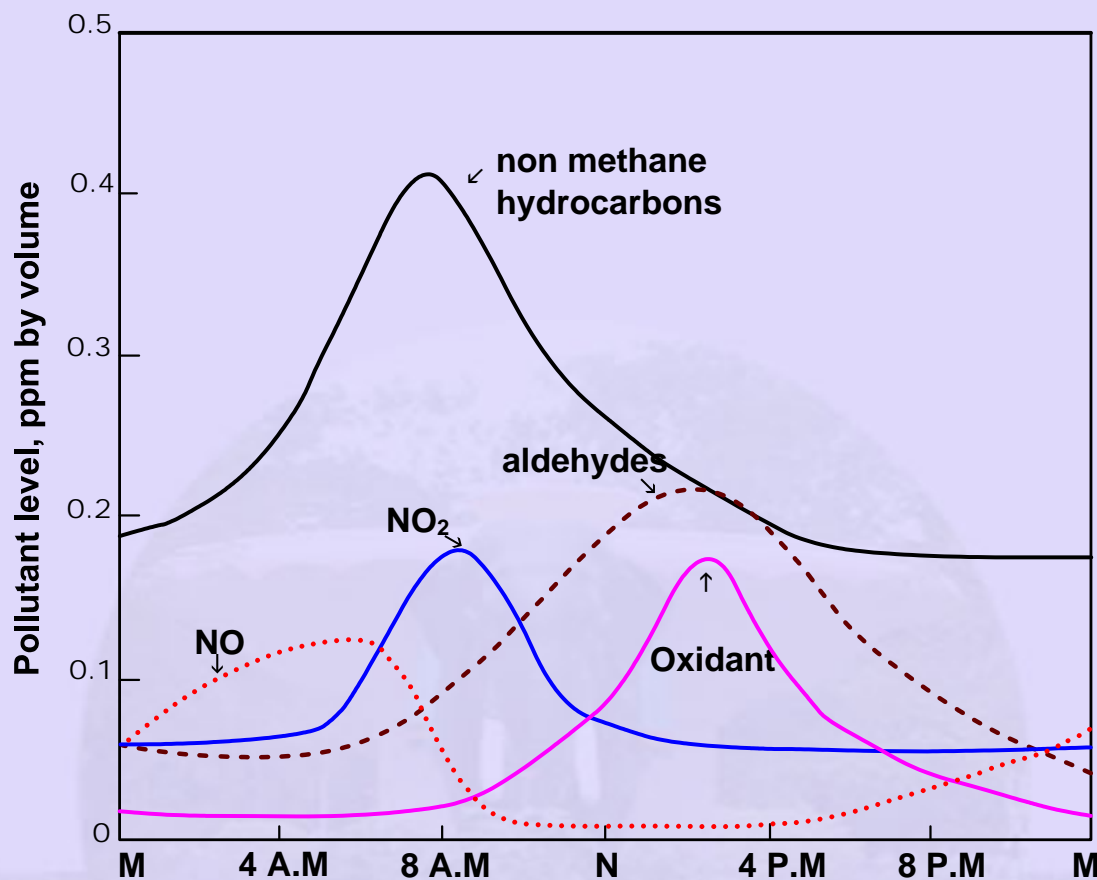
Fig. 1 Dynamic behaviour of photochemical smog

(Redrawn by permission of Lewis Publishers, Chelsea, Michigan 48118, USA from

Fundamentals of Environmental Chemistry, S.E.Manahan, p.630,1993)

The control of photochemical smog may require substantial reduction in NO_x produced in urban areas. At the same time it is necessary to control the release of hydrocarbons from numerous mobile and stationary sources. Catalytic converters are now used to destroy the pollutants in exhaust gases. A reduction catalyst is employed to reduce NO in the exhaust gas and after injection of air an oxidation catalyst is used to oxidise the hydrocarbon and CO.

