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The chemistry of OH and HO_2 radicals in the earth's atmosphere

Yu M Gershenzon, S G Zvenigorodskii, V B Rozenshtein
Semenov Institute of Chemical Physics, USSR Academy of Sciences, Moscow

ABSTRACT. In the present review the main photochemical mechanisms for reaction of OH and HO_2 with atmospheric components are examined and possible alternative methods of studying them are analysed. The mechanisms governing the change in concentrations of OH and HO_2 radicals cannot be represented without a consideration of other stable and labile minor gas components in the atmosphere. Amongst the latter the most important are ozone, ozone-active radicals and their precursors, stable molecules. In addition to OH and HO_2, NO, NO_2, as well as Cl and ClO are also reactive towards ozone. The destruction cycles for ozone involving these radicals and reactions related to them are also briefly examined in this review together with the heterogeneous processes involving OH and HO_2 that can also substantially affect the gaseous composition of the atmosphere.

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I. Introduction

Atmospheric photochemistry was only recognised and started to develop as an independent branch of chemistry in the middle of the 1970s, although the basic principles of the photochemical theory of the atmosphere had been formulated more than half a century ago.[1,2] This was assisted in many respects by the rapid development of technique for measuring rate constants of fundamental chemical and photochemical processes and of numerical methods for simulating the kinetics of multicomponent chemical systems using computer technology. By using the experience gained in solving kinetic problems in plasma chemistry and photochemistry and also in the calculations of different processes in chemical reactors, it was possible to achieve real progress in the understanding of the nature of chemical processes in the atmosphere and to develop the idea of it as a multicomponent non-equilibrium chemical system. The photochemical models developed from this concept made it possible to predict the gaseous composition of the atmosphere containing many chemical compounds as minor components, which was subsequently confirmed in full-scale experiments. The rapid development of studies in the field of atmospheric chemistry has recently led to its having a reverse effect on traditional areas of chemistry, which has manifested itself in particular in the revision of a whole series of kinetic data of fundamental significance for the representation of photochemical processes in the atmosphere and the development of new experimental methods for measuring rate constants of reactions involving minor gas components.

Although the present-day chemistry of the atmosphere makes use of dozens of molecular and ion-molecule reactions, photodissociation and photoionisation reactions, a special place is occupied amongst them by processes involving OH and HO_2 radicals, which because of their high chemical activity are initiators of a whole range of oxidative reactions in different regions of the atmosphere. The existing theoretical and experimental results provide convincing evidence of the key role of hydrogen radicals in a whole set of problems in atmospheric chemistry. In the lower atmosphere (troposphere) hydroxyl initiates the oxidation of CO, CH_4, C_2H_6, H_2, CH_3Cl, CH_3CCl_3, CH_3Br, H_2S, SO_2, and a number of other components of natural and anthropogenic origin. In the upper atmosphere (stratosphere and mesosphere) reactions involving OH and HO_2 are responsible for changes in the ozone content. Moreover, many questions related to a determination of the strength of atmospheric photochemical sources and sinks of OH and HO_2 and their content in the atmosphere have given rise to considerable controversy.

II. The atmosphere as a multicomponent chemical system

The earth's atmosphere contains a large number of chemical compounds, of which N_2 and O_2 are the most abundant. An important role in atmospheric photochemistry is played by the so-called precursor gases—N_2O, H_2O, CH_4, and freons of natural and anthropogenic origin. When they are oxidised in the lower atmosphere and undergo photodissociation or react with photolysis products in the upper atmosphere, these gases become sources of free radicals and other minor gas components. The content of some of the most important components at different altitudes and their sources are shown in Table 1. More detailed information about the vertical and latitudinal distribution of the minor gas components, their time variations, and determination of the total strengths of their sources can be found in two reviews.[6,7]

In restricting the discussion solely to the neutral components, we shall examine the key channels of photochemical transformation of the gas precursors.

1. Oxygen components

The photodissociation of O_2 results in the formation of atomic oxygen in the ground (^3P) and excited (^1D) states

$$O_2+h\nu\rightarrow O(^1D)+O(^3P),\ (135\ \text{nm} < \lambda < 175\ \text{nm}), \quad (1)$$

$$O_2+h\nu\rightarrow 2O(^3P),\ (175\ \text{nm} < \lambda < 250\ \text{nm}). \quad (2)$$

Ozone is formed as a result of the termolecular reaction

$$O+O_2+M\rightarrow O_3+M, \quad (3)$$

where M are air molecules.

Table 1. Some properties of the most important minor components of the atmosphere.

Gas	Background concentration, mole fractions		Extent of study of global distribution	Main sources	Main sinks
	T	S			
CH_4	$1.6\cdot10^{-6}$	$(15-6)\cdot10^{-7}$	++	B	P
N_2O	$3.2\cdot10^{-7}$	$3\cdot10^{-7}\div3\cdot10^{-10}$	++	B	P
O_3	$(4\div10)\cdot10^{-8}$	$(1\div10)\cdot10^{-6}$	+++	P	P
NO_x	$(4\div10)\cdot10^{-11}$	$1\cdot10^{-10}\div3\cdot10^{-8}$	+++(T), ++(S)	A, P storms	P, W (T)
HNO_3	$(2\div10)\cdot10^{-10}$	$8\cdot10^{-9}\div1\cdot10^{-10}$	++	P	P, W(T)
OH	$1\cdot10^{-13}\div1\cdot10^{-14}$	$3\cdot10^{-13}\div8\cdot10^{-10}$	+	P	P
HO_2	$1\cdot10^{-11}\div1\cdot10^{-14}$	$1\cdot10^{-12}\div6\cdot10^{-10}$	+	P	P
H_2O_2	$1\cdot10^{-9}\div5\cdot10^{-10}$	$1\cdot10^{-12}\div5\cdot10^{-10}$	o	P	P, W (T)
H_2CO	$4\cdot10^{-10}\div2\cdot10^{-11}$	$1\cdot10^{-11}\div1\cdot10^{-10}$	+	P	P
H_2	$5.7\cdot10^{-7}$	$5\cdot10^{-7}\div1\cdot10^{-8}$	++	B, P	P
H_2O	$1\cdot10^{-2}\div2\cdot10^{-5}$	$(1\div6)\cdot10^{-6}$	+++(T), ++(S)	H	W (T), P (S)
CO	$(2\div8)\cdot10^{-8}$	$(0.2\div10)\cdot10^{-8}$	++	A, P	P

Note. The concentrations of minor components are annual average globally mean values and are given mainly from the results of one-dimensional simulation[3] and from the data of four studies.[4-7] Conventional notation: T = troposphere, S = stratosphere, A = anthropogenic, W = rainout, P = photochemical, B = biogenic, o = no reliable measurements, + = individual measurements carried out, ++ = special series of measurements carried out, +++ = regular inspection made, NO_x = NO + NO_2, H = hydrosphere.

Oxygen atoms are consumed in the reactions

$$O+O+M\rightarrow O_2+M, \quad (4)$$

$$O+O_3\rightarrow 2O_2. \quad (5)$$

On photodissociation of ozone, oxygen atoms are again formed in their ground or excited states:

$$O_3+h\nu\rightarrow O_2+O(^3P),\ (\lambda > 320\ \text{nm}), \quad (6)$$

$$O_3+h\nu\rightarrow O_2+O(^1D),\ (\lambda < 310\ \text{nm}). \quad (7)$$

This reaction sequence, proposed by Chapman[1,2] was for a long time considered to be the main route for formation of atmospheric ozone. The sequence of stages (1)–(7) represents a chain reaction for conversion of "odd" oxygen—O and O_3—and it is sometimes called the "odd" oxygen cycle.

2. Sources of OH and HO_2

The reaction of an excited oxygen atom with a water molecule was first regarded as a photochemical source of hydroxyl by Nicolet and Bates.[8,9]

$$H_2O+O(^1D)\rightarrow OH+OH. \quad (8)$$

The formation of OH is also possible in a number of other reactions of $O(^1D)$ with minor atmospheric components:

$$CH_4+O(^1D)\rightarrow CH_3+OH, \quad (9)$$

$$H_2+O(^1D)\rightarrow H+OH. \quad (10)$$

OH and HO_2 are interconverted in reactions involving oxygen species:

$$O_3+OH\rightarrow HO_2+O_2, \quad (11)$$

$$O+HO_2\rightarrow OH+O_2. \quad (12)$$

3. Sources of nitrogen oxides

According to Crutzen[10] the following reaction represents a photochemical source of nitric oxide in the atmosphere:

$$N_2O+O(^1D)\rightarrow 2NO. \quad (13)$$

The concentration of N_2O—a product of the activity of bacteria under anaerobic conditions—rapidly decreases with altitude, ranging from 10^{12} cm^{-3} on the earth's surface to 10^8 cm^{-3} at an altitude of 35–40 km (see Table 1). A photochemical equilibrium in the system $NO-NO_2$ with a typical time of several tens of seconds[6] is established in the atmosphere, being determined mainly by the following reactions:

$$NO+O_3\rightarrow NO_2+O_2, \quad (14)$$

$$NO_2+O\rightarrow NO+O_2, \quad (15)$$

$$NO_2+h\nu\rightarrow NO+O. \quad (16)$$

The photochemistry of the minor gas components, taking into account the specific nature of reactions in different regions of the atmosphere, will be examined in greater detail in subsequent sections.

4. Main cycles of destruction of ozone

One of the principal problems of atmospheric chemistry is the effect of photochemical processes on the protective layer of ozone. It is evident that with the concentrations of ozone that actually exist in the stratosphere, being several orders higher than the concentration of components that are chemically active towards them (see Table 1), the destruction of ozone may be due solely to catalytic cycles of the type

$$\begin{array}{l} X+O_3\rightarrow XO+O_2, \\ XO+O\rightarrow X+O_2, \\ \hline O_3+O\rightarrow O_2+O_2, \end{array} \quad (17)$$

or

$$\begin{array}{l} X+O_3\rightarrow XO+O_2, \\ XO+O_3\rightarrow X+2O_2, \\ \hline 2O_3\rightarrow 3O_2, \end{array} \quad (18)$$

where X = OH, NO, or a chlorine atom which is formed in the

stratosphere by photodissociation of freons. The cycles of ozone destruction involving OH, NO, and Cl are known as the hydrogen, nitrogen, and chlorine cycles respectively. Bromine atoms are also highly effective, but they are present in the atmosphere to a much lesser extent than Cl atoms. A large number of studies have been devoted to stratospheric cycles of ozone destruction, amongst which the two fundamental publications of Johnston[11,12] can be given special mention. The efficiency of action of a catalyst molecule in destruction cycles is determined by the concentration of catalyst in the atmosphere, which depends on the rates of its generation and removal from the cycle.[13] The ratio of the rate of destruction of odd oxygen to the rate of removal of catalyst from the cycle represents the chain length and corresponds to the number of O and O_3 molecules destroyed by a single catalyst molecule. The number of recurrences in the cycle can reach 10^6. In the stratosphere the nitrogen, hydrogen, and chlorine cycles (in order of increasing contribution) are active. Terminations of the chains in the cycles occur as a result of a cross interaction of the homogeneous catalysts between each other

$$OH+HO_2 \rightarrow H_2O+O_2,$$

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

$$ClO+NO_2+M \rightarrow ClONO_2+M$$

or as a result of the heterogeneous destruction of radicals or reservoir gases (HNO_3, $ClONO_2$) on aerosols and water droplets. However, in a number of cases termination is governed not by chemical reactions but by a process of turbulent transfer, resulting in the removal of the catalyst molecule from the stratosphere. Thus, dynamic processes affect the length of the cycles and prove to be an additional important factor that is necessary to take into consideration in simulating the gaseous composition of the atmosphere.

