Tropospheric ozone. 3. Mechanism and factors determining the ozone content in troposphere

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Mechanism and factors determining the ozone content in troposphere, as well as factors participating in the ozone formation and sink are discussed. Photochemical formation of ozone in clear atmospheric conditions, during smogs and lightnings, other photochemical sources of ozone, transport of ozone from stratosphere to troposphere, as well as the ionic cycle are considered.

Introduction

It was considered for a long time that ozone enters the atmosphere mostly from superstrata, i.e., from troposphere, where it is generated under action of the solar UV radiation.[1] However, it has been discovered in the 60s that a significant part of ozone can be formed during photochemical processes directly from precursor gases,[2] as well as there are other mechanisms of ozone formation[3] in troposphere: lightnings,[4,5] ion cycle,[6,7] charged cosmic particles,[8] and so on. This paper is devoted to consideration of these mechanisms and factors.

1. The estimation of tropospheric ozone budget

The estimation of factors involved in processes of ozone formation and sink are presented in Table 1.

As is seen, in Southern and Northern hemispheres almost double difference between individual components can be reached. However, if the difference in ozone sink onto the Earth surface can be explained by different land and sea areas, then it is not clear why the ozone transfer from stratosphere to troposphere in both hemispheres differs so strongly. The comparison of each component in any hemisphere shows that photochemical formation and desruction are of more importance than other factors. Of interest is the difference between estimates of the same components made by different authors.

Later the authors of the listed works tried to improve the first estimates with the use of global and regional models of different complexity. Some results are listed in Table 2.

However, even more sophisticated model methods (Table 2) did not smooth the above difference, although Table 2 contains only a part of available estimates. For example, in Ref. 28 the difference in photochemical generation estimates varies from 2300 to 5300 Tg/year. The same varitaions are seen between other components.

Among other sources of tropospheric ozone lightnings are the most significant. This source is rather variable and its contribution differs significantly depending on the region. So, estimates of contribution of different components to the ozone total balance in the open troposphere in the Mediterranean show that if the ozone total content in the tropospheric air column is 50 DU, then 30% of this magnitude is of stratospheric origin, 13% is formed by lightnings, and 29% have a photochemical origine.[29] Even greater value (37%) was received for Southern Atlantic.[30]

Table 1. The estimations of source and sink power of ozone in troposphere (10^{12} g/year) and its budget (10^{12} g)

Factor	Northern hemisphere	Southern hemisphere	Globe	References
Inflow from stratosphere	420	230	650	9
	430	220	650	10
Photochemical formation	770–2050	320–450	990–2500	11
	330–1240	180–690	310–1930	12
Photochemical sink	1330	1110	2440	12
Sink onto the Earth surface	940–1300	360–760	1300–2100	13
	650	430	1080	14
Budget	94	47	141	15
	158	83	241	16

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Table 2. The estimation of ozone balance (10^{12} g/year) and budget (10^{12} g) by models

Model	Transport from stratosphere	Photochemical components		Deposition onto the surface	Budget	Reference
		formation	destruction			
UTO	846	–	–	1178	370	17
GEOS-CHEM	470	4900	4300	1070	315	18
MATCH	480	3940	3120	1300	–	19
UCI	473	4230	3885	812	288	20
HGISS	400	4100	3680	820	310	21
MATCH-MPIC	540	4560	4290	820	294	22, 23
ECHAM4	590	4375	4300	668	294	24, 25
MCGAT	565	3314	3174	705	216	26
ECHAMS/MESSy1	–	4854	4467	780	319	27

2. Photochemical formation of ozone in troposphere

Photochemistry studies physical and chemical changes of molecules interacting with light.[31] According to the Grotthuss–Draper law, molecular chemical changes are caused only by the light absorbed by a molecule. Chemical changes in molecule occur when it reaches an excited state with the energy sufficient for breaking bonds. The dissociation energy of bonds varies from 1 eV in ozone to 11 eV in carbon dioxide. The corresponding radiation wavelengths are 1.24–0.001 μm and lower. The radiation of microwave (1–10 cm) and IR (1–10 μm) ranges, absorbed by molecule, causes its rotational or vibrational excitation, which is not efficient enough to cause a chemical change.

The second law of photochemistry was formulated by Stark and Einstein.[32] Each molecule participating in a photochemical reaction changes its state when absorbing a single light quantum (the primary photolysis act proceeds under action of one quantum). Further, secondary reactions or even chain processes can proceed,[33] involving in reaction any number of molecules. This number is defined by the character of secondary processes and by the reaction conditions. For example, average number of dissociated molecules of ozone attributed to a single absorbed quantum varies from zero to several tens.[34]

The lifetime of an exited molecule (after the absorption of a light quantum) is usually about 10^{-8} sec. Under standard illumination density, they react or deactivate before absorbing the second quantum, even if the process section is large.[34]

Evidently, all these laws hold for ozone. The theory of ozone photochemical formation was created virtually from two parallel branches: the study of processes of the stratospheric ozone formation and analysis of mechanism of the “dry” smog formation.

Photochemical theory of stratospheric ozone formation has passed several stages in its development. First, S. Chapman has proposed a theory of ozone formation in reactions with participation of particles containing only oxygen[35]:

$$O_2 + h\nu \rightarrow O + O,\ 150 \le \lambda \le 300\ \text{nm},$$

$$O + O_2 + M \rightarrow O_3 + M,$$

$$O_3 + h\nu \rightarrow O_2(^1\Delta g) + O(^1D),\ 180 \le \lambda \le 300\ \text{nm},$$

$$O_3 + O \rightarrow 2O_2.$$

Further, the reactions of vibrational and electron-exited states of the particles were added to this process[36]:

$$\begin{aligned}
O_3 + O(^1D) &\rightarrow 2O + O_2,\\
&\rightarrow 2O_2(^1\Delta g),\\
O_3 + O_2(^1\Delta g) &\rightarrow O + 2O_2,\\
O_2(^1\Delta g) + M &\rightarrow O_2 + M,\\
O_2(^1\Delta g) &\rightarrow O_2 + h\nu,\\
O(^1D) + M &\rightarrow O + M,\\
O + O + M &\rightarrow O_2 + M,\\
&\rightarrow O_2 + (^1\Delta g) + M,\\
O_2(^1\Delta g) + O &\rightarrow O_2 + O,\\
2O_2(^1\Delta g) &\rightarrow 2O_2.
\end{aligned}$$

The Chapman reaction for a long time was sufficient for theoretical analysis of oxygen photochemistry and explanation of a few known facts. The appearance of new experimental data has shown the reaction to be insufficient.