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Chemical reactions involved in smog formation in the atmosphere:

The starting mechanism is the absorption of uv light from the sun by NO_2. This causes the nitrogen dioxide to decompose into nitric oxide.

$$NO_2 + h\upsilon \rightarrow NO + O$$ ....(26)

and reactive atomic oxygen (26). The atomic oxygen initiates oxidising processes or quickly combines with molecular oxygen to form ozone, which itself is reactive and acts as oxidant.
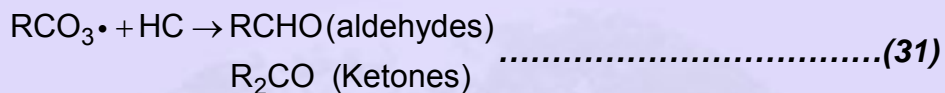
$$O + O_2 + M \rightarrow O_3 + M$$ ....(27)

$$O_3 + NO \rightarrow NO_2 + O_2$$ ....(28)

In equation (27) an energy absorbing molecule or particle (M) is required to stabilise O_3 or else it will rapidly decompose. Under normal conditions, the ozone formed will be quickly removed by reaction with NO to provide NO_2 and O_2 according to equation (28);however when the hydrocarbons are present in the atmosphere, this mechanism is partially eliminated as NO reacts with the hydrocarbon radical peroxyacyl ($RCO_3\bullet$) according to equation (32) $RCO_3\bullet$ also reacts with O_2 to give O_3 (equation 33) and as a result ozone concentration builds up to dangerous levels.

Hydrocarbons, indicated by symbol HC compete for free oxygen released by NO_2 decomposition to form oxygen bearing free radicals such as acyl radical.

$$HC + O \rightarrow RCO\bullet \text{ (acyl radical)}$$ ....(29)

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This radical takes part in a series of reactions involving the formation of still more reactive species , which in turn react with O_2 , hydrocarbons and nitric oxide.

$$RCO\bullet + O_2 \rightarrow RCO_3\bullet \text{ (peroxy acyl radical)} \quad\text{.........................}(30)$$

$$RCO_3\bullet + HC \rightarrow RCHO \text{ (aldehydes)}$$
$$R_2CO \text{ (Ketones)} \quad\text{....................................}(31)$$

$$RCO_3\bullet + NO \rightarrow RCO_2\bullet + NO_2 \quad\text{...}(32)$$

$$RCO_3\bullet + O_2 \rightarrow RCO_2\bullet + O_3 \quad\text{...}(33)$$

Reactions represented by equation(31) are termination reactions forming aldehydes and ketones; however, in equations (32) and (33) the peroxyacyl radical reacts with NO and O_2 to produce another oxidised hydrocarbon radical ($RCO_2\bullet$) as well as more NO_2 and O_3. Further the acylate radical ($RCO_2\bullet$) can react with NO to generate even more NO_2.

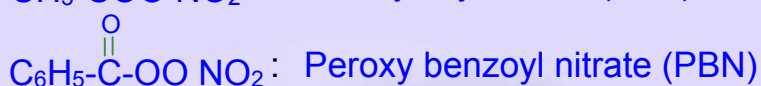$$RCO_2\bullet + NO \rightarrow RCO\bullet + NO_2 \quad\text{......................................}(34)$$

The NO level in the atmosphere eventually drops off with the accumulation of NO_2 and O_3. When the reactions such as these increase the NO_2 level sufficiently, another reaction begins to compete for the peroxyacyl radical.

$$RCO_3\bullet + NO_2 \rightarrow RCO_3 NO_2 \text{ (PANS)} \quad\text{...........................}(35)$$

The end products are known as peroxyacyl nitrates or PANS. Numerous PANS could be formed, corresponding to different possible R groups.

