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Transformation of nitrogen- and sulphur-containing compounds in the atmosphere and procedures for reducing the amounts of nitrogen and sulphur oxides in industrial waste

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Various nitrogen- and sulphur-containing compounds of both natural and anthropogenic origin enter the atmosphere of our planet. Examples of compounds of natural origin are reduced sulphur compounds [H_2S, CS_2, $(CH_3)_2S$, COS] and nitrogen-containing compounds (NH_3, N_2O). The principal sources of nitrogen- and sulphur-containing compounds of anthropogenic origin are nitrogen and sulphur oxides.

Various aspects of the protection of the air on our planet and in the first place the problem of "acid rain" require the knowledge of the mechanisms of the chemical transformations of nitrogen- and sulphur-containing compounds in the atmosphere. It is known that the appearance of "acid" rain may be caused by the increased content in the troposphere of the oxides NO_x and SO_2. The knowledge of the mechanisms of the formation and removal of NO_x and SO_2 from the troposphere is therefore essential. The understanding of the principles governing the self-purification of the tropsphere makes it possible to employ them for the creation of technological processes leading to a decrease in the anthropogenic NO_x and SO_2 waste ejected into the atmosphere.

The gas-phase processes relevant to the problem under consideration have been investigated for several years at the Institute of Chemical Physics of the USSR Academy of Sciences. Problems of practical importance are solved jointly with other organisations. For example, the solution of the problem of the influence of photochemical sources of sulphur and nitrogen compounds on the background level of air pollution on a regional and global scale is being sought jointly with the Laboratory for Atmospheric Monitoring. The development of methods for the purification of industrial gaseous waste is being prosecuted together with the Dzerzhinskii All-Union Thermotechnical Institute (VTI), the Southern Branch of the VTI (YuzhVTI), and the Krzhizhanovskii Energy Institute (ENIN).

Consistent study of the elementary reactions, on the basis of which the mechanisms of the chemical transformation of particular compounds in the atmosphere were devised, served as the starting point for the research being prosecuted. These studies have made a definite contribution to the understanding of the mechanisms of the oxidation of hydrogen sulphide, carbon disulphide, and ammonia in the atmosphere which has been achieved and have made it possible to propose physicochemical models for the technological developments designed to reduce the nitrogen and sulphur oxide waste ejected into the atmosphere.

Table 1. Examples of the elementary processes investigated.

(a) Reactions of radicals with components of the atmosphere (R + M → products)

R	M	Refs.
NH_2	O_2, NO, NO_2, O_3, SO_2	[1–5]
HNO	NO, HNO	[6]
OH	NH_3, CS_2	[7, 8]
HS	O_2, NO_2	[9]
HSO	NO_2, NO	[9, 10]
HO_2	NO, H_2S, HO_2, NH_2, HNO	[11, 12]

(b) Heterogeneous radical destruction processes (R + surface → destruction)

R	Surface	Refs.
HO_2	Teflon, quartz, boric acid, metal oxides, NaCl, etc.	[13, 14]
OH	Quartz, sulphuric acid, Teflon, boric acid, ice, etc.	[15]
NH_2	Quartz, quartz coated by adsorbed NH_3	[16]

(c) Elementary processes with participation of excited species ($A^* + M \rightarrow$ products, $A^* + M \rightarrow A + M$)

A*	M	Refs.
$O(^1D)$	NH_3, H_2, CH_4, O_3	[17, 18]
$NH_2(v)$	O_2, N_2, O_3, CH_4	[19]
$NO_2(v)$	NO_2, CO	[20]
$OH(v)$	N_2, O_2, O_3, CH_4, H_2	[18, 21]
$O_3(v)$	O	[22]

