

Formation of Ozone in the tropospheric

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environment

| Article information | Abstract |
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| <p>Key words Ozone, formation, troposphere</p> <p>Received 26 6 2022, Accepted 15 7 2022, Available online 23 7 2022</p> | <p>Tropospheric ozone (O₃) is formed via transport from stratospheric O₃ and by oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs) in the presence of NO_x (NO + NO₂). In fact, presence of NO_x is important in formation of O₃. In the presence of VOCs and NO_x, chlorine atoms also play a role in the formation of tropospheric O₃. Monitoring the concentration of O₃ 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, O₃) is a reactive oxidant gas produced naturally in the Earth's atmosphere. O₃ 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 O₃ is a little like chlorine. O₃ was discovered in 1840 by the German-Swiss chemist, C. F. Schonbein. Later in the 19th century, O₃ was detected to be present at a higher mixing ratio in the stratosphere than in the troposphere [1]. In the stratosphere, oxygen

(O₂) molecules absorb energy from the energetic ultraviolet (UV) radiation and dissociate to form two individual O atoms. Some of the atoms combined with remaining O₂ to form O₃ 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, O₃ at low altitudes (troposphere) is bad, which is considered as undesirable pollutant. In fact, O₃ 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 10¹¹ molecules / cm³). If present in high concentrations, however, causes health problems. This paper will explore the formation of O₃ 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 O₃ 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 O₃ are measured either as mixing ratio (ppmv), as concentration (molecules / cm³), or as Dobson units “DU” (1DU = 2.69 × 10¹⁶ molecules / cm²)^[1,2]. The use of DU allows one to measure “the total concentration” in a given section of the atmosphere. The levels of O₃ 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, O₃ 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_x and VOCs^[3-5]. The NO_x (NO + NO₂) and VOCs are released into the troposphere from a variety of sources. For example, NO_x are released from soil, fossil fuel combustion, power plants, industrial facilities, and burning of biomass^[6]; while VOCs are released from vegetation, ocean, paints, combustion of fossil fuels, and chemical industry^[1]. Thus, the O₃ cycle starts by the emission of NO_x, CO, and VOCs. The final fate of tropospheric O₃ is to be deposited on the water and soil via both dry and wet deposition. At the same time, some O₃ would be photolyzed by the solar radiation into O₂ and atomic O.

VI- Ozone formation

When it was first established that most O₃ was present in the stratosphere, tropospheric O₃ was believed to originate from the stratosphere. This was based upon the fact that the production of O₃ occurs through the photodissociation of O₂ 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^[1,2]. About 85-90 % of all O₃ is located in the stratosphere. Tropospheric O₃ can be formed through its leakage from the stratosphere as well as photochemicaloxidation processes of CO and VOCs as explained below:

V- Flux of O₃ from the stratosphere to the troposphere

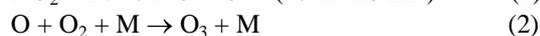
The classical view of the origin of O₃ in the tropospheric environment is that O₃ is transported from the stratosphere^[7]. Levy et al. have reported that an increase in the O₃ mixing ratio with altitude in the troposphere is often interpreted as a result of downward transport from the stratosphere^[8]. However, other researchers show that, the increase of O₃ with altitude can be caused also through its precursors (VOCs and NO_x) and that it is gradually dispersed upward^[9]. About 10 to 15 % of the total atmospheric O₃ is found in the troposphere. In northern hemisphere, the flux of O₃ from the stratosphere to the troposphere has been estimated to fall in the range of (3-8) × 10¹⁰ molecules cm⁻² s⁻¹, while in the southern hemisphere the flux is about half that value^[3,6]. The total

O₃ production in the stratosphere is about 5 × 10¹³ molecules cm⁻² s⁻¹; only about 0.1 % of all O₃ produced in the stratosphere is transported down to the troposphere^[6].

VI- Formation of O₃ by chemical processes

VI- A Role of Nitrogen oxides (NO_x)

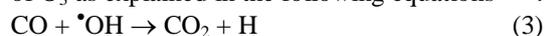
In the tropospheric environment, formation of O₃ via chemical reactions is depending on the concentration of NO_x. NO_x has been suggested to be the controlling parameter; so below the mixing ratio 10-30 pptv, O₃ is photochemically destroyed, while above this concentration, O₃ will be produced^[3]. On the other hand, if NO_x present at high concentration (~ 10 ppbv), NO₂ will react with OH producing HNO₃. Browell et al. have reported that the concentration of O₃ 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_x emission in the northern hemisphere)^[10]. As was mentioned above, NO_x is sum of NO and NO₂. Some NO₂ is emitted directly into the troposphere, while most of it however is formed by the oxidation of NO. Photodissociation of NO₂ (λ ≤ 420 nm) leads to the formation of O₃^[3-5]. The reaction sequence producing O₃ 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 O₃ is NO_x^[11,12]. Thus, increasing anthropogenic emissions of NO_x, hydrocarbons, and CO over the past century have caused appreciable increase of tropospheric O₃ over industrial continents and probably over the globe^[13]. In the early 1970s, Crutzen suggested that tropospheric O₃ originates mainly from production within the troposphere by photochemical oxidation of CO and hydrocarbons catalyzed by NO_x^[4,14].