5. Models of the atmosphere

In photochemical models of the atmosphere use is made of a system of non-stationary diffusion kinetic equations of continuity that generally take the following form:

$$\frac{\partial [n_i]}{\partial t} = P_i - L_i [n_i] - \sum_j \frac{\partial F_{ij}}{\partial x_j}. \qquad (19)$$

Here $[n_i]$ is the concentration of the ith component, P_i and L_i are its photochemical sources and sinks respectively, x_j are Cartesian coordinates, F_{ij} are component fluxes, and t is time. In one-dimensional models, which are the most widely used, only the vertical flux component is considered

$$F_{iz} = K_z [M] \frac{\partial}{\partial z} \left(\frac{[n_i]}{[M]} \right) \qquad (20)$$

where K_z is the globally averaged vertical component of the tensor of the coefficient of diffusion transfer (turbulent or molecular), [M] is the total concentration of air molecules. In the solution of certain problems and at a given ratio between the lifetime in photochemical reactions $\tau_{chem} = 1/L_i$ and the characteristic time of dynamic transfer $\tau_{dyn} = H^2/K_z$, the equation system (19) can be simplified ($H = RT/mg$, the height of uniform atmosphere, R is the gas constant, m is the molecular weight, and g is the acceleration due to gravity).

Quasi-stationary conditions (diagnostic problem), $\partial[n_i]/\partial t = 0$. For long-lived components ($\tau_{dyn} \ll \tau_{chem}$) the system of equations in (19) takes the following form:

$$P_i - L_i [n_i] - \frac{\partial F_{iz}}{\partial z} = 0. \qquad (21)$$

In the case of short-lived components ($\tau_{chem} \ll \tau_{dyn}$) the following photochemical equilibrium is established:

$$P_i - L_i [n_i] = 0. \qquad (22)$$

Within the framework of the diagnostic problem the photochemical balance between the minor gas components is calculated in given regions of the atmosphere and the sensitivity of the equilibrium model concentrations to different perturbation mechanisms and the internal parameters of the model is determined.

Non-equilibrium conditions (prognostic problem). The whole equation system (19) is solved in this case for long-lived components, while in equations for short-lived components the transport term $\partial F_{iz}/\partial z$ can be omitted. The solution of the prognostic problem makes it possible to study the mechanism of the relaxation of the system to equilibrium conditions and to simulate the change in concentration of the minor gas components under atmospheric conditions and to predict the chemical composition in air in the atmosphere at different moments in time.

The relationship between the dynamic and photochemical lifetimes in the atmosphere is relative in nature, since the clearly defined non-uniformity of the atmosphere causes considerable changes (by several orders of magnitude) in τ_{chem} and τ_{dyn}. This factor considerably complicates a numerical solution of system (19), since the retention of the transport component on its right-hand side results in the need to solve a system of second-order partial differential equations when there is a close relationship between the equations because of the high rates of the chemical reactions.

In current photochemical models of the atmosphere, adaptation of the numerical algorithms of system (19) to include transport is considered to be one of the most complex and topical problems. Elucidation of this problem is outside the scope of the present review, but the details can be obtained from four studies.[14–17] Moreover, the need to overcome the difficulties in the calculations had led to the development of a new approach to the analysis of the photochemical parts of the model equations — the application of the concept of families.

This idea involves separating from the whole collection of components included in the scheme of reactions individual groups (families), within which the conditions of photochemical equilibrium are assumed to be fulfilled, whereas dynamic transfer is calculated for the complete family as a whole. This makes it possible to simplify considerably the numerical solution of system (19), having reduced the number of complete equations. In most photochemical models of the atmosphere the following families are usually distinguished: "odd" oxygen $O_y = O(^3P) + O(^1D) + O_3$, "odd" nitrogen $NO_y = N + NO + NO_2 + 2N_2O_5 + HO_2NO_2 + NO_3 + ClONO_2$, "odd" hydrogen $HO_y = H + OH + HO_2 + 2H_2O_2$, and "odd" chlorine $Cl_y = Cl + ClO + HOCl + ClONO_2$. The combination of components on the right sides can be modified according to the choice of reaction scheme and the atmospheric conditions under which they occur. The altitude profiles of the interconversion times for components within a single family [$OH \longleftrightarrow HO_2$ (*1*), $NO \longleftrightarrow NO_2$ (*2*)], the lifetimes of OH radicals (*3*) and families HO_y (*4*) and NO_y (*5*), the conversion time of $HNO_3 \longleftrightarrow NO_y$ (*6*),

and the lifetimes of the chemically inactive gases H_2O and CH_4 are presented in Fig. 1. The high rate of interconversion of the species of the HO_y and NO_y families and the marked difference between the lifetimes of active species and stable gases can clearly be seen in Fig. 1.

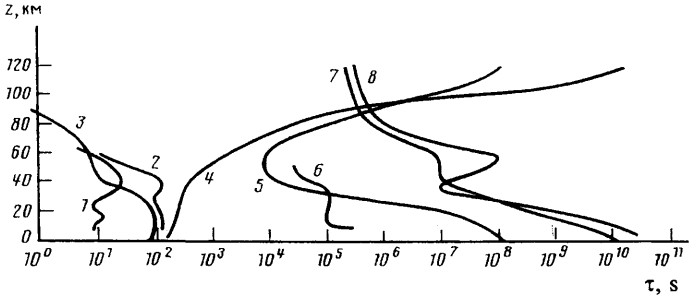


Figure 1. Lifetimes of components of the photochemical reactions of OH (*3*), NO_y (*5*), HO_y (*4*) and the gas precursors CH_4 (*8*) and H_2O (*7*), and also the time for reaching photochemical equilibrium in the systems OH/HO_2 (*1*), NO/NO_2 (*2*), and HNO_3/NO_y (*6*).[6,18]

A distinctive feature of the atmosphere as a medium for photochemical processes is the presence in it of a number of vertically divided regions, each of which is characterised by well-defined specific chemical and physical properties. The lowest region of the atmosphere—the troposphere (up to 12–15 km in altitude)—is characterised by the presence of a considerable amount of water in different aggregate states and an active lower boundary. In photochemical terms this denotes, firstly, the existence of intense heterogeneous reactions involving water droplets, aerosol particles and the earth's surface and, secondly, a greater variability of the chemical composition compared to other regions of the atmosphere as a result of the entry of anthropogenic and natural gases from the lower boundary. In this sense the troposphere may be regarded as a type of filter that limits the transfer of chemically active and water-soluble gas components into the upper layers of the atmosphere.

The stratosphere is considerably less susceptible to the effect of terrestrial sources. The only exception to this is nitrous oxide, from which nitric oxide is formed according to reaction (13), and the "odd" chlorine family, since N_2O and freons, which are inert in the troposphere, are vigorously decomposed in the stratosphere by solar UV radiation. The principal minor gas components O_3, NO, NO_2, OH, HO_2, etc. have only internal photochemical sources in the stratosphere. Also, the stratosphere is quite dry, the relative water vapour content amounting to 10^{-6} and being subject to much smaller variations than in the troposphere. The background concentration of aerosol particles in this region is also small (no more than 20–30 particles per cm^3 in a local maximum—the Junge layer—at an altitude of 16–18 km). All this makes it possible to simulate photochemical processes occurring in the stratosphere in the gas phase, and the stratosphere is characterised as the most favourable region for detailed comparison of theoretical schemes with the results of full-scale observations.

In the upper region of the atmosphere (an altitude range of 50–120 km) the role of photodissociation and photoionisation reactions increases, which helps to increase the concentrations of the atomic components of radicals and causes the formation of excited and ionised molecules and atoms. However, a leading role in the photochemistry of the neutral component of the mesosphere and lower thermosphere is played by OH and HO_2 radicals, which to a considerable extent control the content of components such as O and O_3.

III. Photochemical balance between OH, HO_2, and ozone in the stratosphere

The magnitudes of different sources and sinks of radicals of the hydrogen family are shown in Figs. 2 and 3.

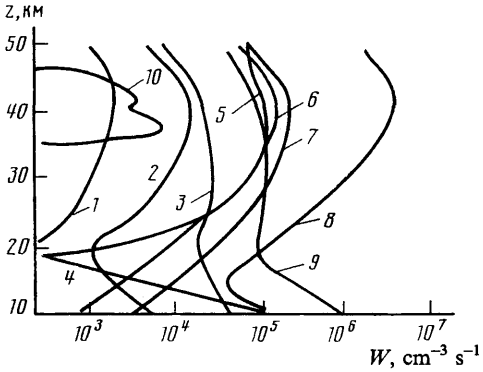


Figure 2. Rates of photochemical formation of radicals of the hydrogen family in the stratosphere:[18] *1*, Cl + H_2; *2*, Cl + H_2CO; *3*, Cl + CH_4; *4*, $CH_3COOH + h\nu \rightarrow CH_3O + OH$; *5*, $H_2O + h\nu \rightarrow H + OH$; *6*, $H_2 + O(^1D)$; *7*, $CH_4 + O(^1D)$; *8*, $H_2O + O(^1D)$; *9*, $H_2CO + h\nu \rightarrow HCO + H$; *10*, generation of OH caused by HNO_3 transport; the rates of processes *5*, *6*, *8*, and *9* are shown on a double scale.

Above 20 km the main source of "odd" hydrogen is provided by the destruction of water vapour

$$O(^1D) + H_2O \rightarrow OH + OH. \quad (23)$$

In the lower stratosphere a similar contribution is made by the photolysis of formaldehyde—one of the intermediates of the oxidation of methane:

$$H_2CO + h\nu \rightarrow HCO + H, (\lambda < 340 \text{ nm}). \quad (24)$$

An alternative channel exists for the photodissociation of formaldehyde

$$H_2CO + h\nu \rightarrow CO + H_2, (\lambda < 340 \text{ nm}) \quad (25)$$

which does not result in the formation of components of the family of "odd" hydrogen. According to Cariolle,[18] the accuracy in determining the quantum yields of these processes is about 40% and for a more rigorous determination of the magnitude of photochemical sources of HO_x in the lower stratosphere careful experimental verification of the relative contribution of each channel in the photodissociation of H_2CO is required.

