

## Lecture 15. Environmental pollution by nitrogen oxides. The formation of nitrogen oxides

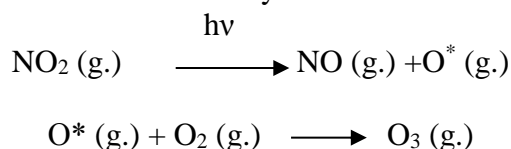
**The purpose of the lecture:** to provide information on environmental pollution with nitrogen oxides, the mechanisms of their formation.

**Expected results:** students gaining knowledge about the ways of environmental pollution with nitrogen oxides and the ways to prevent them.

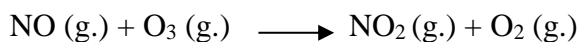
Nitrogen oxides are considered primary atmospheric pollutants. They get into the air during the combustion of various fuels - thermal power plants, oil refineries, flue gases of industrial enterprises and exhaust gases from a motor transport port. Nitrogen oxides  $N_xO_y$  are capable of causing double environmental pollution.

Firstly, they dissolve in water with the formation of nitrous and nitric acid. These acids are among the secondary pollutants and, along with sulfuric and sulfuric acids, lead to acid rain

Secondly, nitrogen oxides can combine with hydrocarbons, which leads to the appearance of photochemical smog. Hydrocarbons, soot also enter the atmosphere as a result of the burning of fossil fuels and are therefore primary pollutants. A photochemical smog arises as a result of a complex sequence of reactions involving radicals. For the first stage of this complex process, the presence of ultraviolet solar radiation is necessary.

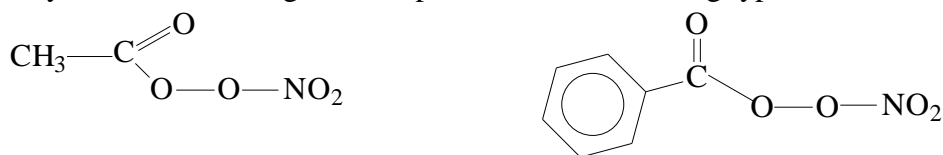


Ozone is a toxic gas for both animals and plants. It is a secondary atmospheric pollutant. If there are no hydrocarbons in it, ozone combines with nitrogen monoxide, resulting in the formation of nitrogen dioxide again:

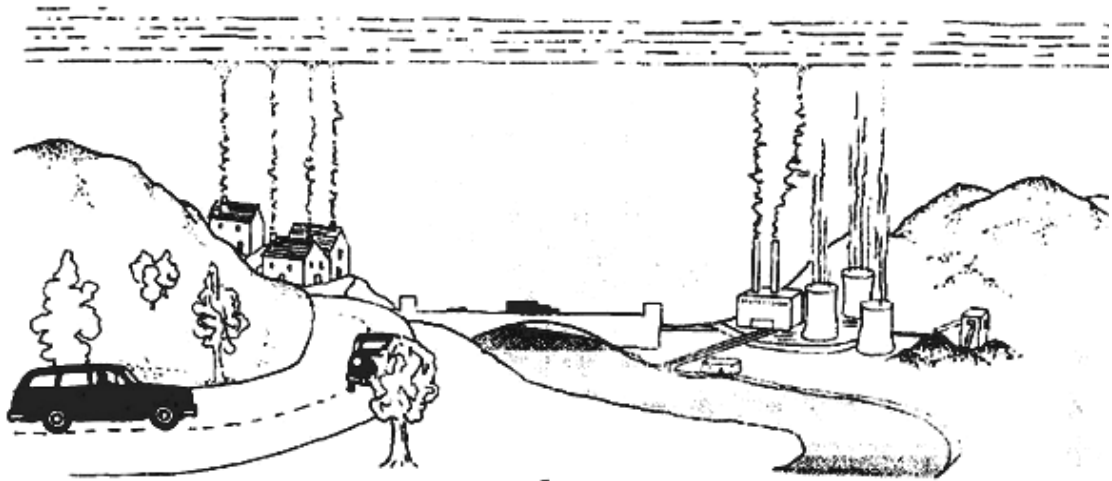


Thus, in the specified "closed cycle" the content of nitrogen dioxide in the atmosphere is maintained at the same level.

However, in the presence of hydrocarbons in the atmosphere, this cycle is violated. Ozone, reacting with unsaturated hydrocarbons, forms organic radicals that combine with nitrogen oxides to form aldehydes and nitrate organic compounds of the following type:



Along with ozone, such compounds are secondary atmospheric pollutants that lead to the appearance of photochemical smog (Fig. 15.1).



