

# Formation of Ozone in the tropospheric

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## environment

Article information	Abstract
<p><b>Key words</b> Ozone, formation, troposphere</p> <p>Received 26 6 2022, Accepted 15 7 2022, Available online 23 7 2022</p>	<p>Tropospheric ozone (O<sub>3</sub>) is formed via transport from stratospheric O<sub>3</sub> and by oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs) in the presence of NO<sub>x</sub> (NO + NO<sub>2</sub>). In fact, presence of NO<sub>x</sub> is important in formation of O<sub>3</sub>. In the presence of VOCs and NO<sub>x</sub>, chlorine atoms also play a role in the formation of tropospheric O<sub>3</sub>. Monitoring the concentration of O<sub>3</sub> in the troposphere "where we live" is very important and that is due to its effect on human's health as well as agricultural crops.</p>

### I. INTRODUCTION

The earth is surrounded by blanket of air, which we are call the atmosphere. It reaches over 500 km from the surface of the earth, so we are only able to see what occurs fairly close to the ground. The blanket moderates temperature, protects us from harmful radiation and supports life. The atmosphere is divided into four regions based on temperature, troposphere, stratosphere, mesosphere, and thermosphere as shown in table 1 below [2].

Table 1: Regions of the atmosphere [2]

Altitude (Km)	Region
0 - 15	Troposphere
15 - 50	Stratosphere
50 - 85	Mesosphere
85 - 500	Thermosphere

The troposphere and stratosphere together account for 99.9 % of the mass of atmosphere; 75 % of which is the mass in the troposphere [2]. Ozone (trioxygen, O<sub>3</sub>) is a reactive oxidant gas produced naturally in the Earth's atmosphere. O<sub>3</sub> is almost colourless and relatively unstable inorganic molecule. The term ozone is derived from the Greek word *ozein*, which means to smell; the characteristic smell of O<sub>3</sub> is a little like chlorine. O<sub>3</sub> was discovered in 1840 by the German-Swiss chemist, C. F. Schonbein. Later in the 19<sup>th</sup> century, O<sub>3</sub> was detected to be present at a higher mixing ratio in the stratosphere than in the troposphere [1]. In the stratosphere, oxygen

(O<sub>2</sub>) molecules absorb energy from the energetic ultraviolet (UV) radiation and dissociate to form two individual O atoms. Some of the atoms combined with remaining O<sub>2</sub> to form O<sub>3</sub> molecules. Fortunately, these molecules are very effective at absorbing the bulk of solar ultraviolet radiation of wavelengths between 240 and 320 nm, which protect the Earth's planet from irradiation by UV light. Such radiation is harmful to humans, animals, and plants.

Ozone in the upper atmosphere (stratosphere) protects us from harmful high energy photons, which could otherwise penetrate to earth's surface, i.e. the ozone shield is essential for our continued well-being. Natural such as volcanoes and human activity depletion the ozone layer. Chlorofluorocarbons (CFCs) destroy stratospheric ozone. Ozone at high altitudes (stratosphere) is good, whereas, O<sub>3</sub> at low altitudes (troposphere) is bad, which is considered as undesirable pollutant. In fact, O<sub>3</sub> is one of the most serious problems of air quality and therefore its concentrations in the troposphere are typically few tens of parts per billion (ppbv) [1] (10 ppbv = 2.5 x 10<sup>11</sup> molecules / cm<sup>3</sup>). If present in high concentrations, however, causes health problems. This paper will explore the formation of O<sub>3</sub> in the troposphere, which includes its leakage from the stratosphere and oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs). The role of atomic Cl in increasing the concentration of tropospheric O<sub>3</sub> as well as effect of ozone on human's health will be discussed.