For example, calculations of global O_3 formation, taking into account only oxygenous reactions, yield a great excess of ozone.[37] It turned out that in reaction of ozone with atomic oxygen only 20% of the formed O_3 is destructed; and the O_3 transfer through the tropopause makes up only 1%. Consequently, there should be additional reactions causing O_3 destruction.

According to Ref. 38, two types of redox transformations are important cycles for ozonosphere:

$$\begin{array}{c} X + O_3 \rightarrow XO + O_2 \\ \underline{XO + O \rightarrow X + O_2} \\ O_3 + O \rightarrow 2O_2 \end{array} \qquad \begin{array}{c} X + O_3 \rightarrow XO + O_2 \\ \underline{XO + O_3 \rightarrow X + 2O_2} \\ O_3 + O \rightarrow 3O_3. \end{array}$$

In this case, the original substance X (catalyst) should be of photochemical origin stipulated by its source, i.e., solar radiation. The photons of solar radiation can take part in catalytic cycle of the following type

$$\begin{array}{c} X + O_3 \rightarrow XO + O_2 \\ XO + O_3 \rightarrow XO_2 + O_2 \\ \underline{XO_2 + h\nu \rightarrow X + O_2} \\ 2O_3 + h\nu \rightarrow 3O_2. \end{array}$$

At the next stage in the development of photochemical theory of ozone formation the hydrogen (hydroxyl) cycle was added to the general scheme. This cycle was discovered in 1950, when V.I. Krasovskii and J. Meinel revealed that OH is a source of the intense infrared radiation of night sky.[39] In the same year D.R. Bates and M. Nicolet revealed an important role of H and OH as catalysts of chemical reactions.[40] According to Ref. 41, H_2O photolysis can be a source of H and OH in the atmosphere:

$$H_2O + h\nu \rightarrow H + OH, \ \lambda < 242 \text{ nm}.$$

As it was noted in Ref. 42, such particles can be the result of $O(^1D)$ reactions with methane, water, and hydrogen.

J. Hampson and B.G. Hant[43–45] added to the analysis the following hydroxyle cycles, separated by Bates and Nicolet:

$$\begin{array}{c} H + O_3 \rightarrow OH + O_2 \\ \underline{OH + O \rightarrow H + O_2} \\ O + O_3 \rightarrow 2O_2 \end{array}$$

$$\begin{array}{c} OH + O_3 \rightarrow HO_2 + O_2 \\ \underline{HO_2 + O \rightarrow OH + O_2} \\ O + O_3 \rightarrow 2O_2 \end{array}$$

$$\begin{array}{c} HO_2 + O_3 \rightarrow OH + 2O_2 \\ \underline{OH + O_3 \rightarrow HO_2 + O_2} \\ O_3 + O_3 \rightarrow 3O_3, \end{array}$$

which made the theoretically derived models of ozone distribution in the atmosphere significantly closer to the experimental ones, however, with numerous discrepancies between them.

Further development of photochemical ozone formation theory was stimulated by introduction of nitrogen cycles.

Having analyzed the above discrepancies, V.N. Konashonok[46] comes to a conclusion that there is an additional ozone loss in the layer below 50 km, caused by the presence of small impurities containing NO, NO_2, and their reactions. Then P. Krutzen have made an assumption that ozone balance in the atmosphere greatly depends on NO_x formed from oxidation of N_2O, which is released from the underlying surface.[47] H. Johnston has attracted attention to a potential danger of the ozonosphere partial destruction by the supersonic aviation, polluting air with nitrogen oxides. Therefore, the nitrogen cycle was introduced:

$$\begin{array}{c} NO + O_3 \rightarrow NO_2 + O_2 \\ \underline{NO_2 + O \rightarrow NO + O_2} \\ O + O_3 \rightarrow 2O_2. \end{array}$$

In 1968, studies of stationary and non-stationary ozone concentration in the atmosphere, containing NO and NO_2, allowed adding the NO_2 photolysis[48] to Chapmen's classical reactions. According to his calculations, the decrease of ozone density at an altitude of 20 km under stationary conditions made 50% as compared to classical equilibrium one.[49]

The second branch of ozone photochemical generation has been developed due to the necessity to define the cause of "dry" smog formation. This special type of atmospheric pollution was first registered in 1944 in Los-Angeles and was called photochemical smog.[50] Unlike the well known London smog, i.e., the dense fog with the impurities of soot and sulfur oxides, the photochemical smog appears due to the influence of sun light (usually under conditions of stable stratification of the atmosphere with low relative humidity). Further investigation justified and made more precise that conception and made it possible to form general idea of smog genesis.[50–51]

It turned out that formation of the photochemical smog starts under impact of solar radiation on nitrogen oxides in the presence of hydrocarbons.[52] The hydroxyl, resulted from these photochemical interactions, oxidizes hydrocarbons.[53] These reactions yield ozone, formaldehyde, peroxyacetylnitrates, and so on. Thus, the same substances as in stratosphere participate in smog formation, except for hydrocarbons.

Both of these branches united, when Demerdjian first formulated the mechanisms of hydrocarbon oxidation in the presence of NO_x with ozone formation in polluted air[54]; and it was found that relatively high stationary concentrations of HO and HO_2 are observed in troposphere under the sun light.[55]

Tropospheric chemistry began its rapid development, when it was discovered that many results obtained for stratosphere can be applied to troposphere.

