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## SHORT COMMUNICATION

Kinetics of nitric oxide oxidation<sup>‡</sup>

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Nitrogen oxides are nowadays a subject of global concern. Several types of nitrogen oxides exist in the environment:  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ . The abbreviation  $\text{NO}_x$  usually relates to nitric oxide  $\text{NO}$ , nitrogen dioxide  $\text{NO}_2$ , and nitrous oxide  $\text{N}_2\text{O}$ . The first two are harmful pollutants for both environment and human health, whereas the third is one of the greenhouse gases. Implementation of stringent  $\text{NO}_x$  emission regulations requires the development of new  $\text{NO}_x$  removal technologies from exhaust gases. One of many proposals for  $\text{NO}_x$  emission reduction is the application of an oxidizing agent which would transform  $\text{NO}_x$  to higher nitrogen oxides with higher solubility in water. The main objective of the paper was to present the rate constant of nitric oxide oxidation, determined in our studies.

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**Keywords:** air pollution, nitrogen oxides, kinetics, oxidation

Environment protection is nowadays a popular subject of social and scientific discussions. Especially in the face of increasing restrictions regarding  $\text{NO}_x$  pollutants emission, followed by high financial penalties. In our opinion, the most dangerous type of environmental contamination is air pollution since it affects the whole ecosystem. Chemicals emitted to the atmosphere can also be easily transmitted into hydro and lithosphere. Furthermore, air pollution has a serious effect on human health. The main source of air contamination are anthropogenic activities such as combustion processes of fossil fuels present in power plants, vehicles and other incineration processes. Key combustion generated pollutants are sulfur oxides (principally  $\text{SO}_2$ ), particulate matter, carbon monoxide, unburned hydrocarbons, and nitrogen oxides ( $\text{NO}_x$ ). In our studies, we have focused on nitrogen oxides because they are responsible for a wide range of environmental problems. Acid rain, photochemical smog, tropospheric ozone, weakening of the ozone layer, and even global warming can be associated with  $\text{NO}_x$  emission.  $\text{NO}_x$  became a subject of interest in 1952, when its role in the formation of pho-

tochemical smog was formulated (Muzio & Quartucy, 1997).

The abbreviation  $\text{NO}_x$  usually stands for nitric oxide ( $\text{NO}$ ), nitrogen dioxide ( $\text{NO}_2$ ), and nitrous oxide ( $\text{N}_2\text{O}$ ), which from the photochemical point of view can be called ‘fresh’, since they reach atmosphere in this form. Both  $\text{NO}$  and  $\text{NO}_2$  are toxic to humans.  $\text{NO}$  is less toxic than  $\text{NO}_2$  but it is unstable and reacts readily with oxygen to form  $\text{NO}_2$ . Even in low concentration it can be a cause of acute lung injury with pneumonitis and fulminant pulmonary edema (Woodrow, 1997). Unlike these two gases,  $\text{N}_2\text{O}$  does not pose a direct threat to human health. However, it is considered as air pollutant because it is one of the greenhouse gases with the absorbency of infrared radiation 270 times higher than that of carbon dioxide ( $\text{CO}_2$ ) (Wright, 2003). Moreover, it indirectly affects the ozone layer through photochemical reactions. A few more nitrogen oxides exist in the environment and they all play an important role in photochemistry of the atmosphere.

By now, the most popular concept of reducing  $\text{NO}_x$  emissions is the selective catalytic reduction

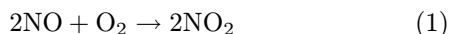
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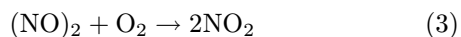
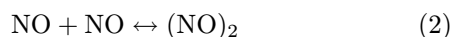
(Brüggemann & Keil, 2008). Other widely used techniques are absorption, adsorption, electrical discharge, etc. Nevertheless, in light of the implemented stringent  $\text{NO}_x$  emission regulations all these methods turn out to be insufficient. Solution to this problem was drawn from the atmospheric chemistry and the fact that nitric oxide constitutes up to 95 % of total  $\text{NO}_x$  emissions from combustion processes, the rest is nitrogen dioxide. Nitric oxide has higher solubility and is thus preferred for absorption processes. What is more, it is said that at low temperatures, below 500 K, the efficiency of selective catalytic reduction is strongly dependant on initial concentration of  $\text{NO}_2$  in the flue gas (Van Durme et al., 2008). Many studies were conducted in order to find a fast, efficient, and cost effective method to increase the  $\text{NO}_2/\text{NO}$  ratio in the exhaust gases (Javed et al., 2007; Mok & Lee, 2006; Mok & Yoon, 2006; Wang et al., 2007). Nitric oxide can be oxidized through chemical or physicochemical processes. Chemical oxidation can be performed by addition of an oxidizing agent: oxygen, ozone, hydrogen peroxide, etc. Non-thermal plasma, electron beam, and photooxidation are physicochemical processes that can enhance the oxidation rate.