### II- Ozone structure and units

The ozone molecule is made up of three oxygen (O) atoms and has angular structure. Both oxygen-to-oxygen bonds are equivalent and have the same length, 1.28 Å. The concentrations of O<sub>3</sub> are measured either as mixing ratio (ppmv), as concentration (molecules / cm<sup>3</sup>), or as Dobson units “DU” (1DU = 2.69 × 10<sup>16</sup> molecules / cm<sup>2</sup>)<sup>[1,2]</sup>. The use of DU allows one to measure “the total concentration” in a given section of the atmosphere. The levels of O<sub>3</sub> may range from ~ 100 to 500 DU depending on the time of year and the region on the earth where the measurements is being taken.

### III- Ozone cycle

Unlike other pollutants, O<sub>3</sub> is not released directly into the troposphere from specific sources. Rather, it is generated in several ways, most importantly by a series of chemical reactions resulting from the interaction of solar radiation with NO<sub>x</sub> and VOCs<sup>[3-5]</sup>. The NO<sub>x</sub> (NO + NO<sub>2</sub>) and VOCs are released into the troposphere from a variety of sources. For example, NO<sub>x</sub> are released from soil, fossil fuel combustion, power plants, industrial facilities, and burning of biomass<sup>[6]</sup>; while VOCs are released from vegetation, ocean, paints, combustion of fossil fuels, and chemical industry<sup>[1]</sup>. Thus, the O<sub>3</sub> cycle starts by the emission of NO<sub>x</sub>, CO, and VOCs. The final fate of tropospheric O<sub>3</sub> is to be deposited on the water and soil via both dry and wet deposition. At the same time, some O<sub>3</sub> would be photolyzed by the solar radiation into O<sub>2</sub> and atomic O.

### VI- Ozone formation

When it was first established that most O<sub>3</sub> was present in the stratosphere, tropospheric O<sub>3</sub> was believed to originate from the stratosphere. This was based upon the fact that the production of O<sub>3</sub> occurs through the photodissociation of O<sub>2</sub> and it was known that this process can only occur at wavelengths < 240 nm, such radiation is present in the stratosphere but not in the troposphere<sup>[1,2]</sup>. About 85-90 % of all O<sub>3</sub> is located in the stratosphere. Tropospheric O<sub>3</sub> can be formed through its leakage from the stratosphere as well as photochemicaloxidation processes of CO and VOCs as explained below:

### V- Flux of O<sub>3</sub> from the stratosphere to the troposphere

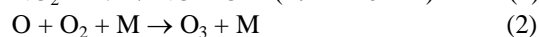
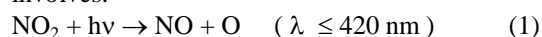
The classical view of the origin of O<sub>3</sub> in the tropospheric environment is that O<sub>3</sub> is transported from the stratosphere<sup>[7]</sup>. Levy et al. have reported that an increase in the O<sub>3</sub> mixing ratio with altitude in the troposphere is often interpreted as a result of downward transport from the stratosphere<sup>[8]</sup>. However, other researchers show that, the increase of O<sub>3</sub> with altitude can be caused also through its precursors (VOCs and NO<sub>x</sub>) and that it is gradually dispersed upward<sup>[9]</sup>. About 10 to 15 % of the total atmospheric O<sub>3</sub> is found in the troposphere. In northern hemisphere, the flux of O<sub>3</sub> from the stratosphere to the troposphere has been estimated to fall in the range of (3-8) × 10<sup>10</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>, while in the southern hemisphere the flux is about half that value<sup>[3,6]</sup>. The total

O<sub>3</sub> production in the stratosphere is about 5 × 10<sup>13</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>; only about 0.1 % of all O<sub>3</sub> produced in the stratosphere is transported down to the troposphere<sup>[6]</sup>.