The photochemical destruction of "odd" hydrogen occurs by a number of processes, resulting in the formation of water molecules:

$$OH+HO_2 \rightarrow H_2O+O_2, \quad (26)$$

$$OH+HNO_3 \rightarrow H_2O+NO_3, \quad (27)$$

$$OH+HO_2NO_2 \rightarrow H_2O+O_2+NO_2. \quad (28)$$

At altitudes of more than 30 km reaction (26) predominates (see Fig. 3). Processes (27) and (28) are predominant at altitudes of 15–30 km. According to one report,[20] the uncertainty factors for the rate constants of these reactions are 1.4 and 2 respectively. Greater accuracy of the kinetic parameters of reactions (23)–(28) is of particular interest currently for processes in the lower stratosphere, where "odd" hydrogen is a key component of the photochemical destruction of ozone.

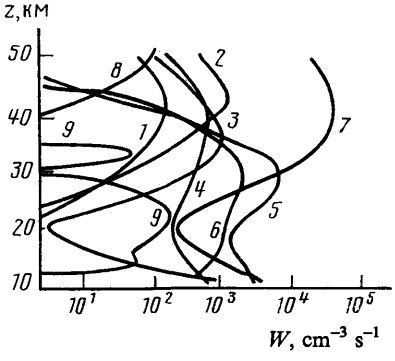


Figure 3. Rates of photochemical destruction of HO_x in the stratosphere[18] (rates of processes *2*, *3*, *5*–*8* are shown on a double scale): *1*, Cl + HO_2; *2*, OH + OH; *3*, OH + H_2O_2; *4*, OH + HCl; *5*, HO_2NO_2 + OH; *6*, OH + HNO_3; *7*, OH + HO_2; *8*, H + HO_2; *9*, depletion of HO_y caused by HNO_3 transport.

The time for equilibrium to be established between the concentrations of OH and HO_2 at stratospheric altitudes does not exceed 10 s (Fig. 1). This is due to the occurrence of a large number of rapid interconversions of OH to HO_2 and the reverse. The vertical profiles of the rates of these reactions are given in Fig. 4.

Despite the comparatively short photochemical lifetimes of the complete family of "odd" hydrogen as a whole and even more so for its individual components (see Fig. 1), dynamic factors can have an averaging effect on the content of HO_y, giving rise to a redistribution of concentrations of the components H_2O and HNO_3 that are important for the balance of HO_y, the lifetimes of which are considerably longer in photochemical reactions.

Virtually all studies in stratospheric photochemistry are in one way or another related to atmospheric ozone—the main component of the oxygen family at these altitudes. The evident progress achieved in this area in recent times does not in any way signify the absence of problems or controversial conclusions, as is reflected by a number of reviews and monographs.[6,7,21–23] We shall only examine certain of those that from our standpoint are of fundamental importance.

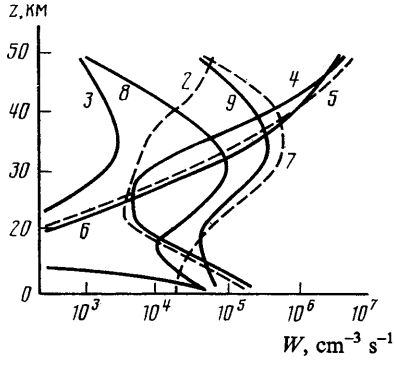


Figure 4. Rates of conversions in the HO_y system (the rates of processes *1* and *3* are shown on a double scale): *1*, $H_2O_2 + h\nu \rightarrow 2OH$; *2*, CO + OH; *3*, $H_2O_2 + h\nu$; *4*, H + O_2 + M; *5*, O + OH; *6*, O + HO_2; *7*, OH + O_3; *8*, HO_2 + O_3; *9*, NO + HO_2.

For several decades the mechanism for the formation and destruction of ozone in the oxygen cycle [reactions (1)–(7)], as proposed by Chapman back in the 1930s, fairly adequately accounted for the results of the majority of full-scale experiments. However, the development of experimental techniques and a refinement of the reaction rate parameters necessitated a review of Chapman's theory, since the stratospheric concentrations of O_3 (particularly in the lower region of the stratosphere) determined by theoretical calculations were considerably higher than the observed concentrations. The possibility that ozone is destroyed in reactions with hydrogen radicals was first demonstrated at the beginning of the 1950s.[8] Subsequently the photochemical destruction of ozone involving nitrogen oxides was examined.[10] A detailed study of the global ozone balance[11] confirmed that in the stratosphere the photochemical generation of ozone substantially exceeds its destruction by the reaction of O + $O_3 \rightarrow 2O_2$, which only accounts for removal of about 20% of the O_3 formed by photolysis of oxygen. The flow of ozone through the tropopause does not exceed 1%. The relative contributions of the nitrogen and hydrogen cycles to the overall photochemical destruction of O_3 (not taking into account the chlorine cycle) from the results of one-dimensional simulation are shown in Table 2. These data are very provisional since similar calculations carried out by different authors suggest that such determinations are sensitive to the rate constants of different reactions and reveal certain quantitative discrepancies. The vertical profiles of the magnitudes of the photochemical destruction of ozone in different cycles are given in Fig. 5.[24] According to current theories the main role in the destruction of ozone in the upper and lower stratosphere is played by the hydrogen cycle while in the middle stratosphere the main role is played by the nitrogen cycle and, to a lesser degree, the hydrogen and chlorine cycles. For the

upper stratosphere the following cycle involving OH and HO_2 is important:

$$\begin{array}{l} OH + O \rightarrow H + O_2, \\ H + O_2 + M \rightarrow HO_2 + M, \\ \hline HO_2 + O \rightarrow OH + O_2, \\ 2\,O \rightarrow O_2 \end{array} \quad (29)$$

In the mesosphere another series of reactions for the destruction of "odd" oxygen is of greater significance:

$$\begin{array}{l} OH + O \rightarrow H + O_2, \\ H + O_3 \rightarrow OH + O_2, \\ \hline O + O_3 \rightarrow 2\,O_2. \end{array} \quad (30)$$

In the region of maximum concentration, destruction occurs via the nitrogen cycle:

$$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2, \\ NO_2 + O \rightarrow NO + O_2, \\ \hline O + O_3 \rightarrow 2\,O_2. \end{array} \quad (31)$$

Below 20 km the principle depletion of ozone takes place by a two-step mechanism

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2, \\ HO_2 + O_3 \rightarrow OH + 2\,O_2, \\ \hline 2\,O_3 \rightarrow 3\,O_2. \end{array} \quad (32)$$

However, at these altitudes when certain ratios exist between the background atmospheric concentrations of components of the families of "odd" nitrogen and hydrogen, the radicals can also become involved in competing "zero" cycles:

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2, \\ HO_2 + NO \rightarrow NO_2 + OH, \\ NO_2 + h\nu \rightarrow NO + O, \\ O_2 + O + M \rightarrow O_3 + M, \end{array} \quad (33)$$

or

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2, \\ HO_2 + NO + M \rightarrow HNO_3 + M, \\ HNO_3 + h\nu \rightarrow NO_2 + OH, \\ NO_2 + h\nu \rightarrow NO + O, \\ O_2 + O + M \rightarrow O_3 + M. \end{array} \quad (34)$$

Cycles of this type play the role of a unique buffer, linking the chemically active nitrogen and hydrogen components and reducing the efficiency of ozone destruction.

Moreover, in the lower stratosphere an important photochemical source of ozone is provided by the oxidation of CO, catalysed by nitrogen oxides

$$\begin{array}{l} CO + OH \rightarrow CO_2 + H, \\ H + O_2 + M \rightarrow HO_2 + M, \\ NO + HO_2 \rightarrow OH + NO_2, \\ NO_2 + h\nu \rightarrow NO + O, \\ \hline O + O_2 + M \rightarrow O_3 + M, \\ CO + 2\,O_2 \rightarrow CO_2 + O_3 \end{array} \quad (35)$$

The source of carbon monoxide in the lower stratosphere (15–20 km) is transport from the troposphere, where CO is mainly formed by oxidation of methane. The strength of this source of ozone (see Table 2) depends mainly on the background concentrations of OH and HO_2 in the lower stratosphere, which remain a subject of controversy even at the present time. That is possibly the reason why in a study of the photochemical balance of the stratosphere[24] carried out using current kinetic data and the results of satellite probing of the global distribution of the most important minor gas components, an imbalance of ozone (an excess of production over destruction in the range 25–60%) was again found at altitudes corresponding to the lower stratosphere. Another source of uncertainty in the determination of the photochemical balance of ozone is the presence of two inconsistent sets of data on the cross-sections of molecular oxygen absorption.[25,26] The use of different data on the cross-sections of O_2 absorption results in a corresponding change in magnitude of the imbalance, as is reflected in Fig. 5. The relative contribution of the different cycles of destruction and formation of ozone can vary considerably as a function of the conditions (altitude, time of day, etc.). For example, the roles of the reactions

$$NO_2 + O \rightarrow NO + O_2,$$

and

$$NO_2 + h\nu \rightarrow NO + O,$$

are quite different. In the first reaction an oxygen atom is consumed while in the second it is formed. Destruction (31) or production (35) of ozone takes place in the nitrogen cycle depending on the ratio of rates of these reactions. Therefore, in the middle stratosphere nitrogen oxides catalyse the destruction of ozone while in the lower stratosphere and in the troposphere the same oxides, being catalysts of the oxidation of CO or hydrocarbons (see Table 2 and below), enable an additional amount of it to be produced.