When discussing the data obtained in background conditions, the mechanisms working at smog conditions are often used.[56] However, it was shown[57] that the ozone formation under clear and background conditions differ drastically.

2.1. Photochemical generation of ozone in clear conditions

Heterogeneous tropospheric chemistry, including ozone, is widely discussed in recent years.[57–59] Krutzen and Zimmerman stated[60] that tropospheric ozone makes up 10% of total content and its concentration at the ground layer varies from 15 to 30 ppb, however, playing a key role in tropospheric chemistry, since the photolysis of this small amount gives a rise to a chain of reactions, sometimes leading to smog formation[55]:

$$O_3 + h\nu \rightarrow O^1D + O_2,\ \lambda \le 320\ \text{nm}. \qquad (1)$$

Here, the wavelength of solar radiation is of importance, because at a longer wavelength the ozone decomposition leads to[61]

$$O_3 + h\nu \rightarrow O^3P + O_2,\ 320 < \lambda < 400\ \text{nm}. \qquad (2)$$

Interacting with an oxygen molecule the occurred oxygen atom leads to ozone retrieval:

$$O^3P + O_2 + M \rightarrow O_3 + M,\ M = N_2,\ O_2. \qquad (3)$$

About 90% of O^1D, formed through the reaction (1), goes to a lower state due to the interaction with air molecules[62]:

$$O^1D + M \rightarrow O^3P + M, \qquad (4)$$

then ozone is retrieved through the reaction (3).

Under standard conditions the remained 10% of O^1D react with water vapor, yielding the hydroxyl[55]:

$$O^1D + H_2O \rightarrow 2OH. \qquad (5)$$

Note that the reaction (5) is ten-fold faster than cycles (4) and (3).

Besides, O^1D can react with nitrous oxide, which is present in air, yielding rather reactive nitrogen oxide[3]:

$$N_2O + O^1D \rightarrow 2NO \qquad (6)$$

or with methane and hydrogen, yielding hydroxyl

$$N_2O + O^1D \rightarrow CH_3 + OH, \qquad (7)$$

$$H_2 + O^1D \rightarrow H + OH, \qquad (8)$$

as well as with such stable molecules[34] as CO_2:

$$O^1D + CO_2 \rightarrow CO_3, \qquad (9)$$

$$CO_3 + M \rightarrow CO_2 + O^3P + M, \qquad (10)$$

$$O_2 + O^3P + M \rightarrow O_3$$

with further formation of ozone molecule.

Further behavior of air system depends on the concentration of trace gases. In the absence of CO and hydrocarbons, a photochemical balance between nytrogen oxides and ozone[69] is established in troposphere:

$$NO + O_3 \rightarrow NO_2 + O_2, \qquad (11)$$

$$NO_2 + h\nu \rightarrow NO + O^1P, \qquad (12)$$

$$O + O_2 + M \rightarrow O_3 + M. \qquad (13)$$

If CO or other hydrocarbons are present in the atmosphere, then this balance becomes broken and OH becomes the principal reactant, generated through the reaction (5).

The hydroxyl concentration on the average is equal to $7.7 \cdot 10^5$ molec/cm^3 [Ref. 64]. It increases up to $2–8 \cdot 10^6$ molec/cm^3 due to photochemical processes, leading to their self-maintainance or even strengthening.[60] Apparently, the OH is one of the strongest oxidizers in the atmosphere. Not without reason it is called the tropospheric cleaner.[65] Hydroxyl reacts with CO, CH_4, and hydrocarbons of different origin.

Depending on the nitrogen oxide concentration in the atmosphere, further transformation of substances (CO, in particular) can go in two ways[63]:

$$\begin{array}{c}
\text{I.}\quad CO + OH \rightarrow H + CO_2 \\
H + O_2 + M \rightarrow HO_2 + M \\
H_2O + NO \rightarrow OH + NO_2 \\
NO_2 + h\nu + NO + O \quad \lambda \le 400\ \text{nm} \\
O + O_2 + M \rightarrow O_3 + M \\
\hline
CO + 2CO_2 \rightarrow CO_2 + O_3
\end{array} \qquad (14)$$

$$\begin{array}{c}
\text{II.}\quad CO + OH \rightarrow H + CO_2 \\
H + O_2 + M \rightarrow HO_2 + M \\
HO_2 + O_3 \rightarrow OH + 2O_2 \\
\hline
CO + O_3 \rightarrow CO_2 + O_2.
\end{array} \qquad (15)$$

According to the first cycle, ozone concentration at $NO \ge 4 \cdot 10^{-12}$ (4 ppt) increases from 20 to 100 ppb. The transition to the second cycle occurs at $NO < 2 \cdot 10^{-14}$.

The occurrence of additional ozone by the first cycle converts NO into other nitrogen oxides[63]:

day

$$NO + O_3 \rightarrow NO_2 \qquad (16)$$

$$NO_2 + OH + M \rightarrow HNO_3 + M,$$

night

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (17)$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M.$$

A part of reactions can proceed only in the presence of HO_2 yielding H_2O_2, which can be formed by the following cycle[63]:

$$\begin{array}{c}
CO + OH \rightarrow H + CO_2 \\
H + O_2 + M \rightarrow HO_2 + M \\
HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \\
H_2O_2 + h\nu \rightarrow 2OH,\ \lambda \le 350\ \text{nm} \\
\hline
2CO + O_2 \rightarrow 2CO_2.
\end{array} \qquad (18)$$

Further, H_2O_2 takes part in the catalytic reaction

$$\begin{array}{c}
HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \\
H_2O_2 + OH \rightarrow HO_2 + H_2O \\
\hline
OH + HO_2 \rightarrow H_2O + O_2.
\end{array} \qquad (19)$$