### VI- Formation of O<sub>3</sub> by chemical processes

#### VI- A Role of Nitrogen oxides (NO<sub>x</sub>)

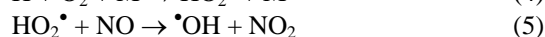
In the tropospheric environment, formation of O<sub>3</sub> via chemical reactions is depending on the concentration of NO<sub>x</sub>. NO<sub>x</sub> has been suggested to be the controlling parameter; so below the mixing ratio 10-30 pptv, O<sub>3</sub> is photochemically destroyed, while above this concentration, O<sub>3</sub> will be produced<sup>[3]</sup>. On the other hand, if NO<sub>x</sub> present at high concentration (~ 10 ppbv), NO<sub>2</sub> will react with OH producing HNO<sub>3</sub>. Browell et al. have reported that the concentration of O<sub>3</sub> in the northern hemisphere is higher than its concentration in the southern hemisphere, which is consistent with a larger photochemical production (as a result of higher NO<sub>x</sub> emission in the northern hemisphere)<sup>[10]</sup>. As was mentioned above, NO<sub>x</sub> is sum of NO and NO<sub>2</sub>. Some NO<sub>2</sub> is emitted directly into the troposphere, while most of it however is formed by the oxidation of NO. Photodissociation of NO<sub>2</sub> (λ ≤ 420 nm) leads to the formation of O<sub>3</sub><sup>[3-5]</sup>. The reaction sequence producing O<sub>3</sub> involves:



That is due to the fact that solar radiation within this region down to about 300 nm can reach the earth's surface. Other researchers are in agreement with this mechanism and have reported that one of the essential precursors of tropospheric O<sub>3</sub> is NO<sub>x</sub><sup>[11,12]</sup>. Thus, increasing anthropogenic emissions of NO<sub>x</sub>, hydrocarbons, and CO over the past century have caused appreciable increase of tropospheric O<sub>3</sub> over industrial continents and probably over the globe<sup>[13]</sup>. In the early 1970s, Crutzen suggested that tropospheric O<sub>3</sub> originates mainly from production within the troposphere by photochemical oxidation of CO and hydrocarbons catalyzed by NO<sub>x</sub><sup>[4,14]</sup>.

#### VI- B Role of carbon monoxide (CO)

The simplest atmospheric carbon species is CO. Carbon monoxide is introduced into the tropospheric environment from both natural and anthropogenic sources and is usually in the range of 50-150 ppbv. These sources include emission by vegetation, burning of biomass, oxidation of hydrocarbons, and combustion of fossil fuels<sup>[1,15]</sup>. It estimated that about 60-70 percent of the CO emission results from human activities<sup>[1]</sup>. CO plays a central role in the formation of tropospheric O<sub>3</sub> via its reaction with •OH in the presence of sufficient concentrations of NO<sub>x</sub>; that would lead to the formation of O<sub>3</sub> as explained in the following equations<sup>[3,5]</sup>:



Recall equation 1

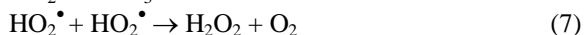
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$  ( $\lambda \leq 420 \text{ nm}$ ) (1) Ozone is then formed as a result of combination of O atom with molecular oxygen ( $\text{O}_2$ ) as shown above in equation 2.

The fate of the  $\text{HO}_2^\bullet$  depends on the ambient concentration of NO. If sufficient NO is present, it converts NO to  $\text{NO}_2$ .  $\text{NO}_2$  absorbs visible and ultraviolet radiation from the sunlight ( $\lambda \leq 420 \text{ nm}$ ) and this leads to its photolysis when ground state O atoms are produced.  $\text{NO}_2$  is the only significant source of the atomic O in the troposphere. Then atomic O reacts rapidly with  $\text{O}_2$  in the presence of a third body (M, usually  $\text{O}_2$  or  $\text{N}_2$ ) in order to produce  $\text{O}_3$ . Therefore, reaction (1) is an extremely important because it leads to the formation of tropospheric  $\text{O}_3$  (equation 2).

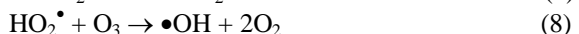
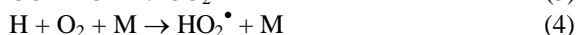
$\therefore$  net reaction:



In contrast, in a NO-poor environment, reaction (5) will not consume all of the  $\text{HO}_2^\bullet$ , and hence what occurs is either the self-reaction of two radicals or the reaction of  $\text{HO}_2^\bullet$  with  $\text{O}_3$ .



