Smog Formation Review

SMOG FORMATION

Pollutants can be divided into two groups: Primary pollutants are directly emitted to the atmosphere. Secondary pollutants occur by chemical and photochemical reactions of primary pollutants after they have been admitted to the atmosphere by the aid sunlight. Unburned hydrocarbons, NO, particultes are among the primary pollutants. Ozone and peroxyacetly nitrate are the examples of secondry pollutants. Some pollutants can be counted in both categories. NO2 is emitted from vehicles, it is also formed from NO photochemically. Aldehydes are the products of exhaust emission. They also occur as the result of the photochemical oxidation of hydrocarbons. CO is emitted from vehicles and it is also the product of atmospheric hydrocarbon oxidation.

Smog is ground level photochemical ozone formation which is the consequence of the reactions between NOx and hydrocarbons.

Ozone is a strong oxidizer which affects the respiratory system, leading to damage of lung tissues. Chronic exposures to elevated ozone levels are responsible for losses immune system functions, accelerated aging and increased susceptibility to other infections. In addition due to its nature an oxidizer, there are prospects for permanent loss of the alveoli cells.[2]

PHOTOCHEMICAL BACKGROUND

The initial step in photochemical reactions is the absorption of a photon by an atom, molecule, free radical or ion. The result of this absorption is strongly dependent on the energy , in other word the wavelength of the photon. Visible and ultraviolet portion of the light is required to start the photochemical reactions. The absorption can generate dissociation, internal rearrangement, flourescence, or excited species. Species which absorb a photon and then dissociate are the fundamental in the occurrence of

Table 1. Properties of ozone

Physical state	Colorless gas
Chemical formula	O3
Molecular weight	48
Melting point	-197.2
Boiling point	-111.9
Specific gravity (relative to air)	1.658
Vapor density @ 0 C, 1 atm	2.14 g/lt
Vapor density @ 25 C, 1 atm	1.96 g/lt

Solubility @ 0 C, 1 atm	0.494 ml/100 ml water

Photochemical smog

Primary photochemical reactions occur because of photon absorption and dissociation. Secondary photochemical reactions occur due to availability of these primary products. The process can be summarized as follow:

$$A + h\nu \rightarrow A'$$

dissociation of A' into products

$$A' \rightarrow A_1 + A_2$$

In Los Angeles, in 1950s researchers noticed that the sharp increases in NO and non-methane hydrocarbon concentration due to starting of the traffic. By late morning, hydrocarbons and NO concentrations began to decrease whereas, NO2 concentrations began to increase. At mid-day an increase of the concentrations of NO2 occurs along with the rising in the concentrations of oxidants, especially ozone. As the afternoon proceeded and the sun started to fall, the decrease in the oxidant concentrations occured. In the late afternoon, the declining of the NO and NO2 levels was observed. These observations made researchers conclude the availability of a relationship between sunlight, hydrocarbons/volatile organic components, NO and NO2.

It was also observed that CO show an increase in the early morning and late afternoon periods. CO takes an important role in the smog formation process by reacting with OH free radicals to produce free radicals to generate a free hydrogen atom. Consequently, free hydrogen atom reacts with oxygen rapidly to form the hydroperoxy free radical (HO2). This radical gets involve in the formation of ozone.

DISSOCIATION OF NO2

Photodissociation of NO2 is a specific example of photochemical reaction. NO2 absorbs over the whole of the visible and ultraviolet range of the solar spectrum with a decrease in absorption in the longer wavelength visible portion. The color of the gas is reddish-brown during the reaction. The energy requirement to break the bond between the NO and NO2 is approximately 72 kilocalories/g-mole at 25 C. From the table 1.7, it can be seen that required light of wavelength is less than about 0.4 (4000 A). The dissociation is dependent on wavelength. Above 4200 A, due to insufficient energy to achieve dissociation, other photochemical effects like fluorescence occur. Below about 3700 A the rate of molecules undergoing process per photon absorbed is more than 90 %. In typical sunlight the half life of NO2 is approximately two minutes.

Table 2 Photon energy as a function of wavelength.

