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Experimental data on the influence of oxygen on the rate of formation of N_2 , N_2O , and CO_2 were obtained for a wide range of conditions, the goal being to substantiate and develop a previously proposed mechanism and reaction kinetics for the reaction of CO with NO and O_2 . The effect of the reversibility of the NO adsorption step on the kinetics of the process was also analyzed. The conditions necessary for acceleration of the reaction of CO + NO by oxygen were obtained. Good correspondence was also obtained between the calculated and experimental kinetic dependences.

In [1], we formulated a mechanism for reactions taking place in the $CO-NO-O_2$ system on a palladium catalyst, and singled out several consequences of the kinetics, in particular the nature of the influence of oxygen on the transformation rate of NO. In the present work, ideas for the mechanism and kinetics of the interaction process of CO with NO and O_2 which we introduced in [1] are confirmed and developed on the basis of experimental data pertaining to the influence of oxygen on the formation rate of N_2 , N_2O , and CO_2 . These data were obtained under a wide range of conditions.

Experiments were conducted in a gradientless reactor with a piston vortex generator at atmospheric pressure over a Pd (0.5% by mass)/SiO₂ catalyst. To obtain the catalyst, the support was soaked with a solution of Pd(NO₃)₂, and was then dried and calcined in air at 673-723K over the course of 2 h. The dispersion of the palladium, determined by chemisorption of oxygen in a static volume chamber, amounted to ~ 0.05 (the average size of the particles being ~ 20 nm). The flow rate of the reaction mixture was 0.1 liters/min, the mass of the catalyst being 1 g (grain size of 2-3 mm). The initial concentrations of reagents varied within the limits: CO $(0.25 \pm 8\%)$; NO $(0.25 \pm 8\%)$; O₂ $(0.05 \pm 10\%)$ by volume. Helium was used as a carrier gas. The analysis of the components of the reactant mixture and reaction products was conducted chromatographically in columns with molecular sieves of CaA (H₂, O₂, N₂, NO, CO), and with polysorb-1 (CO₂, N₂O).

The experimental temperature dependences of the degree of conversion of reagents X in the reaction of CO with O_2 ($C_{NO} = 0$) and CO with NO ($C_{O_2} = 0$) are presented in Fig. 1a (an excess of CO) and 1b (an excess oxidizer). In Fig. 2A, experimental data on the effect of the initial concentration of oxygen on the rate of formation of N_2 , N_2O , and CO_2 are cited for various temperatures and ratios of CO to NO in the initial reaction mixture. A qualitative analysis of the experimental data was conducted with the aid of the mechanism proposed



Fig. 1. Dependence of the degree of conversion of reagents X on temperature: a) in an excess of reducer: 1) NO in N₂ and N₂O (1.5% NO + 8% CO); 2) NO in N₂O (1.5% NO + 8% CO); 3) O₂ in CO₂ (0.75% O₂ + 8% CO); b) in an excess of oxidizer: 1) CO in CO₂ (1% CO + 8% NO); 2) CO in CO₂ (1% CO + 4% O₂).

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	$N^{(1)}$	$N^{(2)}$	$N^{(3)}$	$N^{(4)}$	N ⁽⁵⁾		
1) NO + $2Z \rightleftharpoons ZN + ZO$,	1	2	0	0	1		
2) $ZN + NO \rightarrow Z + N_2O$,	1	0	0	0	1		
3) $2ZN \rightarrow 2Z + N_2$,	0	1	0	0	0		
4) $CO + ZO \rightarrow Z + CO_2$,	1	2	2	0	0		
5) CO + $Z \rightleftharpoons Z$ CO,	0	0	0	2	0		
6) $ZCO + ZO \rightarrow 2Z + CO_2$,	· 0	0	0	2	0		
7) $O_2 + 2Z \rightleftharpoons 2ZO$,	0	0	1	1	-1		
8) $N_2O + Z \rightarrow ZO + N_2$	0	0	0	0	1		
$N^{(1)}$: CO + 2NO = CO ₂ + N ₂ O,							
$N^{(2)}:$ 2CO + 2	$2\mathrm{CO} + 2\mathrm{NO} = 2\mathrm{CO}_2 + \mathrm{N}_2,$						
$N^{(3)}, N^{(4)}: 2CO + O$	$2\mathrm{CO} + \mathrm{O_2} = 2\mathrm{CO_2},$						
$N^{(5)}: 2NO = 1$	$2\mathrm{NO} = \mathrm{N_2} + \mathrm{O_2},$						