Therefore, under these circumstances, oxidation of CO by  $\bullet\text{OH}$  can proceed according to the following steps, which leads to the destruction of  $\text{O}_3$ : Recall equations 3 and 4



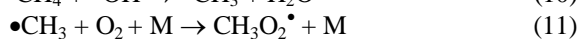
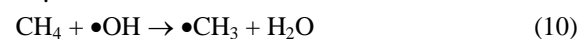
$\therefore$  net reaction:



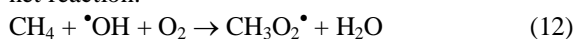
Because the rate constants at 298 K (all in units  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) have been suggested to be  $8.3 \times 10^{-12}$  for reaction (5),  $5.6 \times 10^{-12}$  for reaction (7), and  $2 \times 10^{-15}$  for reaction (8), thus, the rate constant for reaction (5) is about 4000 times faster than that for reaction (8) [15]. In most cases, oxidation of CO by  $\bullet\text{OH}$  can be considered to be a source of tropospheric  $\text{O}_3$ .

#### VI- C Role of volatile organic compounds (VOCs)

The oxidation pathways of VOCs are more complex than those of CO. Similarly to CO; the oxidation of VOCs may or may not lead to  $\text{O}_3$  production, depending on the  $\text{NO}_x$  level. In the presence of  $\text{NO}_x$ , oxidation of VOCs (such as methane,  $\text{CH}_4$ ) plays a pivotal role in tropospheric  $\text{O}_3$ . Using  $\text{CH}_4$  as an example because it has been suggested to have the largest concentration of any hydrocarbon in the global atmosphere (its mixing ratio is 1.7 ppmv) [2], further it is the principal hydrocarbon species in the chemistry of the background troposphere [1]. Once again, it has to emphasize that there has to be NO present in order the reaction to occur. Thus, in NO-rich environments, oxidation of  $\text{CH}_4$  occurs as follows [4,5].

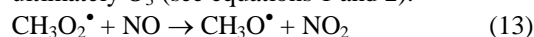


net reaction:



Again the fate of the peroxy radical,  $\text{CH}_3\text{O}_2^\bullet$ , depends on the ambient concentrations of NO. Under tropospheric conditions, the methyl peroxy radical can react with NO.

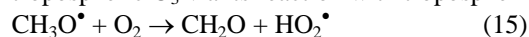
This reaction will lead to the formation of the methoxy radical ( $\text{CH}_3\text{O}^\bullet$ ) and  $\text{NO}_2$  (equation 13). Photolysis of the latter ( $\text{NO}_2$ ) leads to the formation of atomic O and then ultimately  $\text{O}_3$  (see equations 1 and 2).



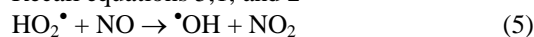
net Rn:



Methoxy radical contributes also in the formation of tropospheric  $\text{O}_3$  via its reaction with tropospheric  $\text{O}_2$ .



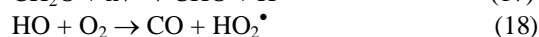
Recall equations 5,1, and 2



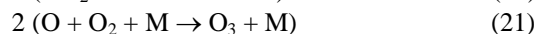
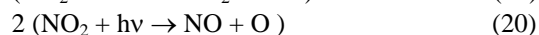
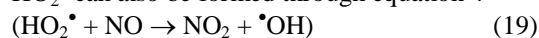
net Rn:



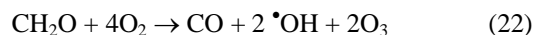
Photolysis of formaldehyde leads to additional production of  $\text{O}_3$



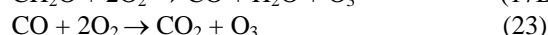
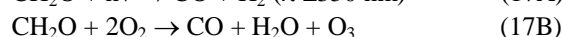
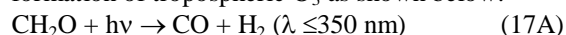
$\text{HO}_2^\bullet$  can also be formed through equation 4