If only non-organic gases were in the atmosphere, then in photochemical cycles the approximate balance $NO \approx O_3$ would hold. However, the balance is impossible due to the presence of hydrocarbons of natural and anthropogenic origin. One of the most controlled mechanisms is methane oxidation. This mechanism can also ramify[33]:

$$\begin{array}{c}
\text{I.}\quad NO \sim 1\ \text{ppb} \\
CH_4 + OH \rightarrow CH_3 + H \\
CH_3 + O_2 + M \rightarrow CH_3 \\
CH_3O_2 + NO \rightarrow CH_3O + NO_2 \\
CH_3O + O_2 \rightarrow CH_2O + HO_2 \\
HO_2 + NO \rightarrow OH + NO_2 \\
NO_2 + h\nu \rightarrow NO + O,\ \lambda < 400\ \text{nm} \\
O + O_2 + M \rightarrow O_3 + M \\
\hline
CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3
\end{array} \tag{20}$$

$$\begin{array}{c}
\text{II.}\quad NO < 4\cdot 10^{-12}\ (4\ \text{ppt}) \\
CH_4 + OH \rightarrow CH_3 + H_2O \\
CH_3 + O_2 + M \rightarrow CH_3O_2 + M \\
CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \\
CH_3O_2H + h\nu \rightarrow CH_3O + OH,\ \lambda < 330\ \text{nm} \\
CH_3O + O_2 \rightarrow CH_2O + HO_2 \\
\hline
CH_4 + O_2 \rightarrow CH_2O + H_2O
\end{array} \tag{21}$$

$$\begin{array}{c}
\text{III.}\quad NO < 10^{-14} \\
CH_4 + OH \rightarrow CH_3 + H_2O \\
CH_3 + O_2 + M \rightarrow CH_3O_2 + M \\
CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \\
CH_3O_2H + OH \rightarrow CH_2O + H_2O + OH \\
\hline
CH_4 + OH + HO_2 \rightarrow CH_2O + 2H_2O.
\end{array} \tag{22}$$

An important fact for the first mechanism is a formation of two O_3 molecules simultaneously with OH, HO_2, NO, and O_2 molecules, acting as catalysts in further cycles. Five O^1D atoms are formed for one OH radical.[57]

Provided the NO content in the atmosphere is low, the methane reaction proceeds by II type with formation of such toxic component as formaldehyde.

Finally, if NO concentration is very low, then the alternative mechanism is realized. According to this mechanism, OH and HO_2 are spent, that causes complete termination of photochemical reactions.

However, under the influence of ultraviolet radiation the ozone sink by the third mechanism can be broken because of formaldehyde oxidation with formation of 0.8 HO_2 per 1 CH_2O. This process can also ramify:

$$\begin{array}{c}
\text{I.}\quad CH_2O + h\nu \rightarrow H + CHO,\ \lambda \le 350\ \text{nm} \\
H + O_2 + M \rightarrow HO_2 + M \\
CHO + O_2 \rightarrow CO + 2HO_2 \\
\hline
CH_2O + 2O_2 \rightarrow CO + 2HO_2
\end{array} \tag{23}$$

$$\begin{array}{c}
\text{II.}\quad CH_2O + OH \rightarrow CHO + H_2O \\
CHO + O_2 \rightarrow CO + HO_2 \\
\hline
CH_2O + OH + O_2 \rightarrow CO + H_2O + HO_2
\end{array} \tag{24}$$

$$\text{III.}\ CH_2O + h\nu \rightarrow CO + H_2,\ \lambda \le 350\ \text{nm}. \tag{25}$$

Hydroxyl can react with more complex carbohydrates. This reaction will be discussed in the following sections. Here we present the scheme of ethane oxidation, as an example[65]:

$$\begin{array}{c}
C_2H_6 + OH \rightarrow C_2H_5 + H_2O \\
C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M \\
C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2 \\
C_2H_5O + O \rightarrow CH_3CHO + HO_2 \\
CH_3CHO + h\nu \rightarrow CH_3 + CHO
\end{array} \tag{26}$$

and further the process follows one of the schemes of the ethane oxidation.

The reaction constants are given in Refs. 66–70.

Now we present the results from Ref. 71 to demonstrate the complexity of the tropospheric ozone problem. The author presents the reactions of ozone generation from classical precursors, which can not be realized in troposphere.[72–74] It is stated that ozone formation in real atmosphere proceeds through the following reactions:

$$RH + 3O_2 + h\nu \rightarrow \text{products} + 2O_3, \tag{27}$$

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3, \tag{28}$$

$$CH_4 + 2O_2 + h\nu \rightarrow H_2CO + O_3, \tag{29}$$

$$H_2CO + 2O_2 + h\nu \rightarrow H_2O + CO + O_3. \tag{30}$$

Only reaction (30) from the above list can be taken into consideration, because formaldehyde photolysis is positively affected here by the solar radiation with a necessary wavelength. Reactions (27)–(29) can be actualized only in the upper atmosphere.

Finally, we should underline that the ozone generation processes are non-linear, even though some components behave in time inphasely or are in antiphase.[72–74]

2.2. Generation of ozone in photochemical smogs

The study of ozone formation has always been of great importance, because the influence of high ozone concentrations on the living and non-living objects has a profound negative effect.[75–95] Numerous investigations allowed the building of a general scheme of smog generation followed by the fast increase of the ozone concentration.

The formation of photochemical smog starts with the influence of solar radiation on nitrogen oxides in the presence of hydrocarbons.[96] In a series of chemical cycles these primary components transform into different secondary impurities (especially into such oxidants as ozone, oxygen, nitrogen dioxide, and peroxyacetylnitrates).

As it was shown above, ozone is generated in the atmosphere by the following basic cycle:

$$\begin{gathered} NO_2 + h\nu \rightarrow NO + O \\ O + O_2 \rightarrow O_3 \\ O_3 + NO \rightarrow NO_2 + O_3. \end{gathered} \qquad (31)$$

However, the transformations of only NO_2 can not provide for high ozone concentrations observed in photochemical smogs, because O_3 and NO_2 constantly decompose and reduce without any significant change in their mean concentrations. Consequently, some process is necessary, which breaks the cycle, i.e., nitrogen oxide is transformed into dioxide without the change in the ozone amount.