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^[1,15]. It estimated that about 60-70 percent of the CO emission results from human activities^[1]. CO plays a central role in the formation of tropospheric O₃ via its reaction with •OH in the presence of sufficient concentrations of NO_x; that would lead to the formation of O₃ as explained in the following equations^[3,5]:



Recall equation 1

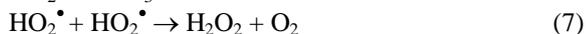
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ ($\lambda \leq 420 \text{ nm}$) (1) Ozone is then formed as a result of combination of O atom with molecular oxygen (O_2) as shown above in equation 2.

The fate of the HO_2^\bullet depends on the ambient concentration of NO. If sufficient NO is present, it converts NO to NO_2 . 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. NO_2 is the only significant source of the atomic O in the troposphere. Then atomic O reacts rapidly with O_2 in the presence of a third body (M, usually O_2 or N_2) in order to produce O_3 . Therefore, reaction (1) is an extremely important because it leads to the formation of tropospheric O_3 (equation 2).

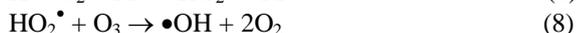
\therefore net reaction:



In contrast, in a NO-poor environment, reaction (5) will not consume all of the HO_2^\bullet , and hence what occurs is either the self-reaction of two radicals or the reaction of HO_2^\bullet with 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 O_3 : Recall equations 3 and 4



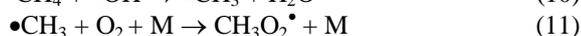
\therefore net reaction:



Because the rate constants at 298 K (all in units $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) have been suggested to be 8.3×10^{-12} for reaction (5), 5.6×10^{-12} for reaction (7), and 2×10^{-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 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 O_3 production, depending on the NO_x level. In the presence of NO_x , oxidation of VOCs (such as methane, CH_4) plays a pivotal role in tropospheric O_3 . Using 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 CH_4 occurs as follows [4,5].

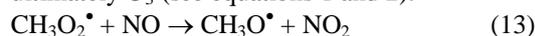


net reaction:



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.

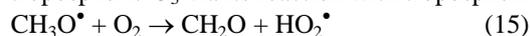
This reaction will lead to the formation of the methoxy radical ($\text{CH}_3\text{O}^\bullet$) and NO_2 (equation 13). Photolysis of the latter (NO_2) leads to the formation of atomic O and then ultimately O_3 (see equations 1 and 2).



net Rn:



Methoxy radical contributes also in the formation of tropospheric O_3 via its reaction with tropospheric O_2 .



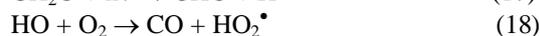
Recall equations 5,1, and 2



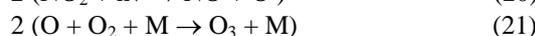
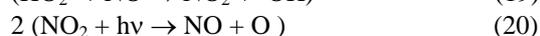
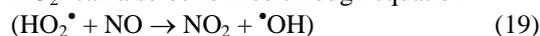
net Rn:



Photolysis of formaldehyde leads to additional production of O_3



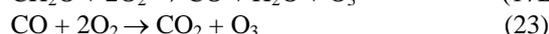
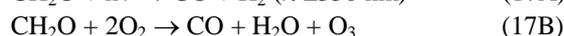
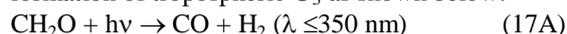
HO_2^\bullet can also be formed through equation 4



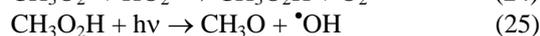
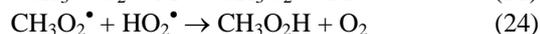
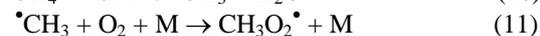
Net Rn:



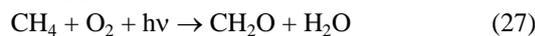
Both photolysis and / or oxidation of CH_2O produce CO. The latter reacts with O_2 , which contributes to the formation of tropospheric O_3 as shown below:



From the above reactions, it is clear that oxidation of VOCs in the presence of NO is important in the production of O_3 in the tropospheric environment. Conversely, if NO is present in a very small concentration, the oxidation of CH_4 in the troposphere occurs as illustrated in the following reactions [14]. Recall equations 10 and 11

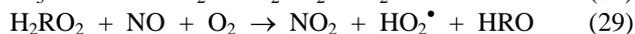
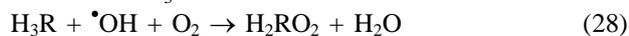


Net Rn:



Thus, reactions 10, 11, 24-26 show clearly that the oxidation of CH_4 in the troposphere (under conditions of low NO concentration) will not produce O_3 . However, photolysis of formaldehyde and / or its reaction with O_2 (equations 17A and 17B) produces CO. Oxidation of CO in the presence of NO produces O_3 as explained above (reactions 3-5,1,2,6, and23). Because the rate constants for reactions 13 and 24 are 7.6×10^{-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

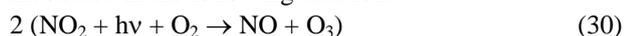
methane is chosen because of its high concentration but the reaction is rather slow and reacts more rapidly with other VOCs. The reaction can be initiated either by the abstraction of H or by $\bullet\text{OH}$ addition. For simplicity, oxidation of all other hydrocarbons (non methane hydrocarbons, H_3R) in the presence of NO can be presented in the following equations, which leads to the formation of O_3 [16].