The majority of the gas-phase reactions in the atmosphere involve the participation of radicals. For this reason, three types of elementary processes were investigated: the reactions of radicals with the components of the atmosphere; the radical-destruction reactions on surfaces close in chemical composition to that of aerosols; elementary processes with participation of excited species (Table 1). The present day requirements are such that virtually only studies of elementary processes by direct spectroscopic methods are of practical value. For this reason, we developed new effective methods for the investigation of elementary processes based on advances in laser and computer techniques.[23]

It is possible to differentiate three types of methods. Intracavity laser spectroscopic (IRLS) methods[24] were developed jointly with members of the Lebedev Physical Institute. Priority on a worldwide scale has been achieved in these methods. The laser magnetic resonance (LMR) method in the IR range combined with EPR spectroscopy is the second procedure. An apparatus of this kind was first devised by Gershenzon and co-workers to investigate elementary processes.[25] The third procedure is the laser-induced fluorescence method combined with laser photolysis.[26]

These methods are highly sensitive ($\sim 10^7$ particles cm^{-2}), possess high time (10^{-7} s) and spectral (10^{-2} cm) resolutions, and make it possible to investigate various types of elementary processes.

With the aid of the above methods, we investigated the elementary reactions of the NH_2, HS, HSO, OH, HO_2, and HNO radicals with the components of the atmosphere (Table 1). On the basis of the results obtained in these studies and the available literature data, the mechanisms of the oxidation of ammonia, hydrogen sulphide, and carbon disulphide in the atmosphere were established.

It was assumed previously that minor components of the atmosphere are oxidised via the mechanism

$$M \xrightarrow{+OH} R \xrightarrow{+O_2} \ldots,$$

where M is a minor component of the atmosphere and R a radical. This mechanism involves two postulates. Firstly, as a rule the primary reaction of the minor component M is with a hydroxyl radical. Secondly, the main reaction of the R radical formed is with molecular oxygen. However, studies in recent years have shown that each minor component M can exhibit its specific features in its chemical transformation in the atmosphere and the above postulates are not general.

As suggested earlier, the mechanism of the oxidation of ammonia corresponds to the traditional mechanism

$$NH_3 \xrightarrow{+OH} NH_2 \xrightarrow{+O_2} NH_2O_2 + \ldots .$$

It has been shown[1,2] that the radical NH_2 hardly reacts with molecular oxygen at room temperature. The theoretical explanation of this finding is that the adduct NH_2O_2 has a weak N–O bond and rapidly decomposes in the reverse direction with formation of an NH_2 radical. The reactions of the NH_2 radical with the minor components of the atmosphere NO_2, NO,[3] and O_3[4] were investigated and it was shown that these reactions are fairly effective. The mechanism of the oxidation of ammonia in the atmosphere can be represented as follows:

$$NH_3 + OH \rightarrow NH_2 + H_2O, \quad (1)$$

$$NH_2 + NO_2 \rightarrow N_2O + H_2O, \quad (2)$$

$$NH_2 + NO \rightarrow N_2 + H_2O, \quad (3a)$$

$$NH_2 + NO \rightarrow N_2 + H + OH, \quad (3b)$$

$$NH_2 + O_3 \rightarrow NH_2O + O_2. \quad (4)$$

Reactions (2) and (3a) lead to the removal of nitrogen oxides, since the stable products NO_2 and N_2 are formed. A product of reaction (4) is the NH_2O radical whose reactions have not so far been investigated because of the lack of spectroscopic data for this radical. Nevertheless, our experimental data demonstrate qualitatively that the chemical transformation of this radical can lead to the formation of HNO and then NO_x, i.e.

$$NH_2O \rightarrow HNO \rightarrow NO_x.$$

There are two opposed views in the literature concerning the role of ammonia in the formation of nitrogen oxides in the atmosphere: some workers believe that the oxidation of ammonia is a major source of NO_x in the troposphere, while others believe that ammonia hardly contributes to the formation of NO_x in the troposphere. Within the framework of the mechanism established one may introduce the parameter α defined as the ratio of the rates of removal and formation of NO_x:

$$\alpha = \frac{k_2[NO_2] + k_3[NO]}{k_4[O_3]},$$

where k_2, k_3, and k_4 are the reaction rate constants and $[NO_2]$, [NO], and $[O_3]$ are the concentrations of the corresponding compounds in the troposphere.