This process exists due to the presence of hydrocarbon compounds in automobile and industrial emissions. The interaction between organic compounds and hydroxyl radicals leads to the consecutive reactions[97]:

$$\begin{gathered} RH + OH \rightarrow R + H_2O \\ R + O_2 + M \rightarrow RO_2 + M \\ RO_2 + NO \rightarrow RO + NO_2 \\ RO + O_2 \rightarrow HO_2 + RCHO \\ HO_2 + NO \rightarrow OH + NO_2 \\ 2(NO_2 + h\nu \rightarrow NO + O) \\ 2(O + O_2 + M \rightarrow O_3 + M) \\ \text{Total: } RH + 4O_2 2h\nu \rightarrow RCHO + 2H_2O + 2O_3. \end{gathered} \qquad (32)$$

In order to continue the *chain,* the active center OH should constantly return to the beginning of the cycle (32), because the hydroxyl concentration in the atmosphere is low (see the previous section). This can be realized through photolysis of the formed aldehydes (usually, formaldehyde) or by the scheme[98–101]:

$$\begin{gathered} CH_2O + h\nu \rightarrow HCHO \\ H + O_2 + M \rightarrow HO_2 + M \\ CHO + O_2 \rightarrow CO + 2HO_2 \\ \text{Total: } CH_2O + 2O_2 \rightarrow CO + 3HO_2. \end{gathered} \qquad (33)$$

And then the formed HO_2 rapidly reacts with nitrogen oxide

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (34)$$

or follows the above scheme of CO oxidation.

Studying the process of photochemical smog formation, V.A. Isidorov pointed to several ways of its possible development.[102] At a relatively high content of aromatic hydrocarbons in air the ozone concentration and the rate of ozone accumulation decrease to some extent because of low outcome of peroxide radicals and elimination of a part of nitrogen oxides in the form of nitrophens. The same result takes place at formation of alkylnitrates and nitrites, peroxyacetylnitrates and inorganic nitrogen compounds, such as water-soluble N_2O_5 and HNO_3. Consequently, the ozone accumulation depends on the relation between initial concentrations of organic compounds, i.e., precursors of peroxide radicals and nitrogen oxides:

$$D[O_3]/dt = k[NO_x + RO_2]/[NO][RO_2]. \qquad (35)$$

At a low ratio the speed of NO conversion into NO_2 is also low and nitrogen oxide becomes involved in the process of ozone destruction [the last reaction in the system (31)]. Ozone is not accumulated also at very high ratio due to nitrogen dioxide binding with organic radicals:

$$RO + NO_2 \rightarrow PAN \qquad (36)$$

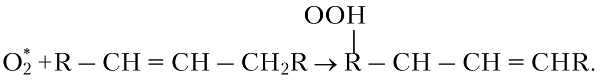
or due to reaction of the formed O_3 with hydrocarbons:

$$O_3 + RH \rightarrow \text{products}.$$

Apart from this basic mechanism, one more mechanism has been considered,[103] which suggests that free radicals, formed in the reaction of the atomic oxygen with hydrocarbons, can be bound with molecular oxygen, yielding the organic peroxyl radicals RO_2, which then react, yielding ozone

$$RO_2 + O_2 \rightarrow RO + O_3. \qquad (37)$$

This could explain the effect of the increase of ozone equilibrium concentrations in the presence of hydrocarbons. The reaction of molecular oxygen in singlet state with olefines, yielding the hydroperoxides, is also possible:



$$O_2^* + R-CH=CH-CH_2R \rightarrow \overset{\displaystyle OOH}{\overset{|}{R}}-CH-CH=CHR. \qquad (38)$$

This reaction is followed by hydroperoxide decay and generation of radicals of RCO type. After that the following reactions can proceed[103]:

$$\begin{gathered} RCO + O_2 \rightarrow RCO_3 \\ RCO_3 + NO \rightarrow RCO_2 + NO_2 \\ RCO_3 + O_2 \rightarrow RCO_2 + O_3. \end{gathered} \qquad (39)$$

To the present, smog situations are studied rather thoroughly in natural and model experiments, conducted in smog chambers. Let us consider some of them.

So, it was informed in Ref. 104 on generation of 10 ozone molecules from each emitted NO_x molecule in the period of smog formation (Tenessee, USA).

Of interest are results of comparison of compositions of organic compounds in air and in industrial emissions[105] (Table 3).

As is seen, the initial, intermediate, and final transformation products are present in atmospheric air simultaneously. Only 7 organic compounds were under monitoring; and 6 of them were in the emissions, while only one in products of transformation.[105] Consequently, it is impossible to improve the situation with photochemical smog without monitoring reactive organic gases and decreasing NO emissions.[106]

Table 3. The composition of organic compounds in emissions of industrial plants and in atmospheric air[105]

Compound	Emissions into atmospheric air		Identified in atmospheric air in the city		
	Mass, ton	Number of substances	Total	Coinciding with emissions	The absence of coinciding
Hydrocarbons	298.7	32	55	28	27
Including:					
saturated	–	–	29	–	–
unsaturated	–	–	16	–	–
cyclic	–	–	10	–	–
aromatic	535.7	13	31	9	22
clorinated	2.3	1	3	–	3
spirits	21.1	2	4	1	3
Ethers	6.9	3	–	–	–
organic oxides	0.4	1	–	–	–
aldeghydes	–	–	11	–	–
Ketones	66.5	2	4	2	2
Esters	29.1	3	4	3	1
nitrocompounds	53.3	1	2	–	2
volatile oils, terpenes	–	–	3	–	3
Total	1014	58	117	43	74