Region of Spectrum	Microns	E, kilocalories per g-mole

Ultraviolet	0.3	95.3
Violet, visible limit	0.38	75.1
Visible	0.7	40.8
Red-visible limit	0.76	37.6
Infrared	1	28.6

CONTRIBUTION OF HYDROCARBONS TO SMOG FORMATION

In the terms of reactivity, some hydrocarbons emitted are worse than the others. It means that some hydrocarbons are more likely to get involved in these chemical reactions than other groups. However, the criteria should be defined for reactivity. In the event of using nitric oxide photooxidation rate as a basis, then the reactivity of several hydrocarbons can be calculated, Fig 1.2. Photooxidation implies the rate at which the hydrocarbons cause NO to be oxidized to NO2 , given in parts per billion per minute.

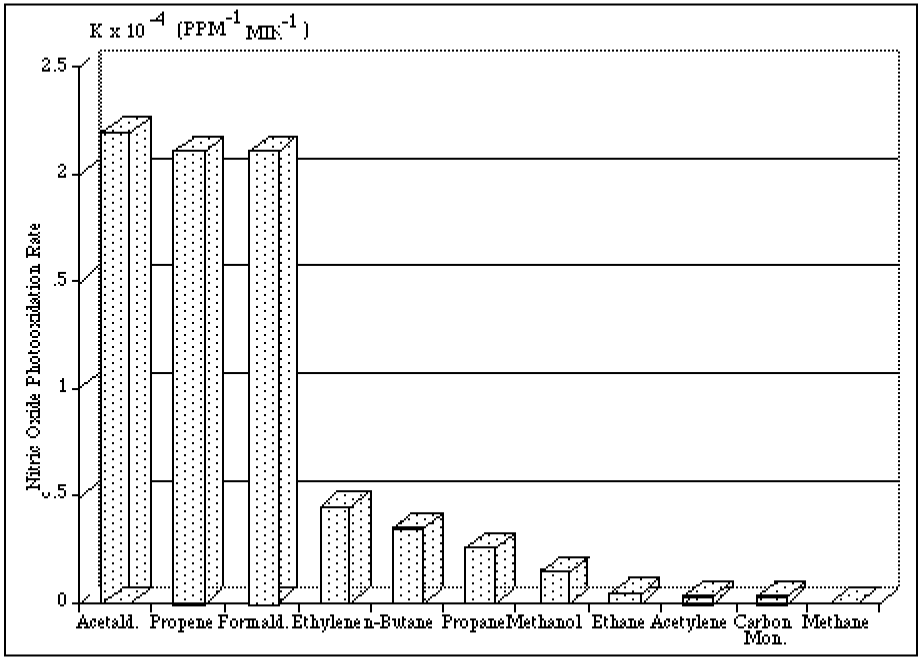

Figure 1. Reactivity index of several compounds.

To control the emission of more reactive hydrocarbon compounds means that the control of the photochemical smog. This can be possible by reducing the emission of internally double-bonded olefins, the diolefins, and the cycloalkanes . It should be noted that the level of different hydrocarbons varies during the day. The concentrations of more reactive hydrocarbons like olefins and diolefins (alkenes and alkadiens) like ethylene, propylene, butadiene decrease dramatically. The drop in the concentrations of cycloalkenes such as cyclopentene is apparent. However the alkanes such as methane and ethane are collected in the atmosphere, since they do not react with other components.

PHOTOLYTIC CYCLE

In first step, NO2 is disassociated NO and an free radical oxygen atom by ultraviolet light. Then, appearing oxygen atom quickly makes a combination with molecular oxygen to form ozone.

$$NO_2 + h\nu \Rightarrow NO + O^{\bullet}$$

$$O^{\bullet} + O_2 + M \Rightarrow O_3 + M$$

M represents any other molecule especially N2 or O2 which absorb the energy of the reaction. Without the M body, only oxygen exchange within an oxygen molecule would occur. Although a triple reaction is required, the reaction is kinetically fast. The third reaction completes the cycle.

$$O_3 + NO \Rightarrow NO_2 + O_2$$

This reaction also occurs fast. Constant level of each compounds, NO, NO2, and O3 could be formed when these three reaction are happened. The steady-state ozone formation can be predicted as a function of initial NO2 concentration. O3 steady-state concentration increases with decreasing concentration of nitric oxide and vice versa.

$$[O_3] = \frac{k_2[NO_2]}{k_1[NO]}$$

(k2 and k1 indicate the rate constants for the reactions, k2/k1 is approximately 1.2 ppm for the Los Angeles noonday condition.[])

Calculations by Stephens show that 10 pphm NO2 causes approximately 2.7 pphm ozone. In fact, most of the NOX emitted from combustion process is NO and levels does not usually exceed 10 pphm. But ozone level usually reaches to 50 pphm for 1 hour peak average.