Since the temperature dependences of the rate constants have been determined, it follows that, knowing the profiles of nitrogen oxides and ozone with respect to altitude and humidity, it is easy to calculate the influence of ammonia on the formation and elimination of NO_x. Estimates have shown that there may be regions in the lower troposphere for which α may be both greater and less than unity. However, if ammonia enters the stratosphere, then it undoubtedly removes nitrogen oxides, i.e. promotes the conservation of the ozone layer.[27]

As examples of the oxidation of reduced sulphur compounds, we shall consider the mechanisms of the oxidation of carbon disulphide and hydrogen sulphide. The mechanism of the oxidation of carbon disulphide in the troposphere can be represented as follows:

$$CS_2 + OH \longrightarrow CS_2OH \xrightarrow{O_2} COS + HSO_2.$$

According to this mechanism, the primary reaction is the association of CS_2 with the hydroxyl radical to form the adduct CS_2OH.[7] The adduct can decompose in the reverse reaction or can react with molecular oxygen.[28] It is then that further reactions of CS_2OH in the presence of oxygen lead to the formation of carbonyl sulphide and sulphur dioxide.[29] One can therefore postulate that the primary products are COS and HSO_2. The reactions of the radicals will be discussed below, but it is clear that it is in fact the reactions of HSO_2 with the components of the atmosphere which lead to the formation of sulphur dioxide.

The classical mechanism proposed previously for the oxidation of hydrogen sulphide was the reaction of hydrogen sulphide with the hydroxyl radical which affords the HS radical, which then reacts with molecular oxygen. However, it was found that the HS radicals react effectively with minor components of the atmosphere (nitrogen dioxide, ozone),[9,30] whereas the reaction with molecular oxygen is fairly slow. Although the existing estimate of the rate constant for the reaction of the HS radical with oxygen[31] still does not permit its complete exclusion, nevertheless one can assume at the present time the following sequence of principal reactions:

$$H_2S \xrightarrow{+OH} HS \xrightarrow{+NO_2,\ O_3} HSO \xrightarrow{+O_3,\ NO_2} HSO_2 \xrightarrow{O_2} SO_2.$$

In this chain of elementary reactions,[7,9,10,30,31] virtually all the rate constants are known. We investigated the reactions of the HS and HSO radicals.[7,9]

As already stated, in the majority of the mechanisms considered, the primary oxidation reaction was assumed to be the reaction with the hydroxyl radical. This seemingly natural hypothesis was based on the fact that this radical is very reactive and its concentration in the atmosphere is adequate. However, data have been obtained recently[32] showing that the reaction of H_2S with the relatively unreactive HO_2 radical proceeds effectively:

$$HO_2 + H_2S \rightarrow HSO + H_2O. \quad (5)$$

This finding was checked both as regards the kinetics of the decrease in the HO_2 concentration and as regards the accumulation of HSO. The rate constant for this reaction is virtually the same as for the reaction of the hydroxyl radical with hydrogen sulphide. Since the concentration of the HO_2 radicals is approximately 100 times greater than the concentration of the OH radicals, we postulated a new mechanism for the oxidation of hydrogen sulphide:

$$H_2S + HO_2 \rightarrow HSO + H_2O,$$
$$HSO + NO_2 \rightarrow HSO_2 + NO,$$
$$HSO + O_3 \rightarrow HSO_2 + O_2,$$
$$HSO_2 + O_2 \rightarrow HO_2 + SO_2.$$

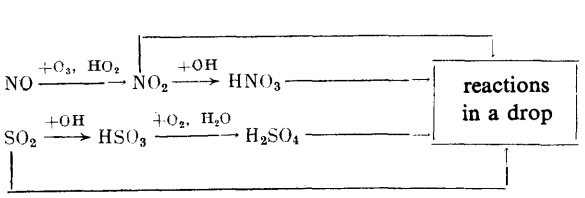
This is a chain mechanism of the oxidation of H_2S. The chain carriers are only two radicals—HO_2 and HSO. The rate constants for these reactions are known. The formation of HSO_2 in the reaction of HSO with ozone is tentative.