Table 2. Formation and destruction of ozone in the troposphere (0–14 km) and stratosphere (14–50 km).[39]

Method of calculation	Formation of O_3					Destruction of O_3				
	Process	in the troposphere		in the stratosphere		Process	in the troposphere		in the stratosphere	
		Rate 10^{11} mol cm^{-2} s^{-1}	%	Rate 10^{11} mol cm^{-2} s^{-1}	%		Rate 10^{11} mol cm^{-2} s^{-1}	%	Rate 10^{11} mol cm^{-2} s^{-1}	%
A	Via CH_4	2.9	59.2	0.78	0.3	In the O_x cycle	0.13	0.05	13	5.65
						In the HO_x cycle	3.5	71.4	86	37.4
	Flux from above	2.0	40.8	—	—	In the NO_x cycle	—	—	130	56.5
						Depletion on the earth's surface	1.4	28.6	—	—
B	Via CH_4	33.1	95	12.2	5	In the O_x cycle	—	—	10.1	4,2
						In the HO_x cycle	28.7	83	132	54.5
	Flux from above	1.74	5	—	—	In the NO_x cycle	—	—	100	41.3
						Depletion on the earth's surface	5.9	17	—	—

Note. *A*—when $F_{NO_x} = 10^9$ cm^{-2} s^{-1} and $[CH_4]/[M]$ $(z = 0) = 1.6 \times 10^{-6}$; *B*—when $F_{NO_x} = 10^{10}$ mol cm^{-2} s^{-1} and $[CH_4]/M$ $(z = 0) = 25 \times 10^{-6}$; F_{NO_x} is the flux of nitrogen oxides from the earth's surface, $[CH_4]/[M]$ $(z = 0)$ is the ground level mole fraction of methane.

The depletion of ozone in the chlorine cycle

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2, \\ \underline{O + ClO \rightarrow Cl + O_2,} \\ O + O_3 \rightarrow 2O_2 \end{array} \qquad (36)$$

is most significant at high altitudes (30–50 km). The maximum decrease in $[O_3]$ through reactions (36) at the currently accepted levels of freon emissions is estimated at 70% for an altitude of 40 km.[27] In the region of maximum concentration of ozone (20–30 km) the content of ClO and Cl are such ($\sim 10^{-10}$ of [M] at an altitude of 25 km) that the chlorine cycle is not able to compete with the nitrogen cycle (31). Hence, with the flux of freons from the earth currently accepted in calculations, there should be no decrease, rather an increase in $[O_3]$ at altitudes of 15–30 km. The increase in $[O_3]$ is due to the following reaction taking place

$$ClO + NO_2 + M \rightarrow ClONO_2 + M,$$

as a result of which NO_2, the main agent responsible for destruction of ozone, undergoes binding, and hence there is a decrease in photochemical ozone destruction. The increase in concentration of stratospheric ozone due to the flux of freons at altitudes of 15–30 km is 3%. It is thought[27] that at present freons do not cause a significant change in the total content of ozone at middle latitudes, but prognostic calculations indicate the necessity for urgent curtailment of their production.

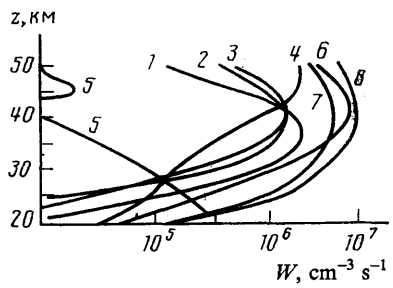


Figure 5. Rates of photochemical destruction and production of ozone in the stratosphere:[24] *1*, nitrogen cycle; *2*, chlorine cycle; *3*, oxygen cycle; *4*, hydrogen cycle; *5*, depletion of ozone through migration; *6*, overall destruction; *7*, overall production at low values of absorption cross-section σ_{O_2}; *8*, the same at higher values of σ_{O_2}.

The decrease in concentration of nitrogen oxides in the middle stratosphere assists an increase in concentration of OH through a reduction in rate of the reaction

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

On the other hand, an increase in [OH] is inhibited by the reaction

$$OH + HCl \rightarrow H_2O + Cl,$$

in which the primary loss of ClO and Cl is compensated.

Thus, all the families and destruction cycles of ozone prove to be interrelated by a system of complex feedbacks.

An example of the effect of freons is evidently provided by the recently discovered vernal (October–November) "holes" in the ozone layer in Antarctica.[28] The vernal decrease in $[O_3]$ above Antarctica was first noticed in 1979 when it amounted to 10%. From 1959 to 1979 this phenomenon had apparently not yet occurred, while in 1986 the fall in the concentration of ozone was as high as 50%. This recently developed vernal fall in the concentration of Antarctic ozone is most probably due to the effect of ClO radicals.[29–31]

IV. Reactions of OH and HO_2 in the troposphere and oxidation of hydrocarbons. Tropospheric ozone

1. Sources and sinks of "odd" hydrogen in the troposphere

Photochemical sources of HO_x in the troposphere are similar to those in the stratosphere—reaction of water molecules with $O(^1D)$ and the photolysis of formaldehyde, an intermediate in the oxidation of methane. However, under tropospheric conditions, in contrast to those of the stratosphere, it is a considerably more complex task to determine the relative contribution of each of the channels for formation of HO_x in view of the well-known variability of the background concentrations of H_2O and the passage of solar radiation in the region of photodissociation of H_2CO and O_3 and also because of a number of other factors, some of which will be examined below. The mean daily profiles of intensity of the above-mentioned channels under standard atmospheric conditions at 15 and 45 °N are shown in Fig. 6.[32]

The gas-phase photochemical sinks of HO_x in the troposphere are related to reactions in which H_2O molecules are formed:

$$OH + H_2O_2 \rightarrow H_2O + HO_2, \qquad (37)$$

$$OH + CH_3OOH \rightarrow CH_3OO + H_2O, \qquad (38)$$

$$OH + HO_2 \rightarrow H_2O + O_2. \qquad (39)$$

Morover, the presence of water in liquid droplet form in the lower troposphere results in an increased role of heterogeneous processes in the destruction of "odd" hydrogen. This, in particular, denotes that the rainout of a number of reservoir components formed by reactions involving OH and HO_2 in the gas phase

$$OH + NO_2 + M \rightarrow HNO_3 + M, \qquad (40)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (41)$$

constitutes a depletion for the HO_x family in the lower troposphere (Fig. 6).

In the troposphere hydroxyl plays a special role by acting as a unique "cleaning agent". In fact, as follows from Fig. 7, the vast majority of oxidative cycles involving anthropogenic and natural components of gases start with a reaction in which OH participates. At the same time the change in concentrations of hydroxyl and its global distribution have not been studied in sufficient detail in full-scale experiments. This is suggested particularly by the lack of consistency in the results of measurements of the OH content in the troposphere. One of the methods, in which ^{14}CO is used as a tracer for the determination of the average concentrations of tropospheric hydroxyl, yields a value of 1.2×10^6 molecules cm^{-3} for the northern hemisphere.[33] Another, more recent, method is based on measurement of the content of methylchloroform CH_3CCl_3.[34]

This component has an anthropogenic origin that is amenable to global quantitative determination and its sole photochemical tropospheric depletion process is the reaction with OH.

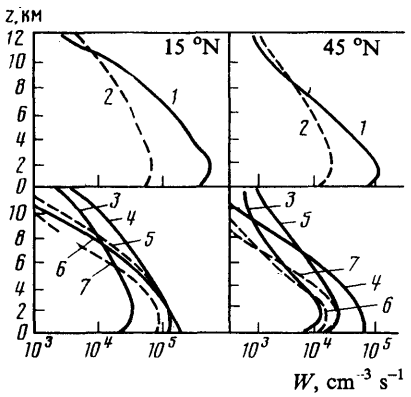


Figure 6. Mean daily rates of photochemical production and destruction of HO_x in the troposphere at 15 and 45 °N:[32] *1*, $O(^1D) + H_2O$; *2*, $H_2CO + h\nu \rightarrow H + HCO$; *3*, $OH + HO_2$; *4*, rainout of H_2O_2; *5*, $OH + H_2O_2$; *6*, $CH_3OH + OH$; *7*, rainout of CH_3OOH.

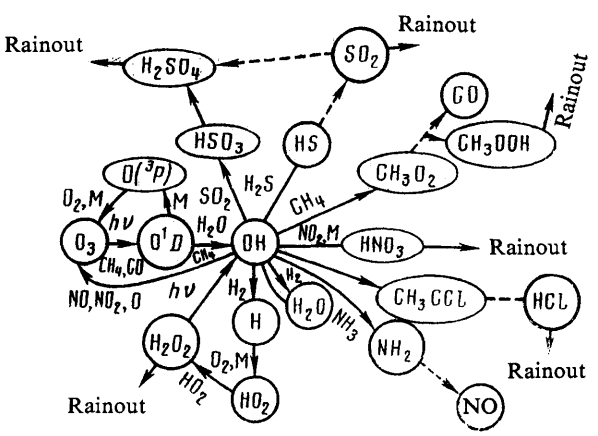


Figure 7. Scheme of photochemical processes involving OH in the troposphere.

Using this method the concentration of hydroxyl is estimated at $3-5 \times 10^5$ molecules cm^{-3} for the northern hemisphere and $0.8-2 \times 10^6$ molecules cm^{-3} for the southern hemisphere.[34] On the whole lower concentrations were generally obtained in model calculations of the global distribution of hydroxyl which were carried out recently compared to the original theoretical predictions.[35] The considerable differences in the content of tropospheric hydroxyl and hydroperoxyl may be due to certain natural factors. Thus, for example, the content of water vapour in the lower troposphere may change over relatively short intervals of time by a factor of 10 or more.[36] Then, since the rate of photolysis of gases in the atmosphere is determined as a convolution of the form

$$j_{A\rightarrow B} = \int_{\Delta\lambda} \sigma_\lambda^A q_\lambda^{A\rightarrow B} F_\lambda d\lambda, \qquad (42)$$

where $\Delta\lambda$ is the spectroscopic range of photodissociation, σ_λ^A is the cross-section of absorption of gas A at wavelength λ, $q_\lambda^{A\rightarrow B}$ is the quantum yield of the reaction, and F_λ is the flux of radiation at that wavelength. The dependence of the average concentrations of OH and HO_2 on incoming solar radiation is evident. The magnitude of F_λ, calculated from the numerical integration of the equation for transmission of solar radiation in the atmosphere, depends on the content of ozone in a column of the atmosphere, molecular and aerosol dispersion, cloud cover, etc.,[32,37] which in turn leads to different concentrations of OH and HO_2. The role of all of the factors listed above is illustrated in Fig. 8, where calculated profiles of the concentration of hydroxyl in the troposphere under different conditions are shown.