Table 4. Concentration of olefines (ppb) in clear (*) and polluted cities

Compound	Ayantepau*	Budja*	Amsterdam*	Pariagun	Kantaura	USA (39 cities)
Ethane	1.06	1.31	0.40	37.7	57.4	21.4
Ethylene	0.60	1.52	0.54	1.08	3.53	–
Acetylene	0.13	–	–	–	–	–
Propane	0.10	0.32	0.15	19.30	27.30	7.7
Propylene	0.38	0.63	0.31	0.43	0.85	
Isobutane	0.03	0.09	0.02	4.27	6.21	2.95
n-butane	0.04	0.02	0.05	5.59	8.61	2.95
Isopentane	0.11	0.10	–	2.05	3.10	1.70
n-Pentane	0.06	0.11	0.07	1.53	2.16	3.60
Hexane	0.04	–	–	0.43	0.30	0.50
Isoprene	1.60	–	–	0.59	3.20	–
References	107	107	108	107	107	109

The data on the concentration ozone cycle components in smog and standard situations are presented in Table 4.

Note that processes of smog formation can proceed not only in the atmosphere but also in the polluted room air.[110]

2.3. Other photochemical sources of ozone

As it is known, a certain amount of sulfur dioxide is present in troposphere (even in the background one). The following mechanism of ozone generation in the process of photochemical oxidation of this gas[111] is possible:

$$SO_2 + h\nu + O_2 \rightarrow SO_2^{+},\ \lambda < 390\ \text{nm}, \qquad (40)$$

$$SO_2^{+} + O_2 \rightarrow SO_3 + O_3. \qquad (41)$$

A similar mechanism is described in Ref. 112. It starts with transition of SO_2 molecules into active state through the reaction

$$SO_2 + h\nu \rightarrow SO_2\,(^3B_1),\ 340 < \lambda < 400\ \text{nm}, \quad (42)$$

and then reacts with O_2SO_4

$$SO_2(^3B_1) + O_2SO_4 \rightarrow SO_3 + O_3, \qquad (43)$$

or

$$SO_2(^3B_1) + O_2 \rightarrow SO_3 + O(^3P) \qquad (44)$$

with following formation of ozone

$$O(^3P) + O_2 + M \rightarrow O_3 + M.$$

Apparently, the mechanisms of sulfur dioxide oxidation are not efficient for troposphere, because we failed to find in literature any estimates of their significance.

A great number of researchers studied the role of halogens in ozone destruction in stratosphere in connection with formation of ozone holes. It was found in a series of works that under conditions close to tropospheric ones, ozone can be formed in reactions with bromine compounds[113]

$$HO_2 + BrO \rightarrow HBr + O_3,$$

which can proceed at the room temperature.

The authors of Ref. 114 investigated the oxidation of ethylene and acetylene in the presence of bromine oxides. It turned out that after a series of chain reactions, OH and O_3 are also formed along with organic products. The measurements conducted in Alerto have shown that the behavior of C_2H_2, C_2H_4, and O_3 is synchronous. This can indicate the importance of such mechanisms for tropospheric pollution.

3. Ozone formation at lightnings

The connection between ozone and thunderstorms was noticed in the past century. According to the recent conceptions,[39] the ozone formation in troposphere can occur under the influence of electric discharges of two types: silent (corona) and thunderstorm (lightning). Lightning discharge produces a wide spectrum of electromagnetic radiation, including ultraviolet. At $\lambda \le 250$ nm the latter can generate excited molecules of oxygen in $O_2(^3\sum{}^+u)$, state, which are then involved in the reaction:

$$O_2(^3S^+i) + O_2 \rightarrow O_3 + O + 41.9\ \text{kJ} \cdot \text{mol}^{-1},$$

$$O + O_2 + M \rightarrow O_3 + M.$$

The initial estimates of ozone amount produced by that scheme were done in Refs. 115 and 116, where the presented high values were comparable with those for the ozone content in the atmosphere.

However, it was later shown that the main source of ozone is just the silent discharge, because the ozone concentration rises long before the beginning of a thunderstorm.[117] The increase in the magnetic field intensity in thunderstorm situations leads to producing of silent discharges in tops of trees, bushes, and even grass. The discharge initial intensity is 8–9 V/cm. Three hours before thunderstorm about $3–10^5$ μg/sec is generated in a volume of 1 liter in the ground layer, i.e., 0.03 μg/m^3. Taking into account a high possibility of ozone loss in the ground layer, this process can be considered as locally significant and not important for the total balance of tropospheric ozone. The scheme of its formation can be the following.

Electrons with the energy higher than 5.09 eV can dissociate oxygen molecules both in silent and lightning discharges

$$1/2O + e \rightarrow e + O.$$

The energy, spent for this process, is equal to 109.5 kJ · mol^{-1}, Then ozone is formed through its typical reactions. If the energy of an electron is lower (3–5 eV), then the dissociative adherence can take place

$$e + O_2 \rightarrow O + O^- - 347.8\ \text{kJ} \cdot \text{mol}^{-1}.$$

Then either the classical reaction or the reaction of the type follow

$$O^- + O_2^- \rightarrow O_3 + e - 41.9\ \text{kJ} \cdot \text{mol}^{-1}.$$

The following processes can proceed in parallel:

$$O^- + O_2 + O_2^- > O_3 + O_2 + 54.5\ \text{kJ} \cdot \text{mol}^{-1}$$

$$e + O_2 + O_2^- \rightarrow O^- + O_3 - 251.4\ \text{kJ} \cdot \text{mol}^{-1}.$$

Ions and electrons of atomic oxygen can break ozone through the reactions

$$O^- + O_3 \rightarrow O_2 + O_2^- + 347.8\ \text{kJ} \cdot \text{mol}^{-1},$$

$$e + O_3 \rightarrow O_2 + O + 41.9\ \text{kJ} \cdot \text{mol}^{-1}.$$

On the whole, as it was found out later, these processes have only a local significance,[118] therefore they are ignored in calculations of the total ozone balance in the atmosphere (Table 5, borrowed from Ref. 119).