If our data for reaction (5) are correct, then the mechanism of the oxidation of carbon disulphide should also be revised. In this case, one can postulate the following mechanism:

$$HO_2 + CS_2 \rightarrow CS_2HO_2 + O_2 \rightarrow COS + HSO.$$

As regards other reduced compounds, the mechanism of their oxidation in the air has been less well investigated and therefore will not be discussed. One can only note that the principal product of the oxidation of these compounds is sulphur dioxide.

Nitrogen and sulphur oxides are removed from the atmosphere in two ways:[33] as a result of the dry deposition of SO_2 and NO_x and as a result of washing out by rain. There are in the latter case two ways in which nitrogen and sulphur oxide enter a rain drop, which can be illustrated by the following scheme:



The nitrogen dioxide and sulphur dioxide molecules can dissolve in water drops. The rate of their removal can then depend significantly on the concentrations in the drops of other substances, because if the latter react chemically with nitrogen dioxide and sulphur dioxide, then the ability of drops to absorb these gases will increase significantly compared with the level determined by Henry's law. The second channel leading to their removal involves gas-phase reactions with the formation of nitric and sulphuric acid molecules which enter the water drops.

Water drops containing nitrogen and sulphur oxides fall on the surface of our planet as rain. In certain regions, where there is much ammonia in the sinks for nitrogen oxides, the NH_2 radical can play a role analogous to that of hydroxyl radicals (its gas-phase reactions with nitrogen and sulphur dioxide):

$$NH_2 \xrightarrow{+NO_2} N_2O + H_2O,$$

$$NH_2 \xrightarrow{+SO_2} NH_2SO_2.$$

The latter reaction has been recently investigated.[34]

It follows from the foregoing that the OH and HO_2 radicals play an important role in the gas-phase atmospheric chemistry. It is therefore important to understand how the heterogeneous processes involving the destruction of these radicals on aerosols influence the nitrogen and sulphur formation and elimination processes. Processes leading to the destruction of the OH and HO_2 radicals on different surfaces, presented in Table 1, have been investigated.[13–15] The experiments were performed using surfaces whose chemical composition was close to that of the aerosols.

By generalising the experimental data obtained, the authors were able to conclude that the accommodation coefficients, i.e. the probability of the destruction of the radicals (γ) per collision with the surface, are within the following ranges for the OH and HO_2 radicals:

$$\gamma_{OH} \approx 10^{-2}—1; \quad \gamma_{HO_2} = 10^{-3}—10^{-2}.$$

Mathematical modelling based on the standard model of the atmosphere at aerosol concentrations typical for urbanised regions has shown that it is necessary to take into account the heterogeneous processes involving the destruction of both OH and HO_2 radicals.[35] The heterogeneous radical destruction reactions lead to an increase in the concentration of pollutants (for example, sulphur dioxide) in the lower atmosphere, which means that the self-purification of the troposphere is impaired with increase in the concentration of aerosols.

The calculations have also shown[36] that the heterogeneous OH radical destruction processes must be taken into account in the chemistry of the stratosphere as well. After volcanic eruptions, droplets of sulphuric acid, on which the heterogeneous destruction of OH radicals takes place very effectively, appear in the stratosphere. Allowance for the destruction of OH radicals leads to an increase in the concentration of nitrogen oxides, which leads in its turn to a decrease in the concentration of nitrogen in the ozone layer.