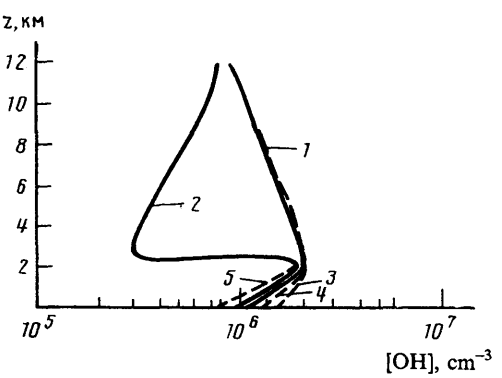
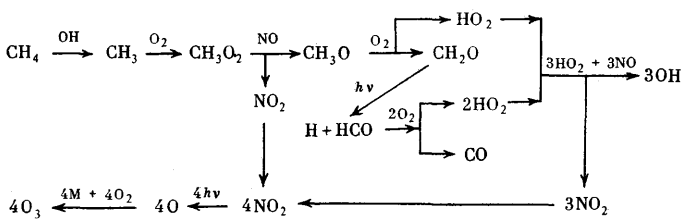


Figure 8. Vertical profiles of the mean daily concentrations of OH for different initial assumptions: *1*, standard atmosphere, contribution of molecular scattering to the photolysis of ozone not taken into account; *2*, profile of H_2O concentration from study of Mastenbrook[36] used for the calculation; *3*, standard atmosphere, contribution of molecular scattering taken into account; *4*, standard atmosphere, molecular scattering and absorption by aerosol taken into account; *5*, standard atmosphere, molecular scattering and absorption by aerosol as well as the effect of globally averaged cloud cover taken into account.

2. Oxidation of methane in the troposphere

The oxidation of CH_4 has a central place amongst the whole set of problems in tropospheric chemistry.[38] It is clear from a simplified scheme of this process that it occurs as a branched chain reaction with degenerate photochemical branching which occurs by photodissociation of formaldehyde. According to scheme (43), three hydroxyl radicals are formed in this case from a single initial one. In reality the branching is of comparatively small importance since a non-radical channel of photodissociation of H_2CO and H_2 and CO exists and because of the high probability of chain termination. It is clear from scheme (43) that on oxidation of a single CH_4 molecule a

maximum of four O_3 molecules can be formed. A further O_3 molecule can be



(43)

formed from carbon monoxide in accordance with reactions (35). In reality less than five ozone molecules are formed by oxidation of a single methane molecule because of destruction of ozone on the earth's surface and in the reactions

$$OH+O_3 \rightarrow HO_2+O_2,$$
$$HO_2+O_3 \rightarrow OH+2O_2,$$

as well as by chain termination in the reactions

$$2HO_2 \rightarrow H_2O_2+O_2,$$
$$HO_2+OH \rightarrow H_2O+O_2,$$
$$OH+NO_2+M \rightarrow HNO_3+M,$$
$$HO_2+NO_2+M \rightarrow HO_2NO_2+M,$$
$$H_2O_2,\ HNO_3,\ HO_2NO_2,\ CH_2O \rightarrow \text{rainout}$$
$$OH,\ HO_2 + \text{aerosol} \rightarrow \text{destruction}.$$

The contribution of the oxidation of methane to the production of O_3 in the troposphere was indicated in Table 2. The concentration of the active species OH, HO_2, and O_3 in the troposphere is markedly dependent on the content of methane and on the rate of its oxidation. The latter in turn is a function of the concentration of nitrogen oxides. Nitrogen oxides enter the troposphere directly from the earth and from the stratosphere, where they are formed by the destruction of N_2O. The best agreement between calculations[39] and the results of measuring the average global concentration of tropospheric ozone is achieved when there is a relative concentration of surface methane of 1.6×10^{-6} and a flux of NO_x from the earth of 1×10^{10} molecules $cm^{-2}\ s^{-1}$. The effect of the flux of nitrogen oxides from the earth and the surface concentration of methane on the minor tropospheric components OH, HO_2, O_3, NO_x are illustrated in Figs. 9–11.

The relationship between the photochemical and dynamic factors that affect the shape of the concentration profile of ozone in the troposphere has been the subject of lively debate for more than two decades.[40] At the beginning of the 1960s, when it was established as a result of a series of full-scale measurements that there was a considerable quantity of ozone in the troposphere, its formation there was linked to a flow from the stratosphere through the tropopause (the "transport" theory of tropospheric ozone).[41] At the beginning of the 1980s quite high positive correlations were found between the content of ozone in the troposphere and a number of radioactive products (^7Be) of stratospheric origin,[42] which served as an additional argument in favour of the transport theory. At the end of the 1970s a theory concerning the presence of considerable local photochemical sources of ozone in the troposphere was advanced in parallel.[38] The discovery of the possibility of generating O_3 by oxidising hydrocarbons in the presence of nitrogen oxides was the basis of this. Subsequent measurements and analysis showed, firstly, that there was a close interrelationship between the content of the gas precursors CO and NO_x and the content of ozone in the troposphere and, secondly, that there was an abnormal distribution of O_3 between the northern and southern hemispheres.[43] The latter fact is due, according to current estimates, to a corresponding lack of similarity in global anthropogenic sources of CO and NO_x in the two hemispheres.

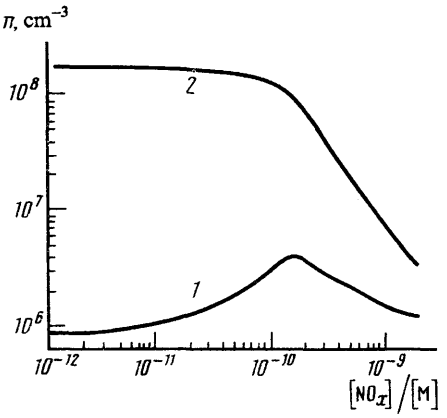


Figure 9. Surface concentrations of OH (*1*) and HO_2 (*2*) as a function of the relative concentration of NO_x, calculated using a one-dimensional model for midday conditions at 45 °N under standard atmospheric conditions ($[CH_4]_{z=0} = 1.6 \times 10^{-6}$).[32]

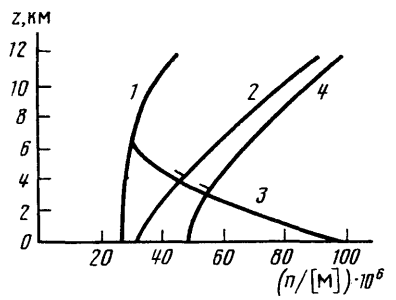


Figure 10. Model concentrations of NO_x (*1* and *3*) and O_3 (*2* and *4*) with different assumptions about the flux of NO_x from the earth's surface[40] and $[CH_4]/[M] = 1.6 \times 10^{-6}$: *1*, *2*, zero flow; *3*, *4*, 2.5×10^{10} molecules $cm^{-2}\ s^{-1}$.

Moreover, there are many feedbacks between the dynamics and photochemistry of tropospheric ozone, which is exhibited particularly in the photochemical destruction of O_3 (including that of stratospheric origin) in the "odd" hydrogen cycle—the main remover of ozone in the troposphere. Furthermore, when there is a high background content of CO, CH_4, and NOx resulting from intense anthropogenic or natural emissions, the role of the photochemical source of ozone increases, the content of O_3 increases

in the troposphere and its flux from the stratosphere to the troposphere decreases because of the levelling out of the vertical gradient of the mole fraction of O_3. The results of numerical simulation, given in Figs. 10 and 11, serve to illustrate the above conclusions. We should note also that all possible types of vertical distribution of ozone concentration in the troposphere observed in full-scale measurements can in principle be simulated by matching the values of the strength of surface sources of the gas precursors of O_3 and the vertical component of the coefficient of turbulent diffusion.[44]

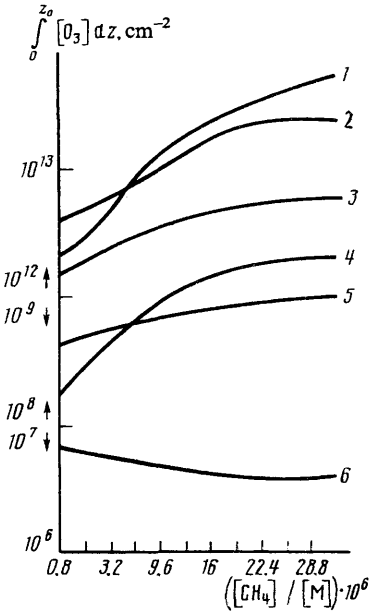


Figure 11. Content of a number of minor gas components in a column of troposphere (0–14 km) as a function of the surface concentrations of methane as determined by one-dimensional simulation.[39] $S_{NO_x} = 10^{10}$ cm^{-2} s^{-1}. *1*, CO × 10^{-5}; *2*, O_3 × 0.5 × 10^{-5}; *3*, NO_2 × 10^{-2}; *4*, CH_3O_2 × 10^{-5}; *5*, HO_2 × 10^{-5}; *6*, OH × 10^{-5}.

The scheme for the oxidation of methane described above can be extended to other members of the hydrocarbon series that are present in the atmosphere of towns and regions with dense anthropogenic sources. Thus, for example, the following sequence of reactions was proposed for ethane:[41]

$$C_2H_6+OH\rightarrow C_2H_5+H_2O,$$
$$C_2H_5+O_2+M\rightarrow C_2H_5O_2+M,$$
$$C_2H_5O_2+NO\rightarrow C_2H_5O+NO_2,$$
$$C_2H_5O+O_2\rightarrow CH_3CHO+HO_2,$$
$$CH_3CHO+h\nu\rightarrow CH_3+CHO$$

and so on in accordance with the methane oxidation scheme (43). The absence of reliable information about the content of C_2H_6 and the intermediate products of its oxidation in the atmosphere and also the insufficient data on the numerical values of the reaction rate constants makes it difficult to determine the role of C_2H_6, C_3H_8, etc. in the photochemistry of the troposphere.

V. Effect of heterogeneous reactions on the gaseous composition of the troposphere and stratosphere

In addition to a large number of different gases, aerosols also form part of the atmosphere. Aerosols are defined as systems in which particles of a solid and liquid substance are dispersed in a gaseous medium, in this case in the air of the atmosphere.[45,46] The size of aerosol particles can vary from several molecular radii to several tens of microns. It is thought that the main ways of forming aerosols are wind erosion of the soil and the release of particles of salt as a result of the bursting of air bubbles in the break-up of ocean waves. In addition to that, a considerable contribution is provided by anthropogenic sources, the relative proportion of which shows a steady tendency to increase. The difference in the mechanisms of formation and the non-uniformity of the global distribution of sources lead to a considerable variability in chemical composition, size of particles, and concentration of the atmospheric aerosol. In the present review we shall confine ourselves to a very brief examination of the physical and chemical properties of an aerosol in relation to the mechanisms of the possible action of aerosol ensembles on the gaseous composition of different regions of the atmosphere.