Further research has been showed that there should be a mechanism which convert NO to NO2 without consuming O3.

The overall higher production of ozone can be explained by the impact of reactive hydrocarbons. Olefins is the most reactive group because of double bond. Oxygen atom attack olefin and divide it into two parts.(Ozone also can do that but reaction with oxygen is faster). Highly reactive free radical which is an incomplete hydrocarbon appears and

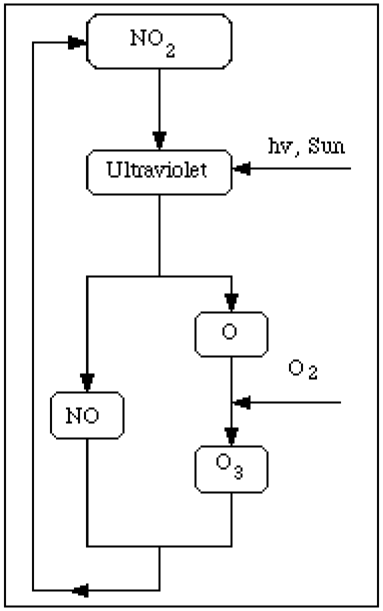

Figure 2. Photolysis of NO2 and generation of O3

continues to get involved in other reactions.

$$O + Olefin \Rightarrow R^{\bullet} + R'O$$

$$R^{\bullet} + O_2 \Rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + NO \Rightarrow NO_2 + RO^{\bullet}$$

Compound which is noted RO2 stands for peroxy radicals. Because, each hydrocarbon molecule requires one oxygen atom to start its oxidation, one hydrocarbon molecule dissociated cause more than one NO molecule to convert NO2.

then original reactions occur,

$$NO_2 + h\nu \Rightarrow NO + O^{\bullet}$$
$$O^{\bullet} + O_2 + M \Rightarrow O_3 + M$$

where: h : Ultraviolet radiation

R : Hydrocarbon group like CH3

* : Free radical

The other radical denoted as R'O might be an aldehyde, since aldehydes are among the products of the reaction between olefins and O.

Photolysis of the formaldhyde results in:

$$HCHO + h\nu \Rightarrow H + HCO$$

Consequently, the fast reaction of the products with O2 :

$$H + O_2 \Rightarrow HO_2$$
$$HCO + O_2 \Rightarrow HO_2 + CO$$

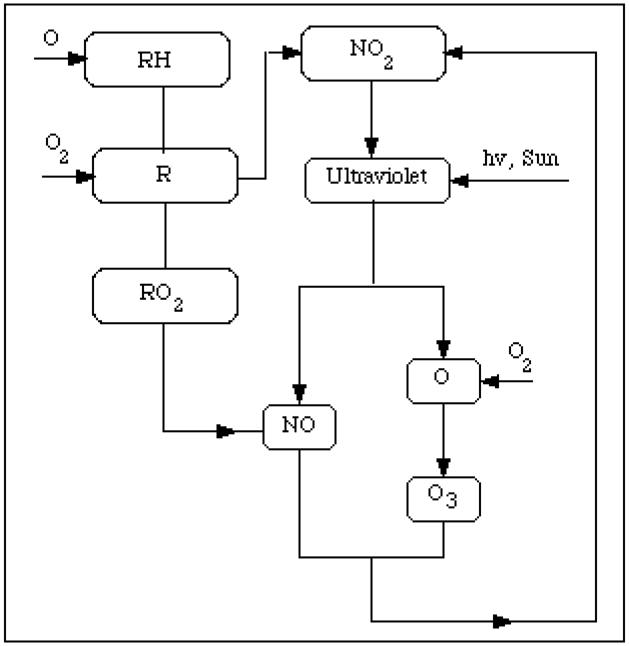

Figure 3.The effect of hydrocarbons in the ozone cycle.