*Fig. 15.1.* Atmospheric conditions favoring the formation of photochemical smog

In many cities around the world this problem is complicated by the formation of the so-called inversion layer in the atmosphere. It provides a layer of heated air, which is located above the city and does not allow the lower layer of colder air to exit. This heated layer is usually moisture free and has maximum transparency for solar radiation.

The result is the accumulation of secondary pollutants held in the lower layer of air. The photochemical smog arising under such conditions can often be observed as a haze hanging over the city in hot weather. This haze is caused by smog particles.

### **The formation of nitrogen oxides**

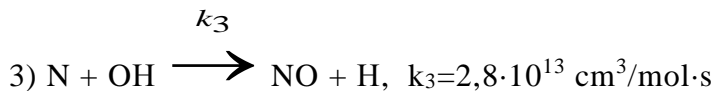
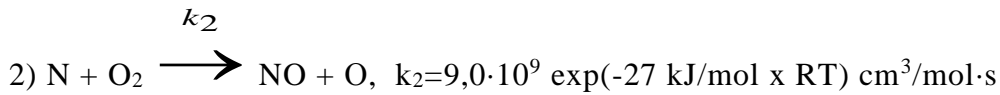
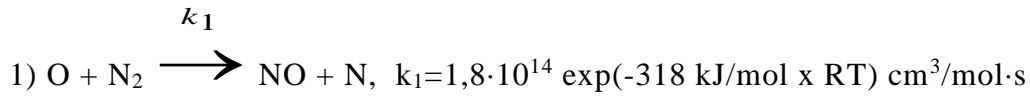
Since the use of hydrocarbon fuels in combustion processes is constantly increasing, combustion products are clearly becoming a powerful source of environmental pollution. The main combustion products are carbon dioxide (carbon dioxide -  $\text{CO}_2$ ) and water. Until recently, these products were considered absolutely harmless. Currently, even carbon dioxide is becoming an important component in the balance of the atmosphere, and it is with an increase in its concentration in the atmosphere that an increase in the global greenhouse effect is associated.

Nitrogen oxides are also combustion products, although they are not formed in such large quantities. In the second half of the twentieth century, it became apparent that the nitrogen oxides  $\text{NO}$  and  $\text{NO}_2$ , collectively called  $\text{NO}_x$ , are the main reagents in the formation of photochemical smog and ozone in the atmosphere of cities, and in general in the troposphere. In addition,  $\text{NO}_x$  participate in chain reactions, removing ozone from the stratosphere, which causes the growth of ultraviolet radiation reaching the Earth's surface. Consequently, reducing the formation of nitrogen oxides has become one of the most important burning problems. As before, the hope for a decrease in nitrogen oxide emissions is associated with the development of increasingly detailed and complex mechanisms of chemical reactions describing the formation of  $\text{NO}_x$ , and with an understanding of the interaction of chemical kinetics and gas dynamics. Such models indicate new ways to reduce these harmful emissions.

Currently, four different ways of formation of  $\text{NO}_x$  are distinguished. This is the thermal path, the rapid formation of  $\text{NO}$ , the formation of nitrogen oxides through the formation of  $\text{N}_2\text{O}$  and the formation of nitrogen oxides from fuel nitrogen. We will discuss each of these paths in sequence. In addition, examples of some primary methods for reducing the amount of formed nitrogen oxides  $\text{NO}_x$  (modification of the combustion process itself) and some secondary methods (processes for burning the fuel) that chemically convert  $\text{NO}$  to harmless products (such as  $\text{H}_2\text{O}$  and  $\text{N}_2$ ) will be given.

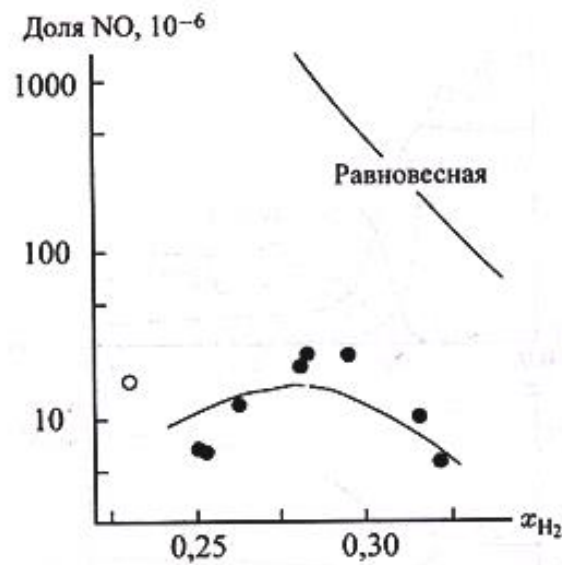
### Thermal path of NO formation (formation of NO by the Zeldovich mechanism)

The thermal path of NO formation, or the formation of NO by the Zeldovich mechanism (postulated in 1946 by Ya.B.Zeldovich) consists of the following elementary reactions.