1. Tropospheric aerosol

In recent studies of tropospheric aerosol[47–49] it has been customary to subdivide it according to the size of particles into three characteristic bands (modes). The first mode—condensation nuclei—is made up by particles with a radius of less than 0.2 μm, the second mode contains chemically formed and growing particles of radius 0.2–1 μm, and particles with a radius of more than 1μm belong to the third mode—the dispersion mode. The distribution in size of a tropospheric aerosol is usually represented by various approximating relationships using exponential or gamma functions. The vertical profiles of particle concentration can be conveniently defined as exponential functions, the parameters of which are determined from the conditions of the full-scale experiment:

$$N_z = N_0 e^{-z/H_0}, \quad (44)$$

where N_z is the concentration of particles at altitude z, N_0 is their concentration at the surface, H_0 is an experimentally determined parameter. The following model of altitude distribution of an aerosol in the troposphere has been put forward on the basis of statistical treatment of the results of full-scale soundings:[49] the first mode: $N_0 = 10^3-10^5$ cm^{-3}, $H_0 = 2-3$ km; second mode: $N_0 = 5-300$ cm^{-3}, $H_0 = 1.5-2$ km; third mode: $N_0 = 10^{-2}-10^{-4}$ cm^{-3}, $H_0 = 0.5-1$ km. The selection of parameters N_0 and H_0 for specific calculations is determined by the characteristics of the region and the atmospheric conditions (temperature, humidity, etc.).

In the aerosol model of Toon and Pollock[50] the following particle composition in the troposphere was postulated: up to an altitude of 3 km—sulphates 50% [ammonium sulphate $(NH_4)_2SO_4$ is the main form], soil particles (SiO_2, Al_2O_3, Fe_2O_3, etc.) 35%, sea salt (NaCl) 15%; above 3 km—sulphates 60% and soil particles 40%.

According to this model the soil particles have the following elemental composition: SiO_2 53%, Al_2O_3 17%, Fe_2O_3 7%, and other compounds 23%.

2. Stratospheric aerosol

From numerous studies on samples of stratospheric aerosol it can be considered an established fact that its main chemical component under background (undisturbed) conditions is a 75% solution of H_2SO_4. The chemical homogeneity and unimodal distribution of particles by size (usually approximated by the ZOLD function) suggests that a single mechanism for formation of aerosol in the stratosphere predominates It is assumed that this mechanism involves the photochemical conversion of sulphur dioxide and carbonyl sulphide (COS) to sulphuric acid vapour followed by generation of the dispersion fraction as a result of nucleation and condensation. The nature of these processes has so far not been established with sufficient certainty but the most probable channel of SO_2 oxidation is thought to be the following sequence of reactions:

$$SO_2+OH+M\rightarrow HSO_3+M, \quad (45)$$

$$HSO_3+OH\rightarrow H_2O+SO_3 \quad (46)$$

or

$$HSO_3+O_2\rightarrow SO_3+HO_2, \quad (47)$$

$$SO_3+H_2O\rightarrow H_2SO_4. \quad (48)$$

Considerable disturbances of the chemical composition and concentrations of stratospheric aerosol occur after volcanic eruptions. This is due to the injection of a large quantity of sulphur compounds and particles of volcanic ash having a varied elemental composition through the tropopause. Typical profiles of the concentration of aerosol particles under different conditions are shown in Fig. 12.

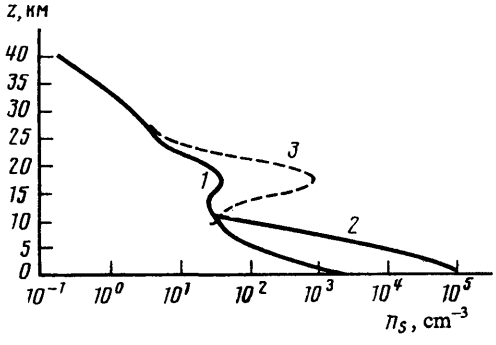


Figure 12. Vertical profiles of the concentration of aerosol particles under different atmospheric conditions: *1*, background (pure) atmosphere; *2*, urban areas; *3*, volcanic clouds.

3. Interaction in the system gases — aerosol. Heterogeneous reactions

Because of the presence of a large number of particles of varied chemical composition in the atmosphere the question as to whether a homogeneous model is applicable for the representation of atmospheric photochemical processes can be raised. In fact, it may be assumed that in a number of situations (urban areas, volcanic aerosol clouds, etc.) heterogeneous destruction on the surface of certain aerosol particles can be an additional form of depletion for chemically active minor gas components. Assuming that under the conditions of a free-molecule system ($Kn = l/\bar{r} \gg 1$) that is characteristic of the stratosphere heterogeneous decomposition occurs as a first-order reaction, the flux of molecules on to a unit surface of aerosol can be given by

$$P = \frac{[n_i]\,\bar{v}}{4} \quad (49)$$

where l is the length of the mean free path, $\bar{r}$ is the average radius of aerosol particles, Kn is the Knudsen number, $\bar{v} = (8RT/\pi\mu)^{1/2}$ is the average arithmetical thermal velocity of the molecules. If γ is the probability of a reaction occurring on collision of a molecule with an aerosol particle, then the number of interactions per unit area per second is

$$Q = \frac{[n_i]\,\bar{v}}{4}\cdot\gamma \quad (50)$$

For a spherical particle the rate of heterogeneous depletion of gas is given by the relationship[51]

$$\frac{d[n_i]}{dt} = -\frac{1}{4}\left\{\frac{8RT}{\pi\mu}\right\}^{1/2}\cdot A\cdot\left(\sum_{j=1}^{k}\gamma_j n_j\right)\cdot[n_i], \quad (51)$$

where $[n_i]$ is the concentration of reacting gas, R is the universal gas constant, T is the temperature, μ is the molecular weight, n_j is the proportion of an aerosol substance of type j relative to the total weight of aerosol, k is the number of possible chemical fractions in the aerosol, $A = 4\pi\bar{r}^2N$ is the specific surface of aerosol particles, $\bar{r}$ is the root-mean-square radius, N is the concentration of aerosol. The last two quantities can be found as the corresponding moments of the given size distribution function of aerosol particles. For small Knudsen numbers ($Kn \lesssim 1$), which is possible in the troposphere, the flow on to a unit of surface can be given by the more general expression:[52]

$$P_1 = \frac{D\,[n_i]}{\bar{r}\,(1+\lambda_0(\gamma))\cdot l/\bar{r}}, \quad (52)$$

where $D = {}^1/_3\bar{v}l$ is the diffusion coefficient, $\lambda_0(\gamma) = \lambda_0(1) + \frac{4(1-\gamma)}{3\gamma}$, with $\lambda_0(1)$ varying monotonically from 1.3 when $Kn \to \infty$ to 0.7 when $Kn = 0$. When $Kn > 1$ and $\gamma \ll 1$ Eqn. (52) transforms to (50). From the relationships obtained it it possible to include heterogeneous processes in equations of the photochemical balance for gas components reacting with the surface of aerosol particles when the corresponding information about their kinetics is available.

4. Model determinations of the possible effect of heterogeneous processes on the gaseous composition of the atmosphere

Before we consider how to represent the results of full-scale studies on the transformation of the gaseous composition of air in the atmosphere in localised zones of aerosol clouds and to a review of laboratory measurements of the rate constants of heterogeneous reactions, let us examine certain boundary measurements obtained with a one-dimensional photochemical model of the atmosphere.[3] The results shown in Figs. 11–13 reflect the degrees of possible variation of the gaseous composition when a model aerosol with given chemical and physical properties is introduced into the

atmosphere. An altitude-invariant profile of the average specific surface of aerosol particles (20 μm^2 cm^{-3}), corresponding to the content of an aerosol in stratospheric volcanic clouds, was used in the calculations.[53] By choosing an altitude-invariant profile it is possible to make a clearer assessment of the sensitivity of different regions of the atmosphere to the introduction of aerosol with given chemical properties. The probability of heterogeneous destruction of the most important minor gas components of the HO_x, O_x, and NO_x families varied over a range of $1-10^{-5}$. The calculations were carried out for a relative surface concentration of methane of 1.6×10^{-6} and a flux of nitrogen oxides $S_{NO_x} = 10^{10}$ molecules cm^{-2} s^{-1}.

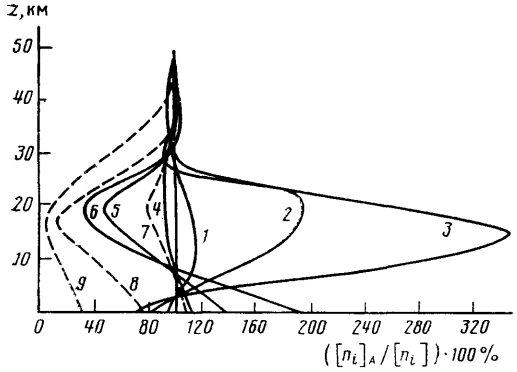


Figure 13. The change in calculated concentrations of certain gases for heterogeneous destruction of O_3 on aerosol particles for different values of y (compared to a purely homogeneous process): *1*, NO_x, $y = 10^{-4}$; *2*, NO_x, $y = 10^{-3}$; *3*, NO_x, $y = 10^{-2}$; *4*, HO_x, $y = 10^{-4}$; *5*, HO_x, $y = 10^{-3}$; *6*, HO_x, $y = 10^{-2}$; *7*, O_3, $y = 10^{-4}$; *8*, O_3, $y = 10^{-3}$; *9*, O_3, $y = 10^{-2}$.

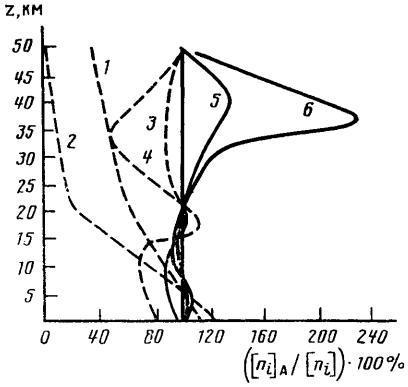


Figure 14. The same as in Fig. 13 but for the case of the destruction of NO_x: *1*, NO_x, $y = 10^{-5}$; *2*, NO_x, $y = 10^{-3}$; *3*, HO_x, $y = 10^{-5}$; *4*, HO_x, $y = 10^{-3}$; *5*, O_3, $y = 10^{-5}$; *6*, O_3, $y = 10^{-3}$.

The changes in concentrations of different gases when an aerosol that destroys O_3 is introduced are shown in Fig. 13. We should note that there is a perceptible deficiency of ozone when $y \geqslant 10^{-4}$, and that heterogeneous destruction of O_3 in the lower stratosphere and upper troposphere (altitude 10–25 km) has the greatest effect on the gas composition. A decrease in the concentration of ozone as a result of its heterogeneous destruction gives rise to a corresponding change in the concentrations of the other components that react with O_3, since the photochemical equilibrium of the system as a whole undergoes an overall shift. It can be established that the calculated deviations in the content of HO_2 and NO_x are generally in good agreement with the main photochemical mechanisms of the stratosphere and troposphere that were examined in the previous sections. Thus, for example, the depletion of ozone in the stratosphere, where the nitrogen cycle is the main cycle of its destruction in the gas phase, results in an increase in concentration of NO_x at these altitudes. In the troposphere, where the destruction of ozone in the hydrogen cycle predominates, the concentration of gases of this family, in particular HO_2, increases.