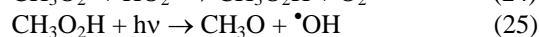
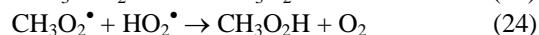
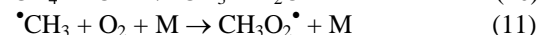
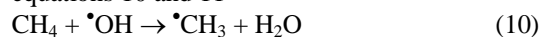
Net Rn:



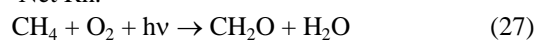
Both photolysis and / or oxidation of  $\text{CH}_2\text{O}$  produce CO. The latter reacts with  $\text{O}_2$ , which contributes to the formation of tropospheric  $\text{O}_3$  as shown below:



From the above reactions, it is clear that oxidation of VOCs in the presence of NO is important in the production of  $\text{O}_3$  in the tropospheric environment. Conversely, if NO is present in a very small concentration, the oxidation of  $\text{CH}_4$  in the troposphere occurs as illustrated in the following reactions [14]. Recall equations 10 and 11

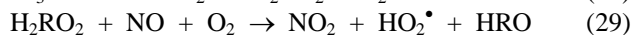
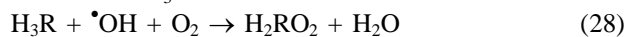


Net Rn:



Thus, reactions 10, 11, 24-26 show clearly that the oxidation of  $\text{CH}_4$  in the troposphere (under conditions of low NO concentration) will not produce  $\text{O}_3$ . However, photolysis of formaldehyde and / or its reaction with  $\text{O}_2$  (equations 17A and 17B) produces CO. Oxidation of CO in the presence of NO produces  $\text{O}_3$  as explained above (reactions 3-5,1,2,6, and23). Because the rate constants for reactions 13 and 24 are  $7.6 \times 10^{-12}$  and  $3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, the removal of  $\text{CH}_3\text{O}_2^\bullet$  by reaction 13 is almost equal to that by reaction 24. Therefore, in NO rich environment, removal of  $\text{CH}_3\text{O}_2^\bullet$  occurs according to reaction 13, while in the absence of NO, reaction 24 will be the dominant [15]. Although

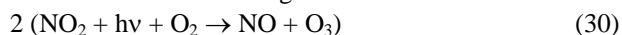
methane is chosen because of its high concentration but the reaction is rather slow and reacts more rapidly with other VOCs. The reaction can be initiated either by the abstraction of H or by  $\bullet\text{OH}$  addition. For simplicity, oxidation of all other hydrocarbons (non methane hydrocarbons,  $\text{H}_3\text{R}$ ) in the presence of NO can be presented in the following equations, which leads to the formation of  $\text{O}_3$  [16].



Recall equation 5



Photolysis of  $\text{NO}_2$  in the presence of oxygen can be illustrated in the following reaction:



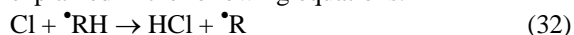
Net Rn:



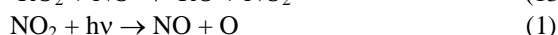
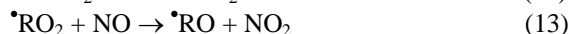
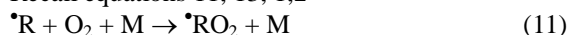
Where R denotes a hydrocarbon radical and HRO represents a carbonyl compound. The carbonyl compounds may undergo further photochemical reactions, which will result in a significant gain of hydrogen radicals. Then the H reacts with  $\text{O}_2$  (reaction 4) to produce  $\text{HO}_2\bullet$ . The latter reacts with NO and that ultimately produces more  $\text{O}_3$  (equations 5,1,2). On the other hand, as was exactly the case for  $\text{CH}_4$ , in the absence of NO, the oxidation of the  $\text{H}_3\text{R}$  will not lead to the production of  $\text{O}_3$  [16].