The third type of elementary processes investigated includes processes involving excited species, which are presented in Table 1. These studies were designed to elucidate the role of vibrationally excited species in the photochemistry of the stratosphere. As was to be expected, vibrationally excited species do not play a significant role in the troposphere.

As already stated, an appreciable amount of N_2O molecules travel from the surface of our planet to the atmosphere. These molecules are chemically inert and therefore readily reach the stratosphere, where they can participate in the formation of nitrogen oxides either under the influence of sunlight or as a result of their reaction with electronically excited oxygen atoms. The movement of NO_x to the troposphere naturally depends on the mechanism of the photochemical reactions in the stratosphere. The experimental data obtained for the deactivation processes and the reactions of excited species have made it possible to analyse the important role of the vibrationally excited species in the photochemistry of the stratosphere. Such species may be the vibrationally excited molecules of ozone $O_3(v)$ and the hydroxyl $OH(v = 9)$ (v is the

vibrational quantum number). The OH(v = 9) molecules are formed in the reaction

$$H + O_3 \rightarrow OH(v = 9) + O_2.$$

The interaction of OH(v = 9) with oxygen can lead either to the deactivation of OH(v = 9) or to the reaction

$$OH\,(v = 9) \xrightarrow{+O_2} H + O_3,$$
$$OH\,(v = 9) \xrightarrow{+O_3} OH\,(v = 8) + O_2.$$

Data obtained recently by Cheskis[37] for elementary processes involving OH(v) have shown that the rate constants for these two processes are comparable and they should therefore be taken into account in the photochemistry of the stratosphere. Allowance for these processes leads to an increase in the calculated ozone concentration in the ozone layer.

The interaction of OH(v = 9) with molecular nitrogen could also occur via two pathways:

$$OH\,(v = 9) \xrightarrow{+N_2} N_2O + H,$$
$$OH\,(v = 9) \xrightarrow{+N_2} OH\,(v = 8) + N_2.$$

Unfortunately there are no data concerning the pathway followed in the reaction of OH(v = 9) with nitrogen. However, estimates have shown that, if the rate constant for this pathway exceeds 3×10^{-15} cm^3 s^{-1}, then, when account is taken of OH(v = 9), the rate of formation of N_2O is comparable to the rate of arrival of N_2O from anthropogenic sources in the atmosphere. Ideas of this kind show that such high effectiveness of the vibrational energy in such reactions is possible.

At high altitudes (80 km), the concentration of oxygen atoms is high and vibrationally excited ozone molecules $O_3(v)$ are formed very effectively by the reaction

$$O + O_2 + M \rightarrow O_3(v) + M.$$

The $O_3(v)$ molecules can be either deactivated or they can enter into a chemical reaction with an oxygen atom:

$$O_3\,(v) \xrightarrow{+O} 2O_2,$$
$$O_3\,(v) \xrightarrow{M} O_3.$$

Experimental studies on the elementary processes with participation of $O_3(v)$ have shown[22] that the vibrational form of energy is effective in the reaction pathway. Estimates demonstrated[38] that processes with participation of $O_3(v)$ should also be taken into account in the mechanisms operating in the chemistry of the stratosphere. This process diminishes the calculated ozone concentration.

The development of methods for reducing the anthropogenic nitrogen and sulphur oxide waste ejected into the atmosphere constitutes an independent and important problem associated with the protection of the atmosphere. The understanding of the natural mechanisms of the elimination of nitrogen and sulphur oxides from the atmosphere and the study of elementary reactions made it possible to put forward chemical models for the reduction of nitrogen and sulphur oxide waste. Table 2 presents three methods for the removal of nitrogen and sulphur oxides from industrial gases. These methods are based to some extent on the principles governing natural sinks for the removal of nitrogen and sulphur oxides from the atmosphere.