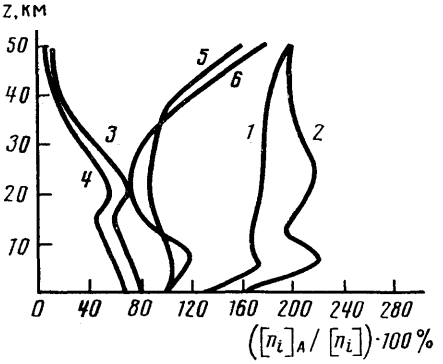


Figure 15. The same as in Fig. 13 but for the case of the destruction of OH: *1*, NO_x, $y = 0.1$; *2*, NO_x, $y = 1$; *3*, OH, $y = 0.1$; *4*, OH, $y = 1$; *5*, O_3, $y = 0.1$; *6*, O_3, $y = 1$.

The second group of model calculations involves a study of the reaction of the system when the heterogeneous destruction of NO_x is introduced (Fig. 14). The critical value of y in this case is about 10^{-5} and the most sensitive region is the upper part of the stratosphere. The nature of the deviations in concentrations of NO_x and HO in Fig. 14 can readily be attributed to the fact that a reduction in $[NO_x]$ causes an increase in O_3 content and increases the consumption of OH and HO_2 in the destruction of ozone. At the same time the content of NO_x increases quite unexpectedly in the lower part of the troposphere despite the development of an additional heterogeneous depletion. This effect may serve as a good illustration of the existence of non-linear feedbacks between the troposphere and stratosphere within the atmospheric photochemical system. In fact the increase in ozone content in the stratosphere as y increases results in a decrease in intensity of the photolysis of ozone via the channel in which $O(^1D)$ is formed in the troposphere because of the screening of UV radiation and hence in a corresponding decrease in the rate of formation of OH by the reaction $H_2O + O(^1D) \rightarrow OH + OH$. This process has the greatest effect on the balance of hydroxyl precisely at altitudes corresponding to the lower troposphere. With a reduced OH content the concentration of NO_x increases, since the effectiveness of its main channel of consumption—$OH + NO_2 + M \rightarrow HNO_3 + M$—is reduced. This

effect more than compensates the heterogeneous destruction of nitrogen oxides in the lower troposphere and becomes more significant when y increases. The calculated data on the change in concentration of the components OH, O_3, NO_x when the heterogeneous destruction of OH is introduced into the model are shown in Fig. 15. A significant change in gaseous composition of the atmosphere is to be expected in this case when $y = 0.1-1$. This change is more apparent in the upper part of the stratosphere, which is quite in accordance with theory. Firstly, the lifetime of HO_x in this region increases in photochemical gas-phase reactions (see Fig. 1), and as a result the relative contribution of heterogeneous depletion to the total destruction of HO_x increases. Secondly, since the hydrogen cycle plays a predominant part in the destruction of ozone in the upper stratosphere, the concentration of O_x increases significantly at altitudes of the order of 40 km when the content of the components at the HO_x family decreases. The introduction of other minor gas components into the balanced equations of heterogeneous depletion has only a slight effect on the calculated concentrations if the aerosol has a specific surface of 20 μm^2 cm^{-3} that is typical of the stratosphere.

Table 3. Probabilities of capture of atmospheric gases by surfaces of different materials.

Gas	Chemical surface	Probability of destruction	Refs.
H_2O_2	H_2SO_4	$7.8\cdot10^{-4}$	[54]
HNO_3	H_2SO_4	$2.4\cdot10^{-4}$	[54]
HO_2NO_2	H_2SO_4	$2.7\cdot10^{-5}$	[54]
N_2O_5	H_2SO_4	$3.8\cdot10^{-5}$	[54]
H_2O	H_2SO_4	$2\cdot10^{-3}$	[54]
NH_3	H_2SO_4	10^{-3}	[54]
OH	H_2SO_4	$5\cdot10^{-4}$	[54]
OH	H_2SO_4	0,1—1	[55]
O_3	Al_2O_3	$(2.3\div8.8)\cdot10^{-5}$	[56]
O_3	H_2SO_4	$\leqslant10^{-8}$	[57]
O_3	H_2SO_4	10^{-10}	[58]
O_3	SiO_2	$\leqslant10^{-4}$	[54]
O_3	Al_2O_3	$5\cdot10^{-5}$	[59]
O_3	SiO_2	10^{-9}	[58]
HO_2	Al_2O_3, Fe_2O_3	$3\cdot10^{-3}$	[60]
OH	SiO_2	$\sim10^{-2}$	[55]
OH	ice	1	[55]

5. Laboratory experiments and stratospheric processes

Examination of models of the chemical composition and the vertical distribution of atmospheric aerosol in combination with the results of numerical simulation indicate that a study of the reactions, of O_3, OH, and NO_x with the surfaces of the most common aerosol particles — H_2SO_4, SiO_2, Al_2O_3, and Fe_2O_3 — is of the greatest interest. In contrast to the rate constants of reactions in the gas phase, comparatively few constants of heterogeneous reactions have been measured, and they have mainly been obtained at room temperature. The existing values, as presented in Table 3, have been obtained during the last 15 years using various experimental techniques. Some of them have been repeatedly verified over this period, since the photochemical balance of ozone is considerably dependent on them. Thus, for example, according to Harker and Ho,[57] the decomposition of O_3 on H_2SO_4 can make a significant contribution to the destruction of stratospheric ozone under background conditions if $\gamma_{O_3} \gtrsim 10^{-4}$. Subsequent experimental measurements[57,58] showed that it does not exceed 10^{-8} even when the surface of sulphuric acid is activated with various metal cations. Thus, even in the presence of volcanic sulphuric acid clouds when the concentration of stratospheric aerosol increases by a factor of 10—100, this process cannot have any substantial effect on ozone depletion. At the same time the results of full-scale probing of the gaseous composition of the stratosphere in localised zones of volcanic aerosol clouds after the powerful eruptions of Agung, St. Helens, and El Chichón suggest that steady negative correlations exist between the concentrations of ozone and aerosol.[61—63] From the value of the probability (0.1—1) of the destruction of OH on the surface of H_2SO_4 obtained using EPR/LMR, Elanskii[63] et al. proposed another mechanism for the deficit of ozone occurring in these situations. It is known from the experimental data that the deficit of ozone in a cloud, reaching a maximum of 30% and with an average value of 7—8%, occurs when the cloud is centred at an altitude of about 20 km. The nitrogen cycle of ozone destruction is characteristic of the photochemistry of the stratosphere in this region, and the conversion of active nitrogen oxides to the buffer components HNO_3 and HO_2NO_2, which are inert towards O_3, mainly involves the members of the family of "odd" hydrogen:

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

and

$$HO_2+NO_2+M\rightarrow HO_2NO_2+M.$$

It is evident that when there is intense heterogeneous depletion of OH on the volcancic sulphuric acid aerosol, the content of hydroxyl and hydroperoxyl must decrease and the concentrations of nitrogen oxides increase in parallel intensifying the destruction of ozone in the gas-phase photochemical "odd" nitrogen cycle. This mechanism was taken as the basis for a one-dimensional simulation[63] (Fig. 16) using actual aerosol profiles obtained in probes of volcanic clouds after an eruption of the El Chichón volcano.[53] Another probable mechanism for the destruction of O_3 involves its decomposition on an aerosol containing Al_2O_3. However, although the aerosol particles containing Al_2O_3 can pass into the stratosphere together with volcanic ash during powerful eruptions, they are not likely to have a significant effect on ozone because of rapid precipitation. The emission of this type of aerosol into the stratosphere in quantities that are capable of giving rise to a competing gas-phase depletion are only possible with intense artificial effects, in particular, from nuclear explosions on the earth's surface. This situation has been analysed in detail by Zvenigorodskii et al.[3]

In summing up let us make two observations of a general nature.

1) Despite the fact that the decomposition constants of O_3 on Al_2O_3 obtained by different authors are in good agreement, the question of the degree of correspondence between the properties of a laboratory sample (pellets of pure Al_2O_3) and those of a real aerosol, in which Al_2O_3 is in the form of conglomerates and undergoes natural ageing and the effect of water vapour, remains open.

2) It is unlikely that the catalytic properties of a stratospheric sulphuric acid aerosol differ very much from the properties of the surface of H_2SO_4 in laboratory experiments. Therefore, the experimentally determined rate constants of the reactions of different gases with H_2SO_4 can be reliably used in solving problems of

atmospheric chemistry. Nevertheless, there is no significant information about the catalytic activity of H_2SO_4 towards nitrogen oxides.

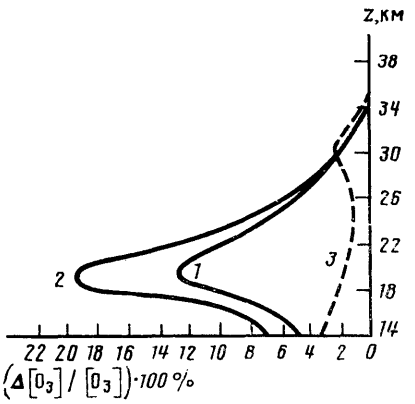


Figure 16. Decrease in the concentrations of ozone in the stratosphere in relation to the capacity and altitude of the maximum of a volcanic aerosol cloud:[63] *1*, maximum at an altitude of 20 km, A_{max} = 20 μm² cm⁻³; *2*, the same, A_{max} = 50 μm² cm⁻³; *3*, maximum at an altitude of 30 km, A_{max} = 20 μm² cm⁻³.

6. Heterogeneous processes in the troposphere

The aerosol fraction in the troposphere varies according to its chemical composition and aggregate state—droplets of moisture and ice crystals, irrigated and unirrigated aerosol particles. If the well-defined variability in the composition of a tropospheric aerosol is also taken into account, this all considerably hinders determinations of the effect of heterogeneous factors on photochemical processes in this region. Moreover, the active lower boundary—the underlying surface—is a sink on a global scale for a whole number of gas components. Originally, in studying heterogeneous processes in the troposphere research workers confined themselves to two mechanisms: rainout of gases that are soluble in water by precipitation (wet rainout) and the destruction of gas-phase components on the underlying surface (dry deposition). The dry deposition of gases occurs through their adsorption or destruction in chemical reactions on the surface. The evident consequence of a chemically active lower boundary is the presence of a concentration gradient and diffusive flow of molecules directed towards the surface that react with the earth, which in atmospheric chemistry can be identified with the "deposition" of a complete column of reacting gas. The rates of dry deposition of a number of gases have been measured under artificial conditions[64–66] above different underlying surfaces. This process can have a definite effect on the content of chemically active gases in the lower part of the troposphere, for example, in seasonal changes in the nature of the surface (Fig. 17).[67]

Wet rainout in the troposphere was for a long time reduced to the removal of precipitation of soluble gases and those reacting in water. A typical time for this process according to initial estimates corresponds to the time of global cycle of tropospheric moisture and amounts to about 10 days. It is evident that such a scheme for representing heterogeneous processes in the troposphere, also accepted in a number of current photochemical models designed for studying mechanisms of the global distribution of gas components, is a considerable simplification of the real picture.