Our studies are focused on NO oxidation by means of oxygen, basically as an introduction to studies on NO ozonation and in order to obtain reference data for further kinetic investigations.

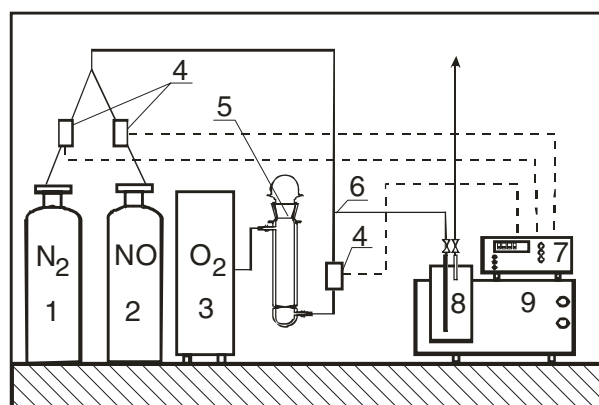
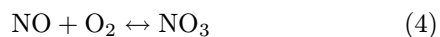
First studies on the kinetics of NO homogenous reaction with oxygen were conducted in 1918 by Bodenstein and Wackenheim



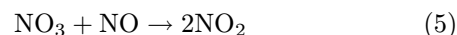
As Tsukahara et al. (1999) reported, three different mechanisms for NO oxidation have been proposed by now. The first mechanism suggests a termolecular reaction, where three molecules have to collide simultaneously (two molecules of NO and one of  $\text{O}_2$ ) to form a transient complex which, in a single step, forms two molecules of  $\text{NO}_2$ . An alternative proposal involves two steps and the existence of an intermediate. For example a pre-equilibrium mechanism with the dimer of NO as intermediate



In this mechanism, the reaction represented by Eq. (2) is fast and the reaction in Eq. (3) is slow and determines the rate of the overall NO oxidation process. Another proposition is that NO is first involved in a reversible reaction with  $\text{O}_2$  forming an intermediate,  $\text{NO}_3$ , which reacts further with NO as follows



**Fig. 1.** Experimental set-up: 1 – nitrogen gas cylinder, 2 – nitrogen oxide gas cylinder, 3 – oxygen generator, 4 – mass flow meters, 5 – drying jar, 6 – ‘T’ shaped joint, 7 – mass flow meters regulator, 8 – gas cuvette, 9 – FTIR spectrometer.



In this case, the rate determining step is the second reaction (Eq. (5)) (Tsukahara et al., 1999; Wink & Ford, 1995).

An overview of the experimental set-up is given in Fig. 1. The gas mixture was prepared by mixing  $\text{N}_2$  (1) with a small amount of NO nitric oxide (2) using mass flow meters Brooks Instruments 5850 TR (4). Both gases were purchased from Linde-Gas. NO and  $\text{N}_2$  mixture was combined with an oxygen stream in a ‘T’ shaped joint (6). Oxygen was obtained from air by a PSA (Pressure Swing Adsorption) oxygen generator AirSep (3) and then passed through a drying jar (5). Gaseous reagents were analyzed using a Fourier Transform Infrared spectrometer Jasco FTIR-4200 (9) equipped with a  $0.4 \text{ dm}^3$  gas cuvette (8) which was used as a batch reactor.

Series of experiments were conducted for NO initial concentrations ranging from 150–540 ppm with an excess concentration of oxygen at the temperature of  $20^\circ\text{C}$ . Then, other series of experiments were performed for NO concentrations 165 ppm, 190 ppm, and 308 ppm with a smaller amount of oxygen at the temperature of  $20^\circ\text{C}$ . However, calibration curves for NO (0–550 ppm) and  $\text{NO}_2$  (0–580 ppm) had first to be determined. Two calibration gas mixtures (1 % of NO in  $\text{N}_2$  and 1 %  $\text{NO}_2$  in air) provided by Linde-Gas were used for calibration purposes. All calculations were performed for standard conditions. During all FTIR measurements, the IR spectra from  $4000 \text{ cm}^{-1}$  to  $700 \text{ cm}^{-1}$  were monitored with a  $4 \text{ cm}^{-1}$  resolution.