It is seen that ozone inflow from stratosphere is equal to 15–25%.

Table 5. The balance of ozone generation and sink in troposphere (10 mol · cm^{-2} · sec^{-1})

Process	Northern hemisphere		Southern hemisphere	
	generation	sink	generation	sink
Transfer from stratosphere	6.5	–	4.5	–
Photolysis	–	–10	–	7
Photochemical formation	29	–	15.5	–
CO	15.5	6.2	–	–
CH_4	5.5	5.3	–	–
Hydrocarbons	8	4	–	–
Photochemical sink	–	–12	–	8
Sink onto the surface	–	–13.5	–	5
Total	35.5	–35.5	20	10

Thus, data of Table 5 prove that basic amount of tropospheric ozone is resulted from photochemical processes; and the initial impurities indicated for the northern hemisphere are simultaneously the source and the sink of ozone. The second significant source of the ozone formation is its transfer from stratosphere.

4. The ozone transfer from stratosphere to troposphere

Stratosphere is one of the main perpetually acting sources of tropospheric ozone. The knowledge of ozone characteristics is important both for estimation of O_3 content balance in troposphere and from the practical point of view. For example, to develop the high-altitude aviation, it is necessary to know mechanisms of O_3 transfer and chemical interaction with aircraft emissions.[120]

The inflow of ^{210}Pb, ^{7}Be natural radionuclides formed in stratosphere[121–126] proves the fact that ozone is transferred from stratosphere into troposphere sinking onto the underlying surface. More accurate methods based on isotope analysis of the components, which directly take part in ozone cycles, are used at present.[127–131]

As is known,[132] most ozone amount is formed in the upper tropical stratosphere. The main areas of ozone formation are located between 10°S and 35°N in summer and between 38°S and 12°N in winter. Further distribution in the atmosphere of the formed ozone can be considered based on three different mechanisms: molecular diffusion, stipulated by a high concentration gradient; transfer by meridian and vertical downstream ordered air motions in the Bruer–Dobson circulation system; and forcing through tropopause with formation of its folds in jet flow zone.[133]

The idea of ozone turbulent transfer from stratosphere into troposphere was formulated long ago.[134] However, later investigations have shown that this mechanism unlikely is significant in stable conditions of upper troposphere – lower stratosphere. Open atmosphere in this layer is laminar and the turbulent zones are of small horizontal (hundreds of kilometers) and vertical (hundreds of meters) dimensions, appearing in regions with significant wind shifts.[135,136] However, significant turbulence and transfer coefficients were obtained by numerical modeling for some situations.[137,138] However, they were not justified experimentally. Therefore, in case of ozone vertical difference the molecular diffusion in the direction of this difference gradient should be observed.

The ozone, soaked through tropopause, should then be captured downwards by a very strong turbulence in the atmospheric boundary layer.[133] In this case, the ozone distribution in the atmosphere in the absence of advection can be described by the following equation:

$$\frac{\partial O_3}{\partial t} = \frac{\partial}{\partial z}\left(K\frac{\partial O_3}{\partial z}\right) - Q,$$

where O_3 is the ozone concentration; K is the molecular diffusion coefficient; Q is the sink power, g/(g·sec).

The development of the Bruer–Dobson circulation theory has passed several stages.[26] First, they noticed the ozone flow from the equator to the pole,[139] and explained this fact by disturbing waves originating in troposphere. The wave sources they thought the flow interaction with mountains, synoptical weather conditions, and convection penetrating into stratosphere. Entering the stratosphere, the waves dissipate. In the case of thermal wind balance the waves initiate movements directed to the pole, as well as downstream movements in high-latitude troposphere.[141] The mass balance in stratosphere remains stable due to upstream movements in tropical tropopause. P. Fabian was the first who estimated the Bruer–Dobson circulation parameters.[142] It turned out that the meridional speed of the transfer was equal to 0.4 cm/sec and the speed of downstream movement was about 0.1 cm/sec. It was clear that accurate estimating of such quantities was impossible.

To solve this problem, both complex[143–148] and simple models have been tried, which could elucidate at least a part of the process or only one phenomenon.[149–153] All existing methods can be divided into 4 groups[154]:

1) methods based on the Eiler equation for the flows through tropopause and on estimates of individual members of the equation[155–157];

2) the method using estimates of non-advective part of the movement through tropopause[158];

3) trajectory methods based on Lagrange approach[159,160];

4) the methods using transfer schemes with physical parameterization and estimations of tracer transfer through tropopause.[153,161,162]

The calculation results by these and some other models are presented in Table 6.

As is seen, on the whole the yearly globe flow is estimated differently by different authors, sometimes with a four-folde difference: minimum is equal to 343 Tg/year and maximum is equal to 1492 Tg/year. Evidently, such a scatter is conditioned by initial meterological parameters taken for different periods, as well as by different estimates of ozone precursors in models.

Detailed studies of ozone flows from stratosphere into troposphere for different seasons in northern hemisphere[180,181] have shown that a latitude zone of 25–40°N in the area of tropopause discontinuity and subtropic jet stream is most favourable for the stratospheric ozone transfer.