The name “thermal” is used because reaction 1 has a very high activation energy due to the strong triple bond in the  $\text{N}_2$  molecule, and therefore it is fast enough only at high temperatures. Since reaction rate 1 is rather low, this is the limiting stage of the process of thermal formation of NO.

Figure 15.2 shows the results of measurements of the NO concentration in hydrogen-air flames of a pre-mixed mixture and their comparison with the calculation results (at a distance  $z = 3 \text{ cm}$  behind the flame front) according to reaction scheme 1-3. A fairly good agreement was obtained between the calculated and experimentally measured concentrations; the latter indicates that the rate constants  $k_1$ ,  $k_2$ , and  $k_3$  are well known.



**Fig. 15.2.** Experimentally measured and calculated concentrations of NO in hydrogen-air flames depending on the stoichiometric ratio

While the concentration of  $\text{H}_2\text{O}$  or  $\text{CO}_2$  can be roughly predicted using the assumption of reaching an equilibrium state, the concentration of NO can be predicted only very inaccurately from the assumption of equilibrium. Reaction 1 is so slow that equilibrium is achieved only for times that are much longer than typical times the mixture was in the high-temperature region (usually a few milliseconds).

In accordance with reactions 1-3, for the rate of formation of NO, we obtain

$$\frac{d[\text{NO}]}{dt} = k_1[\text{O}][\text{N}_2] + k_2[\text{N}][\text{O}_2] + k_3[\text{N}][\text{OH}] \quad (1)$$

Because the

$$\frac{d[N]}{dt} = k_1[O][N_2] - k_2[N][O_2] - k_3[N][OH] \quad (2)$$

and we can assume that the quasistationary condition (fast reactions 2 and 3) is satisfied for nitrogen atoms, i.e.

$$\frac{d[N]}{dt} = 0$$

for the rate of formation of NO we find

$$\frac{d[NO]}{dt} = 2k_1[O][N_2] \quad (3)$$

Thus, the concentration of NO can be minimized by reducing the concentrations of  $[N_2]$ ,  $[O]$  or  $k_1$  (for example, by decreasing the temperature).

The concentration of  $N_2$  can be measured quite accurately using a probe or accurately estimated under the assumption of equilibrium in a burnt gas. For the concentration of oxygen atoms, it is very attractive to assume that an equilibrium state is reached, which is easily calculated from thermodynamic data. However, the assumption of achieving an equilibrium state, especially at relatively low pressures, gives an error in estimating the concentration of oxygen atoms  $[O]$  by more than 10 times. This super-equilibrium concentration is created by chemical reactions in the flame front.

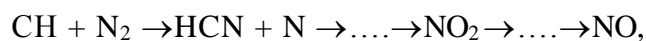
The best approximation for the concentration of oxygen atoms  $[O]$  is the assumption of partial equilibrium. As a result, we get,

$$[O] = \frac{k_{H+O_2} \cdot k_{OH+H_2} \cdot [O_2][H_2]}{k_{OH+O} \cdot k_{H+H_2O} \cdot [H_2O]} \quad (4)$$

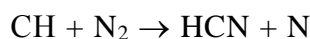
Thus, the concentration of O atoms can be calculated from the concentrations of  $H_2O$ ,  $O_2$  and  $H_2$ , which are easily measured or calculated, since all these products are stable. As shown earlier, the concept of partial equilibrium is valid only for high temperatures (above 1700 K). Here this limitation is not very important, since the rate constant  $k_1$  is small at  $T < 1700$  K.