The gas-phase ammoniacal purification method is based on the reactions which also occur in the atmosphere:

$$OH \xrightarrow{+NH_3} NH_2,$$
$$NH_2 \xrightarrow{+NO} N_2 + H_2O,$$
$$NH_2 \xrightarrow{+NO} N_2 + H + OH,$$
$$NH_2 \xrightarrow{+NO_2} N_2O + H_2O. \qquad (6)$$

The difference is that in the atmosphere there is a sufficiently high concentration of OH radicals (ultimately due to the effect of sunlight) and these processes can occur at room temperature. In the purification method considered, ammonia must be introduced at a fairly high temperature (~1000 K) of the effluent gases, where the branching route (6), capable of maintaining the required concentration of OH and NH_2 radicals, is significant. Studies by this method are conducted jointly with the VTI, where the technological version of this method has been applied. The method has been tested on the experimental industrial plant at the Kirovakan heat and power generating plant. However, an earthquake precluded the completion of these experiments. It has to be said that the method has not found a wide-scale development abroad hitherto, but ways of applying it at lower temperatures are being sought continuously. It is seen from the example of this method that the dry methods for the removal of nitrogen oxides must be based on the preparation of OH and NH_2 radicals at sufficiently high concentrations and low temperatures. These can be chemical, radiation, or photolytic methods.

Table 2. Methods for the removal of NO_x and SO_2 from effluent industrial gases.

Method	Reagent	Gas	Degree of purification, %	Products
Gaseous ammoniacal	NH_3	SO_2	–	N_2, H_2O
		NO_x	80	
Radiation-chemical	without reagents	SO_2	90	HNO_3, H_2SO_4
	NH_3	NO_x	90	$(NH_4)_2SO_4$, NH_4NO_3
Ozone-ammoniacal	O_3, NH_3	SO_2	95	
		NO_x	80	$(NH_4)_2SO_4$, N_2, N_2O

In the radiation-chemical purification methods, the required NH_2 and OH concentrations are established by the reaction of the effluent gas with electrons. Studies conducted recently at the Institute of Chemical Physics of the USSR Academy of Sciences under the supervision of A P Shvedchikov jointly with the State Institute of Non-Ferrous Metals showed that the radiation-chemical method is promising for the purification of not only the effluent gases from heat and power generating plants containing <0.1% of carbon dioxide but also of the waste gases from industrial non-ferrous metallurgical undertakings, where the carbon dioxide content is higher. This leads to the possibility of using industrial electron accelerators not only for reducing the amount of ecologically harmful impurities (SO_2, NO_x) in waste gases but also possibly for

the creation of a new technology for the synthesis of sulphuric acid as a result of the radiation-chemical oxidation of sulphur dioxide.

The ozone-ammoniacal method is based on the principle used by nature to remove NO_x and SO_2 from the atmosphere in which a significant role is attributed to the reactions in the water drops. Ozone is needed only to convert NO into NO_2 in the gas phase:[39]

$$NO \xrightarrow{+O_3} NO_2 + O_2.$$

Next NO_2 and SO_2 enter the water drops where chemical reactions take place and the rate of removal of NO_2 and SO_2 is determined. Studies by V A Lozovskii, Yu N Kozlov, and A N Petrov (Institute of Chemical Physics of the USSR Academy of Sciences) have shown that under optimum conditions the purification process depends significantly on the interaction of NO_2 with SO_2 dissolved in the drops, which can be illustrated schematically as follows:

$$(NO_2)_{gas} \rightarrow (NO_2)_{aq} \rightarrow NO_2^- \xrightarrow{+HSO_3^-} NH_4^+,\ SO_4^{2-},\ N_2,\ N_2O.$$

This method is being developed jointly with VTI, YuzhVTI, and ENIN. It has been tested on the experimental industrial plant of the Moldavian Hydroelectric Power Station. The design of a full-scale plant for the purification of the flue gases from the heat and power generating plant in Dushanbe is now being completed.

It is noteworthy that this method has been designed in the USSR and has many advantages over foreign methods.

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