The reaction of formaldhyde with OH radical yields:

$$HCHO + OH \Rightarrow H_2O + HCO^{'}$$
$$HCO^{'} + O_2 \Rightarrow HO_2 + CO$$

For higher aldehydes, the process is as follow:

$$RCHO + OH \Rightarrow RCO^{'} + H_2O$$
$$RCO^{'} + O_2 \Rightarrow RCOOO^{'}$$

RCOOO8 can react with either NO or NO2

$$RCOOO^{\cdot} + NO \Rightarrow RCOO^{\cdot} + NO_2$$
$$RCOO^{\cdot} + NO_2 \Rightarrow R^{\cdot} + CO_2$$

In the event of reaction with NO2

$$RCOOO^{\cdot} + NO_2 \Rightarrow RCOOONO_2$$

results in peroxyacetyl nitrate (PAN)

OTHER MECHANISMS

Althoughseveral mechanisms are available for photochemical smog formation, the NO2-NO-O3-NO2 cycle is the main part in all the models. Other mechanisms can be listed as follow:

ACETALDEHYDES

The reaction of acetaldehyde with atomic oxygen generates hydroxyl radicals

$$CH_3CHO + O \Rightarrow CH_3CO + OH$$

The second step is the reaction of OH radical with CO

$$OH + CO \Rightarrow CO_2 + H$$

The hydrogen can react with molecular oxygen

$$H + O_2 + M \Rightarrow HO_2 + M$$

Consequently, hydroperoxyl radical oxidize nitric oxide

$$HO_2 + NO \Rightarrow NO_2 + OH$$

It can be seen that the original nitrogen-oxygen cycle is valid in this mechanism. It should be noted the OH is first used as a reactant and generated as a product.

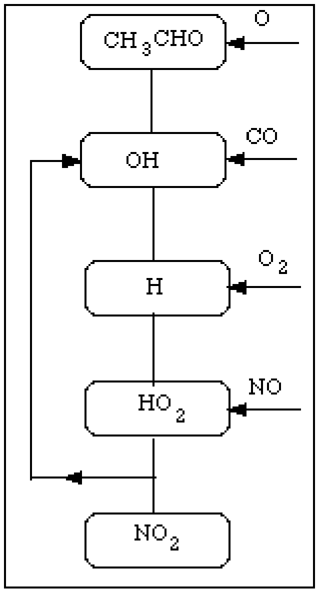

Figure 4. The impact of acetaldehyde on ozone formation.

While nitric dioxide participate in the buildup of ozone, regenerated OH and available CO keep the reaction go on and on. The role of CO in the ozone formation should be underlined.

ALKANES

Alkanes react with OH radicals (daytime) and NO3 (nighttime)

$$RH + OH \Rightarrow R^{'} + H_2O$$
$$RH + NO_3 \Rightarrow R^{'} + HNO_3$$

Reaction of R* with O2 :

$$R^{'} + O_2 \Rightarrow RO_2^{'}$$

The reaction of alky peroxy radical with NO occurs in two ways.

i) For the compounds < C4

$$RO_2^{'} + NO \Rightarrow RO^{'} + NO_2$$

RO: Alkoxy radical

ii) For larger alky peroxy radicals:

$$RO^{'}_2 + NO \Rightarrow RONO_2$$

ALKENES

Gas-phase alkenes react with OH radicals, NO3 radicals, O3 radicals. Among these, reaction with OH radicals is fast. For example, for propylene:

$$CH_3CH = CH_2 + OH \Rightarrow CH_3\,CH\dot{C}H_2OH + CH_3CH\,\dot{C}H_2 - OH$$

The first product is the dominant in this process. The reaction of this radical with O2 results in

$$CH_3CHCH_2OH + O_2 \rightarrow CH_3CCH_2OH - O^{\cdot}$$

beta-hydroxyalkoxy follows two pathways, this radical can react with O2 or decompose. It should be noted that isomerization is not important for smaller alkanes.

$$CH_3CHCH_2OH - O^{\cdot} + O_2 \rightarrow CH_3CCH_2OH = O + HO_2$$

or decomposition of the product,

$$CH_3CHCH_2OH - O^{\cdot} \rightarrow CH_3CHO + CH_2OH$$

The available data shows that the decomposition of -hydroxyalkoxy is the dominant over the first pathway. Then, it can be concluded that OH radical reactions with alkenes lead to the formation of aldhyde and/or ketones.