#### VI-D Role of halogen atoms

Reactive halogen species such as Cl can contribute significantly to or even locally dominate the oxidative capacity in tropospheric marine environment [17-19]. In the gas phase, photolysis of  $\text{Cl}_2$  is the principal pathway of producing Cl atoms in the low level of atmosphere. The final fate of those atoms (Cl) depends on the concentrations of organic species and  $\text{O}_3$ . In addition, the rate constant for the reaction of atomic Cl with most organic species (equation 32) is  $\sim 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is greater than that of  $\text{O}_3$  ( $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (equation 33) [19]. Thus, reaction of atomic Cl with organic species is faster than that of its reaction with  $\text{O}_3$ . Consequently, Cl atoms can be considered as a sink for organics rather than  $\text{O}_3$  in the tropospheric environment. As was noted above, the reaction of  $\bullet\text{OH}$  with alkanes, which of course can occur by only H abstraction mechanism. That reaction is slow and it has been shown that atomic Cl abstracts H from the alkanes is faster than the  $\bullet\text{OH}$  but the opposite is true with alkenes. Reaction of atomic Cl with tropospheric organic species, which explain its contribution in the formation of  $\text{O}_3$ , is explained in the following equations:



Recall equations 11, 13, 1,2



Once the alkyl radical is produced in reaction (32), it reacts in the same manner as outlined above for attack by

$\text{O}_2$  (reaction 11). Then, if sufficient NO is present, this can be considered as another pathway of  $\text{O}_3$  production in the troposphere. Therefore, reactions of Cl atoms contribute to the removal of organics; further in the presence of  $\text{NO}_x$ , it increases the formation of tropospheric  $\text{O}_3$  [18,19]. In another work, Tanaka et al. [20] have show that in the presence of  $\text{NO}_x$ , atomic Cl promotes the formation of  $\text{O}_3$  via its reaction with VOCs but that this depends on the type of VOCs. For instance, in a mixture of VOCs, which do not react rapidly with  $\bullet\text{OH}$  (paraffins as an example) to form  $\text{O}_3$ . So, in the presence of  $\text{NO}_x$ , paraffins react with Cl atoms which contributes to the formation of  $\text{O}_3$ ; that is due to the fact that Cl atoms reacts with paraffins faster than  $\bullet\text{OH}$ . On the other hand, if the mixture of VOCs contains a high concentration of species that react quickly with  $\bullet\text{OH}$  (such as olefins), in the presence of  $\text{NO}_x$  this will lead also to  $\text{O}_3$  production [20]. It can be concluded that formation of  $\text{O}_3$  via the reaction of atomic Cl with organic species is dependent on the type of organics as well as  $\text{NO}_x$  concentration.

#### VII- Ozone issues

##### $\text{NO}_x$ / VOCs ratios:

In the case where the  $\text{NO}_x$  / VOCs ratio is high (meaning a high concentration of  $\text{NO}_2$ ), the  $\bullet\text{OH}$  radicals will not oxidize VOCs in order to produce  $\text{O}_3$ ; instead,  $\bullet\text{OH}$  reacts with  $\text{NO}_2$  to produce  $\text{HNO}_3$ . However, a small fraction of  $\text{NO}_2$  would be photolyzed and that will lead to the production of  $\text{O}_3$ . On one hand, this is good because the production of  $\text{O}_3$  will decrease in the regions where  $\text{NO}_2$  concentration is high. On the other hand,  $\text{NO}_2$  is toxic and if present in high concentrations causes health problems [12]. Therefore, decreasing  $\text{NO}_x$  can lead to an increase of  $\text{O}_3$  formation at high  $\text{NO}_x$  / VOCs ratios.