### **Fast NO formation (formation of NO by the Fenimore mechanism)**

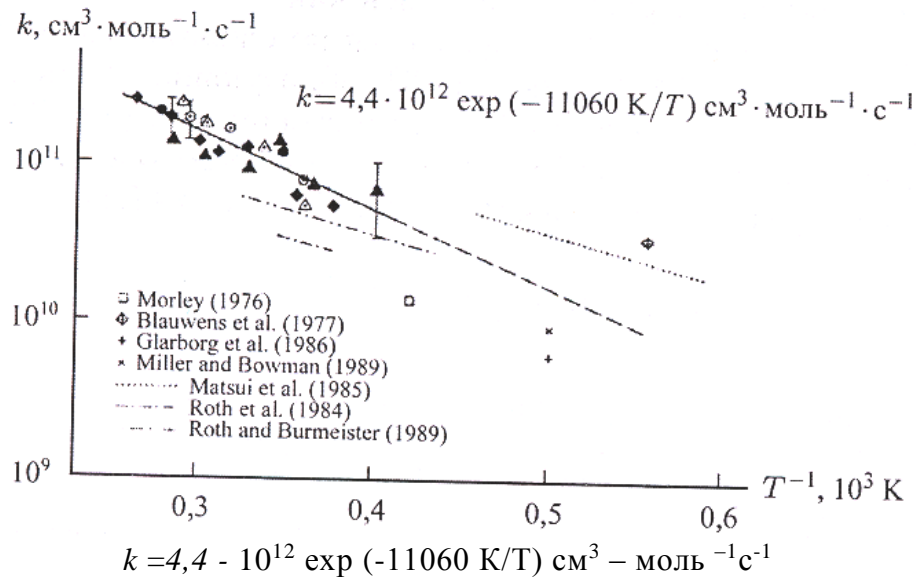
The mechanism of the rapid formation of NO was proposed by Fenimore (1979) based on the results of measurements of the concentration of  $[NO]$  over a flat hydrocarbon flame. He noted that the concentration of  $[NO]$  did not reach zero when the probe reached the flame front downstream from the unburned fresh mixture, as the Zeldovich mechanism predicted. An additional mechanism for the rapid formation of NO in the flame front is more complex than the mechanism of thermal formation of NO, since it involves CH radicals, which were previously considered as an insignificant intermediate component, i.e. NO is formed by a complex reaction scheme. CH radicals formed as intermediate components only in the flame front react with air nitrogen to form hydrogen cyanide acid, which then reacts with the formation of NO



Exact data on the limiting stage

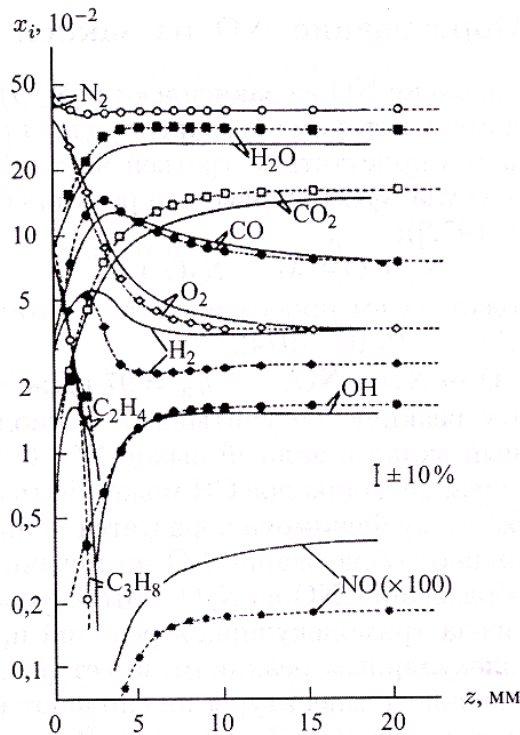


are presented on the graph of the Arrhenius dependence of the rate constant of this reaction in Fig. 15.3. Currently, this constant is known accurate to coefficient 2.



**Fig. 15.3.** The rate constants for the reaction  $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$

Predictions of the formation mechanism of NO Fenimore are less accurate; this can be seen from fig. 15.4, which shows the profiles of the mole fractions of the components in a low pressure flame of a stoichiometric  $\text{C}_3\text{H}_8$ -air mixture. Dots indicate the results of experiments, and lines indicate the results of calculations.



**Fig. 15.4.** Profiles of mole fractions of components in a flame of a stoichiometric propane-air mixture

The activation energy of the  $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$  reaction is only about 75 kJ/mol ( $T_a \sim 9000 \text{ K}$ ), compared with 318 kJ/mol ( $T_a = 38200 \text{ K}$ ) for the thermal formation of NO; therefore, unlike thermal, the rapid formation of NO occurs at relatively low temperatures (about 1000 K).

## Literature

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