During these studies, numerous spectra were obtained; two exemplary ones are shown in Fig. 2. They represent the composition of reaction gases before and after the NO oxidation. In case of the spectrum obtained before the reaction, two peaks representing NO ( $1907 \text{ cm}^{-1}$ ) and  $\text{NO}_2$  ( $1628 \text{ cm}^{-1}$ ) were present, the

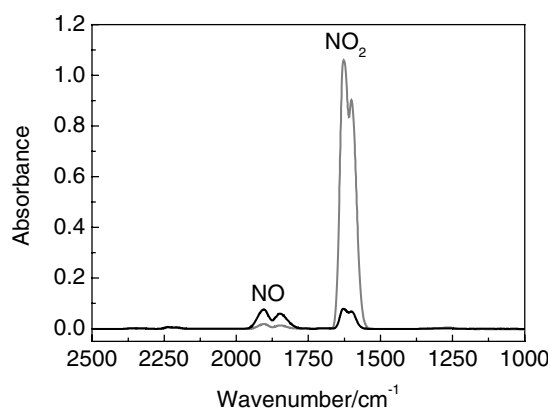


Fig. 2. FTIR spectra for nitrogen oxides (290 ppm) before (black line) and after (grey line) their reaction with oxygen.

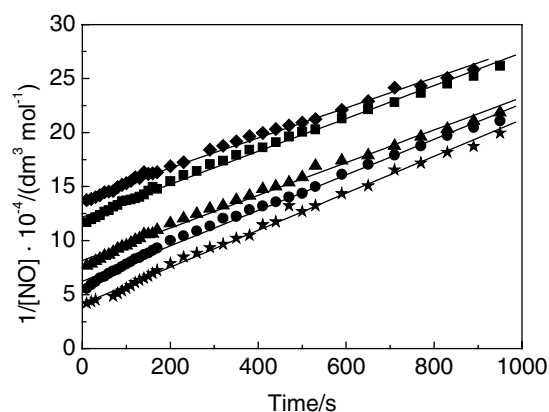


Fig. 3. Oxidation of nitric oxide at different initial NO concentrations:  $7.27 \times 10^{-6} \text{ mol dm}^{-3}$  (◆),  $8.54 \times 10^{-6} \text{ mol dm}^{-3}$  (■),  $1.30 \times 10^{-5} \text{ mol dm}^{-3}$  (▲),  $1.79 \times 10^{-5} \text{ mol dm}^{-3}$  (●),  $2.39 \times 10^{-5} \text{ mol dm}^{-3}$  (\*).

same peaks were observed in the spectrum after the reaction; however, a significant change in their heights was noticed. The extinction coefficient of  $\text{NO}_2$  is much larger than that of  $\text{NO}$  causing a big difference in the peaks heights.

The main goal of the first series of experiments was to evaluate the rate constant for nitric oxide oxidation. Since in both pre-equilibrium mechanisms the rate equations can be simplified to the one that is true for the termolecular mechanism, we decided to calculate the rate constant according to Tsukahara et al. (1999)

$$-\frac{d[\text{NO}]}{dt} = 2k[\text{NO}]^2[\text{O}_2] \quad (6)$$

where  $k$  is the rate constant,  $t$  represents time, and  $[\text{NO}]$  and  $[\text{O}_2]$  denote the concentration of nitric oxide and oxygen, respectively.

Generally, the  $\text{NO}$  oxidation reaction is of the third order; however, it can be simplified to a second-order reaction when excess amount of oxygen is introduced

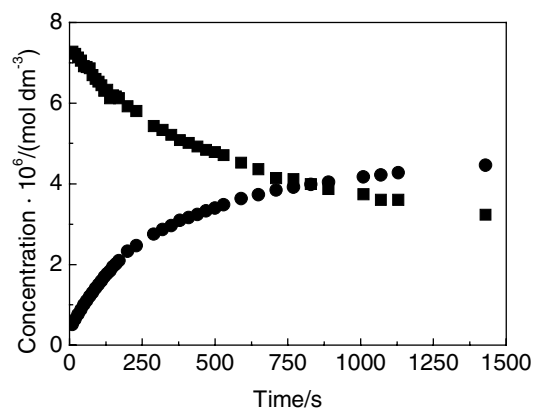


Fig. 4. Formation of nitrogen dioxide (●) from nitric oxide (■). Initial  $\text{NO}$  concentration 160 ppm).

to the reaction space. Then the rate expression becomes

$$-\frac{d[\text{NO}]}{dt} = 2k_1[\text{NO}]^2 \quad (7)$$

where

$$k_1 \cong k[\text{O}_2]_0 \quad (8)$$

and  $[\text{O}_2]_0$  denotes the initial oxygen concentration.