Table 6. Annual ozone flow (Tg/year) from stratosphere into troposphere

Model	Flow, Tg/year	References	Model	Flow, Tg/year	References
UIO	846	17	HGISS-GHM	390	169
GEOS-CHEM	470	18	STOCHEM	432	170
MATCH	1440	19	GISS-GCM	750	171
UCI	473	20	CHASER	593	172
HGISS	400	21	MAZART2	343	173
MATCH-MPIC	630–540	22, 23	LMDz-INCA	523	174
ECHAM-4	459	24, 25	UMD-CTM	479	175
ECHAM-3.2	575	163	IMPACT	663	176
IMAGES	550	164	STOCHEM	395	177
ECHAM/TM3	740–768	165	FRSGC/UCT	519	178
CTMK	1092–1429	166	SUNYA-GCCM	606	179
MOZART	391	167	MIN	343	
MATCH-MPIC	1103	168	MAX	1492	

The contribution of photochemical and stratospheric sources of tropospheric ozone in 30—60°N zone is roughly equal. In the seasonal behavior the winter and spring transfer is maximal.[182–184]

The ozone transfer in tropopause folds [196–199] was revealed in the 60s based on the data of radiolocation and inverse trajectories.[121] Aircraft experiments confirmed this phenomenon.[185–193] The lidars capable of detecting the phenomena with greater temporal and spatial resolution gave even more information.[194,195]

For a long time only downstream branch of spiral circulation, where ozone was transferred, has been fixed. At the present time, there are numerous data, which confirm the existence of the upstream branch and the transfer of minor air components: water vapor,[200–203] methane, nitrous oxide and others[204–206] from troposphere to stratosphere.

Discussions of any atmospheric phenomenon require the knowledge of its repetition and power, i.e., its general significance. This data can be found in Ref. 207, where it is also shown that the largest number of tropopause fold phenomena in the Northern hemisphere is registered in the period from December to January, reaching 700 cases per month. The smallest number is registered in the period from June to July and does not exceed 400 cases per month. The number of such folds in the Southern hemisphere is much less. Their maximum is registered in the cold period from April to June, reaching 340—360 cases per month. The repetition minimum is registered in summer in December and is equal to 260 cases per month.

In a series of research works, ozone flows from stratosphere into troposphere through the tropopause fold were estimated. Some of these estimates are collected in Table 7.

The data of Table 7 reveals 3 peculiarities. The first of them is a great spread of values. The second is the existence of the seasonal trend. The third one states that the method of ozone flow estimation is not important for close seasons. Similar results are presented in Ref. 214.

5. Ion cycle

Charged particles produced under the influence of galactic cosmic rays, solar wind, and radioactive nuclear decay of atmospheric impurities are always present in the atmosphere.[215] The concentration of free electrons in the atmosphere is very small due to the rapid reaction of their adherence to aerosol molecules or particles[215]:

$$e + \mathrm{O_2} + M \to \mathrm{O_2^-} + M.$$

Therefore, the charged part of tropospheric air mainly consists of positive and negative ions.

When considering the ozone formation with the charged particles, the authors of Ref. 6 underline a possibility of the existence of two $\mathrm{O_3}$ generation cycles in the atmosphere:

$$\left.\begin{array}{l}\mathrm{O_2} + \mathrm{O} \to \mathrm{O_3} + e,\\ e + 2\mathrm{O_2} \to \mathrm{O_2^-} + \mathrm{O_2}\end{array}\right\}$$

and

$$\left.\begin{array}{l}\mathrm{O_4^+} + \mathrm{O} \to \mathrm{O_3} + \mathrm{O_2^+}\\ \mathrm{O_2^-} + 2\mathrm{O_2} \to \mathrm{O_4^+} + \mathrm{O_2}\end{array}\right\}.$$

Although, according to their estimates, the contribution of these cycles is very small in comparison with standard reaction of the ozone formation

$$\mathrm{O} + \mathrm{O_2} + M \to \mathrm{O_3} + M.$$

It is noted[216] that the role of nitrogen in the processes of ozone formation and decay is very important. Nitrogen molecules are involved in the trimolecular process. Besides, the excitation of N_2^x molecule can transfer energy to $\mathrm{O_2}$ molecules:

$$\begin{aligned}\mathrm{N_2^+} + \mathrm{O_2} &\to \mathrm{N_2} + \mathrm{O_2^+}\\ &\to \mathrm{N_2} + 2\mathrm{O}.\end{aligned}$$

Ions $\mathrm{N_2^+}$ are involved in recharging of $\mathrm{O_2}$ molecules, which results in formation of ions $\mathrm{O_2^+}$:

$$\mathrm{N_2^+} + \mathrm{O_2} \to \mathrm{N_2} + \mathrm{O_2^+}.$$

Oxygen atoms are formed as a result of reaction of nitrogen atoms and ions:

$$\mathrm{N^+} + \mathrm{O_2} \to \mathrm{NO} + \mathrm{O}$$

$$\mathrm{N^+} + \mathrm{O_2} \to \mathrm{NO^+O}.$$

These processes lead to absorption of radiant energy by nitrogen, which in turn leads to formation of ozone and to processes conditioned by the direct influence of radiation on oxygen. The authors of Ref. 216 point out that this radiochemical process essentially differs from the photochemical one.

Table 7. The estimates of ozone flows from stratosphere to troposphere through tropopause (10^{22} molec/day)

Determination method	Month	Flow	References
Mesoscale model	February	1.8	208
» »	February	7.9	209
» »	April/May	10.4	210
Ozone lidar + Inverse trajectories	March	10.0	211
Radio probing + Inverse trajectories	October	4.0	212
Ozone lidar + Inverse trajectories	November	6.5	213

Conclusion

The analysis of mechanisms and factors determining the ozone content in troposphere shows that the main sources of ozone are: ozone transfer from stratosphere to troposphere, its photochemical formation from precursors, and ozone generation at lightnings.

The transfer of O_3 from stratosphere into troposphere is a stable source with seasonal modulation. In the process of ozone photochemical formation and destruction in troposphere much more O_3 can be generated and decayed than transferred from stratosphere. However, this source has daily and seasonal components. The processes of O_3 generation in background and smog situations should be distinguished.

The amount of ozone, generated during thunderstorms, in some areas can be compared with that generated photochemically and the transfer from stratosphere. However, this phenomenon is of regional character.

Other mechanisms are of less importance.

It is evident that in the open system (like the atmosphere) all the mentioned mechanisms can be realized simultaneously competing with each other in the photochemical component. This fact will be considered in detail by us in future.

New available works on the issue can be of interest to readers, therefore we give their references.[217–228]

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