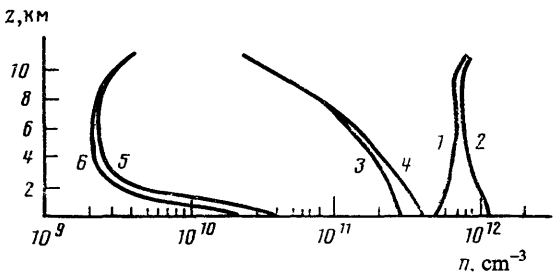


Figure 17. Vertical profiles, of O_3, NO_x, and HO_2 concentrations in the troposphere for different rates of ozone deposition on the surface:[67] *1*, concentration of O_3 for a rate of deposition W_{O_3} = 0.6 cm s⁻¹ (earth); *2*, the same for W_{O_3} = 0.02 cm s⁻¹ (snow); *3*, $[HO_x] \times 10^3$, W_{O_3} = 0.06 cm s⁻¹ (earth); *4*, $[HO_x] \times 10^3$, W_{O_3} = 0.02 cm s⁻¹ (snow); *5*, $[NO_x] \times 10$, W_{O_3} = 0.6 cm s⁻¹ (earth); *6*, $[NO_x] \times 10$, W_{O_3} = 0.02 cm s⁻¹ (snow).

Firstly, atmospheric gases have varying solubility, as determined by Henry's constant.

Secondly, the partial return to the atmosphere of gases that are not dissociated in water on evaporation of water droplets is not taken into account.

Thirdly, an important role is played in the troposphere by heterogeneous processes involving an irrigated and unirrigated aerosol.

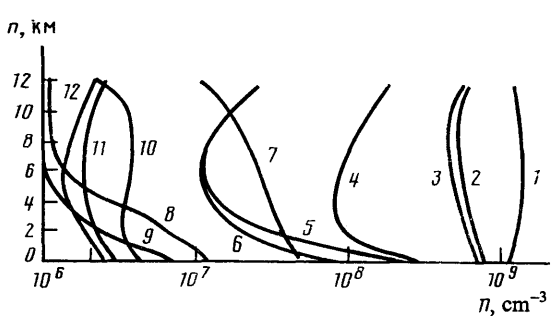


Figure 18. Calculated concentrations of HNO_3 (*1–4*), NO_x (*5–8*), and HO_x (*9–12*) for rate constants of rainout K_z, s⁻¹ of: 0 (*1, 5, 9*); 1.15 × 10⁻⁶ (*2, 6, 10*); 5 × 10⁻⁶ (*3, 7, 11*); 10⁻⁵ (*4, 8, 12*).[67]

It is clear that a description of heterogeneous chemical processes in the troposphere must be based on a consideration of all types of reactions taking into account the individual properties of a reacting

gas. Up to the present time the complete absence of experimental data on the probabilities of capture of molecules which interact with an aqueous surface remains the main problem. The calculation of the integrated rate of washout of gases in atmospheric cloud and aerosol systems based on the solution of kinetic equations for a single particle followed by generalising it for an ensemble of particles with a given size distribution function does not present major difficulties, but in all the overall relationships thus obtained the probability of capture appears as a parameter.[68] The only current method for independent determination of the rates of rainout is based on measurement of the chemical composition of the deposits. However, in this case other sources of uncertainty arise, related to assumptions about the exposure time of the droplet, the chemistry of liquid-phase processes, and errors in the measurements themselves, which considerably reduce the accuracy of the estimates obtained.

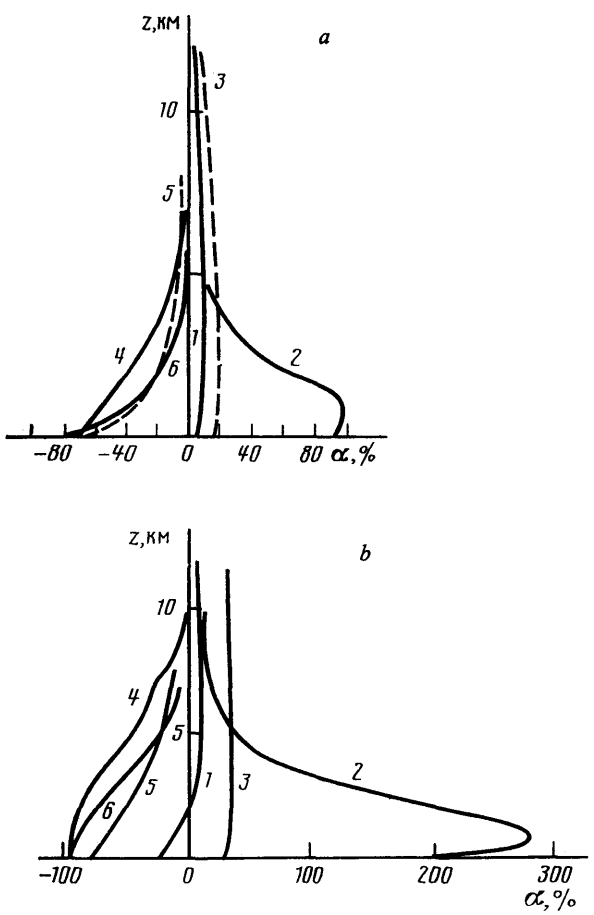


Figure 19. Change in the relative concentrations of O_3 (*1*), NO_2 (*2*), CO (*3*), H_2O_2 (*4*), OH (*5*), and HO_2 (*6*) when the destruction of OH (*a*) and HO_2 (*b*) radicals on aerosols is taken into account: *a*, $\gamma_{OH} = 1$; $N = 5 \times 10^4 \exp(-z)$ cm^{-3}; *b*, $\gamma_{HO_2} = 8 \times 10^{-3}$; $N = 5 \times 10^5 \exp(-z)$ cm^3.

Because of these factors, it would seem natural to assume that the washout constants in the existing photochemical models of the troposphere must differ considerably. And in fact, a scatter of the order of magnitude of 10^{-5} to 10^{-6} s^{-1} is reached. Thus, Logan[32] recommended that for the simulation of wet rainout of H_2O_2, HNO_2, HNO_3, HO_2NO_2, H_2CO, and CH_3OOH the following values of the constants should be used: up to an altitude of $z = 4$ km, $k = 2.31 \times 10^{-6} \exp(1.6-0.4z)$ s^{-1}; and when $z > 4$ km, $k = 2.31 \times 10^{-6}$ s^{-1}. The rate constant of the additional depletion of H_2O_2 on an irrigated aerosol in the continental troposphere was given by the expression: $2 \times 10^{-6} \exp(-z/1.2) + 4 \times 10^{-8}$ s^{-1}. The latter relationship was obtained with the assumption that the whole aerosol is irrigated, H_2O_2 is irreversibly destroyed in the aqueous shell of aerosol particles by interacting with the ferrous cation Fe^{2+} and the probability of capture is the same as for the surface of sulphuric acid,[54] namely 10^{-3}. It has already been mentioned that a general deficiency of current photochemical models of the troposphere that represent rainout of gases by precipitation is the use of the same relationships for a whole series of components that are susceptible to rainout for a determination of the parameters of this process, without taking into account their individual properties. At the same time even the few results of analysis of the chemical composition of deposits show that in the hydrocarbon series, for example, H_2CO is rained out to a much lesser extent than other members of the series, since the concentrations of formaldehyde in the analysed samples of rainwater are low.[69,70] Moreover, as is demonstrated by model calculations, the concentrations of the minor gases in the lower part of the troposphere are very dependent on the rainout rate constants. Numerical experiments to determine the concentrations of minor gases when the rate constants of rainout vary over the wide range of $0-10^{-5}$ s^{-1} (Fig. 18) show that in this case these concentrations vary over several hundred percent.[67]

In recent times because of the problem of acid rain, composite photochemical models of the troposphere that combine theories about the chemical processes in the vapour and liquid phases have started to be developed.[70,71] However, a weak point of these models is still the same lack of data on the coefficients of capture.

Heterogeneous reactions on the surface of an unirrigated aerosol should also be made the subject of careful study. As was indicated earlier, attempts to examine the interaction between an aerosol and gases in the atmosphere that are based on the assumption that the whole aerosol is irrigated frequently yield results that do not correspond to current ideas about the physicochemical processes in this region. The clearest example is provided by the study of Isaksen and Crutzen,[72] in which a similar approach using the assumption of an aerosol sink results in the deviations of the calculated concentrations of H_2O_2 and HO_2 from those observed reaching two orders of magnitudes. The incorrectness of such an approach is suggested also by the results of many experiments on irrigation of aerosols in clouds and mists. Thus, for example, it was found that 100% irrigation only occurs for large submicron particles, whereas out of the total number of particles with a radius of < 0.4 μm, in which about 90% of the total surface of a stratospheric aerosol is concentrated, not more than 2% is irrigated.[46] Thus, it is evident that the role which an unirrigated tropospheric aerosol plays in heterogeneous chemical processes in the troposphere is at least comparable to the role of irrigated and droplet aerosols. Gershenzon et al.[4] studied the change in gaseous composition of the troposphere taking into account the possibility of heterogeneous destruction of OH and HO_2 radicals on the surface of model aerosols. From the results of two studies[55,60] typical values for a tropospheric aerosol are $\gamma_{OH} = 0.1-1$ and $\gamma_{HO_2} = 10^{-3}-10^{-2}$. The results of a calculation[4] of the values of $\alpha = [(n_A - n)/n] \times 100$

(n_A and n are the concentrations of the minor components in aerosol and molecular atmospheres respectively) are presented in Fig. 19. The calculations were carried out for aerosols with an average radius of 10^{-5} for an altitude distribution of their concentration in accordance with the equation $N = N_0 \exp(-z)$. The results suggest that there is a decrease in concentrations of the active compounds of the hydrogen family (OH, HO_2, H_2O_2) and an increase in content of CO, O_3, and NO_x in the aerosol troposphere as a result of the heterogeneous destruction of OH and HO_2.

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