Recall equation 5



Photolysis of 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 O_2 (reaction 4) to produce $\text{HO}_2\bullet$. The latter reacts with NO and that ultimately produces more O_3 (equations 5,1,2). On the other hand, as was exactly the case for CH_4 , in the absence of NO, the oxidation of the H_3R will not lead to the production of 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 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 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 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 O_3 . Consequently, Cl atoms can be considered as a sink for organics rather than 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 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

O_2 (reaction 11). Then, if sufficient NO is present, this can be considered as another pathway of O_3 production in the troposphere. Therefore, reactions of Cl atoms contribute to the removal of organics; further in the presence of NO_x , it increases the formation of tropospheric O_3 [18,19]. In another work, Tanaka et al. [20] have show that in the presence of NO_x , atomic Cl promotes the formation of 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 O_3 . So, in the presence of NO_x , paraffins react with Cl atoms which contributes to the formation of 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 NO_x this will lead also to O_3 production [20]. It can be concluded that formation of O_3 via the reaction of atomic Cl with organic species is dependent on the type of organics as well as NO_x concentration.

VII- Ozone issues

NO_x / VOCs ratios:

In the case where the NO_x / VOCs ratio is high (meaning a high concentration of NO_2), the $\bullet\text{OH}$ radicals will not oxidize VOCs in order to produce O_3 ; instead, $\bullet\text{OH}$ reacts with NO_2 to produce HNO_3 . However, a small fraction of NO_2 would be photolyzed and that will lead to the production of O_3 . On one hand, this is good because the production of O_3 will decrease in the regions where NO_2 concentration is high. On the other hand, NO_2 is toxic and if present in high concentrations causes health problems [12]. Therefore, decreasing NO_x can lead to an increase of O_3 formation at high NO_x / VOCs ratios.

VOCs / NO_x ratios:

At high VOCs / NO_x ratios, the chemistry of NO_x becomes limited; in fact, formation of O_3 depends on how much NO can be oxidized to 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 NO_x as an air mass moves downwind from an urban centre. Due to the large sources of NO_x (such as automobiles and power plants) in the urban areas, NO_x is oxidized to 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 NO_x is needed [12]. On the other hand, at low VOCs / NO_x ratios, NO_x increases and that will lead to the decrease of O_3 . That is due to the fact that $\bullet\text{OH}$ reacts predominantly with NO_2 . Indeed, in most of the troposphere, except areas of strong sources of NO_x , the availability of NO_x governs O_3 production [1].

VIII- Sinks of tropospheric O_3

The principal sink of O_3 in the tropospheric environment is through photochemical reaction. Photolysis of O_3 via the ultraviolet radiation from sunlight produces O atom in the excited state (O^*).



Then the O^* reacts with water vapour (H_2O) to produce highly reactive hydroxyl ($\bullet OH$) radicals.



However, this reaction depends on the tropospheric concentration of H_2O . Otherwise, O^* is quenched back to O via its reaction with N_2 or O_2 (M), which removes the excess energy^[1,2].



Because the tropospheric mixing ratio of H_2O is $\sim 10^4$ 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^* produced reacts with H_2O to produce $\bullet OH$. In fact, photolysis of O_3 accounts for 75 percent of its tropospheric loss. Due to the fact that photochemical destruction of O_3 occurs only during the daytime, dry deposition however, may compete effectively with its chemical removal^[1].

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_3 can amplify the UV radiation causes skin oxinflammation markers^[21]. 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^[22]. It has been suggested that oral intake of vitamin E is beneficial to protect humans from effects of exposure to ozone^[23]. O_3 can also affect the agricultural crops as illustrated by different researchers^[24-26].

Conclusions

By far most O_3 (85-90 %) is located in the stratosphere, from where a downward transport of O_3 into the troposphere takes place to a small extent. In addition, during the oxidation of CO and VOCs, O_3 can be produced in the presence of NO_x . However, in a NO -poor environments, O_3 will be destroyed. The distribution of NO_x molecules in the troposphere is therefore a key factor in O_3 formation. Atomic Cl also promotes the formation of tropospheric O_3 in the presence of VOCs and NO_x . In fact, in most of the troposphere except areas where the concentration of NO_x is high, the availability of NO_x governs the formation of O_3 . Tropospheric O_3 continues to be a significant concern worldwide; that is due to its effect on the agricultural crops and human health.

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