Three of the common members of PAN family are:

$$\overset{\overset{\displaystyle O}{\|}}{H-C}-OO\ NO_2 \quad : \quad \text{Peroxy formyl nitrate (PFN)}$$

$$\overset{\overset{\displaystyle O}{\|}}{CH_3-C}OO\ NO_2 \quad : \quad \text{Peroxy acyl nitrate (PAN)}$$

$$\overset{\overset{\displaystyle O}{\|}}{C_6H_5-C}-OO\ NO_2 \quad : \quad \text{Peroxy benzoyl nitrate (PBN)}$$

The ozone formed according to equations (27) and (33) reacts with hydrocarbons to generate more aldehydes and ketones.

$$HC + O_3 \rightarrow RCO_2\bullet + RCHO, R_2CO \ \textit{.............................(36)}$$
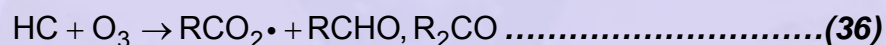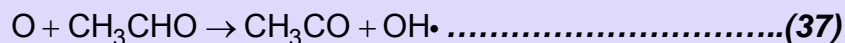
The above equation represent in a broad sense the nature of the overall photochemical reactions leading to the formation of smog.

It has been observed that CO and SO_2 also play a significant part in the process of formation of smog by strongly interacting with many species present in the smog and accelerate the oxidation process.

For example carbon monoxide does this through a series of reactions whose net effect is to convert CO, NO and O_2 into CO_2 and NO_2 thus accelerating the oxidation of NO. First CO is oxidised to CO_2 by OH• radical (equation 38).

n the smogy atmosphere the OH• radical may be produced when aldehydes are attacked by atomic oxygen.
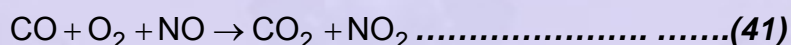
$$O + CH_3CHO \rightarrow CH_3CO + OH\bullet \ \textit{.............................(37)}$$

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$$CO + OH\bullet \rightarrow CO_2 + H\bullet \textit{..(38)}$$

$$H\bullet + O_2 + M \rightarrow HO_2\bullet + M \textit{......................................(39)}$$

The H• radical react with O_2 to form hydro peroxyl radical HO_2• which is the principal agent for rapid conversion of NO into NO_2.

$$HO_2\bullet + NO \rightarrow OH\bullet + NO_2 \textit{......................................(40)}$$

The overall reaction is

$$CO + O_2 + NO \rightarrow CO_2 + NO_2 \textit{....................... ....(41)}$$
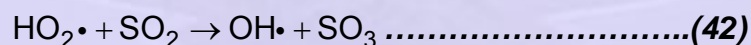
This sequence of reaction provide another route for the oxidation of NO without the participation of O_3 .

Similarly, the reaction of SO_2 with HO_2• radical may be an important step in the mechanism of the oxidation of SO_2 to SO_3 .

$$HO_2\bullet + SO_2 \rightarrow OH\bullet + SO_3 \textit{...........................(42)}$$

In addition, the hydrocarbon radicals may give off an oxygen atom to SO_2 to form SO_3, which in turn is converted to H_2SO_4 droplets resulting in the formation of haze.

Among the important reactions forming nitric acid are the reaction of N_2O_5 with water and addition of hydroxyl radical to NO_2. The oxidation of NO or NO_2 to nitrate species subsequently may occur after the absorption of the gas by aerosol droplet. The nitric acid formed interacts with ammonia in the atmosphere to form salts.

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Organo Nitrogen Compounds:

The different organonitro nitrogen compounds that may be found as atmospheric contaminants may be classified as amines, amides, nitriles, nitro compounds and hetero cyclic nitrogen compounds, The lower-molecular-mass amines which are volatile, are prominent among the compounds giving rotten fish odour. A number of amines are widely used as industrial chemicals and solvents. Decaying organic matter, especially protein wastes, produces amines.

Aromatic amines are of particular concern as atmospheric pollutants, since they are known , to cause bladder cancer in exposed individuals. Aromatic amines of potential concern are aniline,benzidine, 3,3' dichlorobenzidine, naphthylamine, 2-naphthyl-amine, and phenyl-2-naphthyl-amine.They are widely used as chemical intermediates, antioxidants, and curing agents in the manufacture of polymers, drugs, pesticides, dyer, pigments, and inks. These amines also can react with hydroxyl radicals to give rise to harmful products. Being bases they react with acids in the atmosphere.