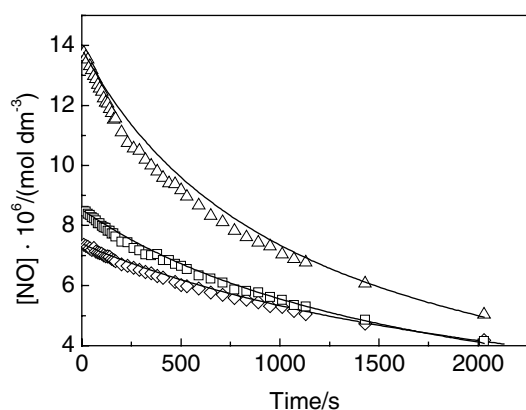
In our experiments, the concentration of oxygen ( $1.41 \times 10^{-2} \text{ mol dm}^{-3}$ ) was approximately  $10^4$  times higher than the initial  $\text{NO}$  concentration. In this case, the mixture of reactive gases consisted of approximately 30 % of  $\text{O}_2$  and 70 % of  $\text{N}_2$  and the concentrations of  $\text{NO}$  and  $\text{NO}_2$  were in the range of ppm values. Fig. 3 shows experimental data, for various initial  $\text{NO}$  concentrations plotted according to the second-order reaction kinetics represented by Eq. (9), which is the integral form of Eq. (6)

$$\frac{1}{[\text{NO}]} - \frac{1}{[\text{NO}]_0} = 2k[\text{O}_2]_0 t \quad (9)$$

$[\text{NO}]_0$  being the initial nitric oxide concentration.

It was found that the rate constant  $k = 5.59 \times 10^3 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ . The obtained value of rate constant fits in the range given by Tsukahara et al. (1999) in their survey of rate constants obtained by various authors. The value of the reaction rate constant is usually in the range of  $1.6 \times 10^3$ – $7.2 \times 10^3 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  under ambient conditions. All values were established in water free systems. In aqueous solutions, the oxidation of nitric oxide follows different mechanism pathways, and the rate constant is much higher than that in the gaseous phase ( $k = 9 \times 10^6 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  (Wink & Ford, 1995) or  $2.1 \times 10^6 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  (Awad & Stanbury, 1993)).

Fig 4. presents the progress of  $\text{NO}$  to  $\text{NO}_2$  oxidation in batch reactor experiments. These data suggest symmetry of  $\text{NO}$  decomposition and  $\text{NO}_2$  formation, additionally confirmed by the small difference between



**Fig. 5.** Changes of NO concentration in time during NO oxidation with oxygen ( $5.6 \times 10^{-3} \text{ mol dm}^{-3}$ ) for various NO initial concentrations:  $7.36 \times 10^{-6} \text{ mol dm}^{-3}$  ( $\diamond$ ),  $8.49 \times 10^{-6} \text{ mol dm}^{-3}$  ( $\square$ ),  $1.38 \times 10^{-5} \text{ mol dm}^{-3}$  ( $\triangle$ ). Solid lines denote theoretical values.

the amounts of NO oxidized and  $\text{NO}_2$  formed in the process, 2 ppm. Considering it all, it may be concluded that the only reaction taking place in the system is reaction Eq. (1), which means that  $\text{NO}_2$  does not undergo further oxidation by oxygen.

The higher is the initial NO concentration the more NO is oxidized to  $\text{NO}_2$ . The highest conversion obtained was 85 % (at initial NO concentration of 534 ppm), whereas the lowest observed conversion was 55 % (at initial NO concentration 163 ppm) which can be easily improved by replacing oxygen with ozone. However, the oxidation of NO by ozone is far more complex. Moreover, when the mole ratio of  $\text{O}_3$  to NO exceeds 1, not only  $\text{NO}_2$  is formed but also  $\text{NO}_3$ , and  $\text{N}_2\text{O}_5$  (Mok & Lee, 2006). Ozonation of NO is the subject of further studies carried out in our laboratory (Skalska et al., 2009).

The aim of the second series of experiments was to verify if the estimated  $k$  value is correct for reactions conducted at lower concentrations of oxygen ( $5.6 \times 10^{-3} \text{ mol dm}^{-3}$ ). Composition of the gas mixture was approximately 10 % of  $\text{O}_2$ , 90 % of  $\text{N}_2$  with NO and  $\text{NO}_2$  concentration in the range of  $10^{-6} \text{ mol dm}^{-3}$ . Fig. 5 presents the comparison of experimental data with the values of NO concentration calculated according to Eq. (9) using the previously determined value of rate constant  $k$ .

Fitting of theoretical curves to experimental points is good, with a slight deviation for the highest initial NO concentration studied. This confirms that even at lower concentrations of oxygen, the oxidation of NO can be described by the second-order kinetics.

The rate of nitric oxide oxidation by means of oxygen can be described by second order reaction kinetics. The rate constant determined experimentally was verified for different concentrations of oxygen and its value is in the range given by others authors. Results of these studies are a good basis for the determination of kinetics of NO reaction with ozone.

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