##### VOCs / $\text{NO}_x$ ratios:

At high VOCs /  $\text{NO}_x$  ratios, the chemistry of  $\text{NO}_x$  becomes limited; in fact, formation of  $\text{O}_3$  depends on how much NO can be oxidized to  $\text{NO}_2$  and then photolyzed in order to produce O atom. This issue is complicated, because the chemical mix of pollutants tends to change from limited VOCs to limited  $\text{NO}_x$  as an air mass moves downwind from an urban centre. Due to the large sources of  $\text{NO}_x$  (such as automobiles and power plants) in the urban areas,  $\text{NO}_x$  is oxidized to  $\text{HNO}_3$ , which removed rapidly from the troposphere either by dry or wet deposition. Decrease of VOCs will not be as rapid because of widespread emission of biogenics as well as less efficient deposition of many organic compounds. Therefore, control of VOC and  $\text{NO}_x$  is needed [12]. On the other hand, at low VOCs /  $\text{NO}_x$  ratios,  $\text{NO}_x$  increases and that will lead to the decrease of  $\text{O}_3$ . That is due to the fact that  $\bullet\text{OH}$  reacts predominantly with  $\text{NO}_2$ . Indeed, in most of the troposphere, except areas of strong sources of  $\text{NO}_x$ , the availability of  $\text{NO}_x$  governs  $\text{O}_3$  production [1].

#### VIII- Sinks of tropospheric $\text{O}_3$

The principal sink of O<sub>3</sub> in the tropospheric environment is through photochemical reaction. Photolysis of O<sub>3</sub> via the ultraviolet radiation from sunlight produces O atom in the excited state (O<sup>\*</sup>).



Then the O<sup>\*</sup> reacts with water vapour (H<sub>2</sub>O) to produce highly reactive hydroxyl (•OH) radicals.



However, this reaction depends on the tropospheric concentration of H<sub>2</sub>O. Otherwise, O<sup>\*</sup> is quenched back to O via its reaction with N<sub>2</sub> or O<sub>2</sub> (M), which removes the excess energy<sup>[1,2]</sup>.



Because the tropospheric mixing ratio of H<sub>2</sub>O is ~ 10<sup>4</sup> ppmv and the rate constant of reaction (30) is about a factor of 10 larger than the rate of reaction (31), therefore, 10 percent of the O<sup>\*</sup> produced reacts with H<sub>2</sub>O to produce •OH. In fact, photolysis of O<sub>3</sub> accounts for 75 percent of its tropospheric loss. Due to the fact that photochemical destruction of O<sub>3</sub> occurs only during the daytime, dry deposition however, may compete effectively with its chemical removal<sup>[1]</sup>.

#### Health effects of ozone

Air pollution has been considered as one of the main risks for human's health. Ozone is one of the gases present in the atmosphere. In fact, ozone has the ability to initiate oxidation reactions and causes skin problems. Ferrara F. et al have reported that O<sub>3</sub> can amplify the UV radiation causes skin oxinflammation markers<sup>[21]</sup>. Inhalation of ozone causes chest tightness, wheezing, throat irritation, coughing, shortness of breath. It may also worsen chronic respiratory disease such as asthma as well as compromise the ability of body to fight respiratory infections<sup>[22]</sup>. It has been suggested that oral intake of vitamin E is beneficial to protect humans from effects of exposure to ozone<sup>[23]</sup>. O<sub>3</sub> can also affect the agricultural crops as illustrated by different researchers<sup>[24-26]</sup>.

#### Conclusions

By far most O<sub>3</sub> (85-90 %) is located in the stratosphere, from where a downward transport of O<sub>3</sub> into the troposphere takes place to a small extent. In addition, during the oxidation of CO and VOCs, O<sub>3</sub> can be produced in the presence of NO<sub>x</sub>. However, in a NO-poor environments, O<sub>3</sub> will be destroyed. The distribution of NO<sub>x</sub> molecules in the troposphere is therefore a key factor in O<sub>3</sub> formation. Atomic Cl also promotes the formation of tropospheric O<sub>3</sub> in the presence of VOCs and NO<sub>x</sub>. In fact, in most of the troposphere except areas where the concentration of NO<sub>x</sub> is high, the availability of NO<sub>x</sub> governs the formation of O<sub>3</sub>. Tropospheric O<sub>3</sub> continues to be a significant concern worldwide; that is due to its effect on the agricultural crops and human health.

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