Dimethyl formamide is the most encountered among the amides as atmospheric pollutant. Most amides have relatively low vapour pressures, which limits their entry into the atmosphere. Acetonitrile and acrylonitrile are the prominent contaminants under nitriles. Both are used in the synthetic rubber manufacture. Acrylonitrile, used to make polyacrylonitrile polymer is the prominant pollutant among the nitrogen containing organic compounds.

The notable pollutants among the nitro compounds include nitromethane and nitrobenzene. The important nitro compound produced by the photochemical oxidation of hydrocarbon in urban atmospheres is peroxy acetyl nitrate (PAN).

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Among atmospheric contaminants nitrosamines are of special concern since they are known to cause cancer. Two nitrosamines have been detected in the atmosphere namely N-nitrosodimethylamine and N-nitroso diethylamine.

Organic Particles In The Atmosphere

The combustion processes of automobile engines produce significant amount of organic particulates. A significant amount of organic particulate matter is produced by automobile engines in combustion processes. The organic particulates of greatest concern are polycyclic aromatic hydrocarbons (PAN), which consist of condensed ring aromatic molecules. The most often cited example of a PAH compound is benz (a) pyrene, a compound that can be metabolized in human body to a carcinogenic form.

PAHs can be synthesised from saturated hydrocarbons under oxygen deficient conditions. Hydrocarbons with very low molecular masses, including even methane, may act as precursors for the polycyclic aromatic compounds. The process of PAH formation from low molar mass. hydrocarbons is called pyrosynthesis. This happens at temperatures exceeding $\approx 500^o$ C at which C-H and C-C bonds are broken to form free radicals. These radicals undergo dehydrogenation and combine chemically to form aromatic ring structures. PAHs also originate from pyrolysis of higher paraffins present in fuels and plant materials.

Soot is formed as a residue during the combustion of fuel in power plants and automobiles. It is due to the incomplete combustion of organic products. It is an impure form of elemental carbon (graphite). Soot particles are roughly spherical, whereas graphite has a layered structure. Soot forms accretion of graphite-like precursors. It is known that most PAH compounds are sorbed on

soot particles. Soot consists of many condensed aromatic rings containing 1-3% H, 5-10% O and trace metals such as Be, Cd, Cr, Mn, Ni and vanadium and also toxic organics such as benzo (a) pyrene. This is illustrated in fig.2.
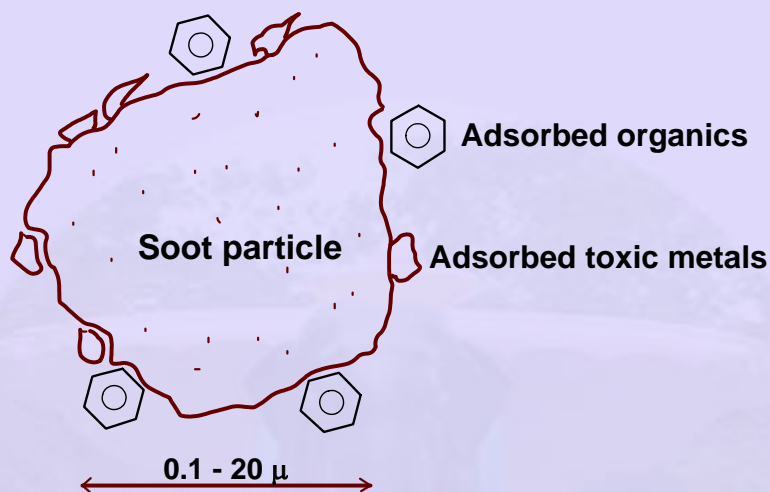
Fig 2. Soot particle from combustion of fossil fuels

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