in [1] plus an additional step (8), the dissociation of N₂0. The constituent parts of the mechanism are the reaction mechanisms for CO with O₂ ($G_{NO} = 0$), CO with NO ($C_{O_2} = 0$), and the decomposition of NO ($C_{CO} = 0$). In numerical simulations carried out in [1] using this kinetic model, the following values were used for constants of the individual steps (in relative units): $k_1 = k_2 = k_7 = 500$; $k_4 = k_5 = 800$; $k_{-1} = 5 \cdot 10^{-4} e^{-26}/RT$; $k_3 = 1 \cdot 10^{+4} e^{-35}/RT$; $k_{-5} = 2 \cdot 10^{+8} e^{-90}/RT$; $k_6 = 1 \cdot 10^{+6} e^{-38}/RT$; $k_{-7} = 5 \cdot 10^{+10} e^{-125}/RT$ (the activation energies are in kJ/mole). The values of k_1 were chosen to bring the calculated and experimental dependences as close together as possible, although in the present work the problem of quantitive modeling of the experiment was not posed (this may be the subject of a separate investigation). Rate constants for steps 4-7 of mechanism (I) are taken to be approximately equal to those obtained in [3] in the analysis of the oxidation of CO by oxygen on a Pd/porcelain catalyst. Approximately the same values for rate constants k_1 , k_5 , and k_7 are confirmed experimentally. In [4], the kinetics of the reaction of NO and mixtures of NO and O₂ with CO on platinum (comparable in its catalytic properties to palladium) were studied at 703K and low pressures (< 10⁻³ Pa). The rate constants for the adsorption of NO, O₂, and CO which we calculated according to the kinetic equations and those measured experimentally in [4] have similar values: $k_1 = 3.6 \cdot 10^{-6}$, $k_5 = 3.2 \cdot 10^{-6}$, $k_7 = 1.5 \cdot 10^{-6}$ moles/cm²·sec·Pa.

In [1], the numerical modeling of the influence of oxygen on the conversion kinetics of NO was carried out for the particular case where $k_{-1} = 0$, i.e., when the adsorption of NO is irreversible. At the same time, the reversibility of this step may appear significant in reactions in which NO takes part. This is clear in the simplified example where CO is absent and only the dissociation of NO with formation of N₂ takes place (steps 1, 3, and 7 of mechanism I). If the NO and O₂ adsorption steps are in quasi-equilibrium, one obtains the dependence of the decomposition rae of NO on reagent concentrations in an explicit form:

$$r_{\rm NO} = 2k_3 (b_1 C_{\rm NO})^2 / [\overline{V b_7 C_{\rm O_2}} (1 + \overline{V b_7 C_{\rm O_2}}) + b_1 C_{\rm NO}]^2, \tag{1}$$

where $b_1 = k_1/k_{-1}$, and $b_7 = k_7/k_{-7}$. From this it follows that the slowing of the reaction by oxygen may appear at low oxygen coverage of the surface, $x(\sqrt{b_7C_{0_2}} << 1)$. Under the additional condition $\sqrt{b_7C_{0_2}} >> b_1C_{NO}$, Eq. (1) simplifies to

$$r_{\rm NO} \cong 2k_3 (b_1 C_{\rm NO})^2 / b_7 C_{\rm O_2}.$$
(2)

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Precisely such a kinetic equation was obtained experimentally for the decomposition of NO on Pt and Pt-Rh contacts (see [5], p. 214). We also note that in the case of irreversible adsorption of NO, the slowing of the NO dissociation is possible only for large values of x, when the blockage of the surface by oxygen begins to manifest itself. In the event that the step is reversible, the inhibiting of the reaction is possible for any, even very small values of x. This is explained by the fact that as x increases (an increase in C_{O_2}), the nitrogen atom surface concentration of n decreases and the reaction rate falls $(r_{NO} = 2k_3n^2)$. The inhibiting effect of oxygen on the transformation of NO for small values of x is possible in the presence of CO. Such a conclusion was made in [4] on the basis of kinetic data obtained on Pt at extremely low reagent partial pressures (< 10^{-3} Pa) for the CO-NO, CO-NO-O₂ systems. For these conditions, the surface coverage of adsorbed particles is insignificant; the strong slowing effect of 0, on the conversion rate of NO was interpreted in [4] to be a result of the influence of x on the atomic nitrogen surface concentration owing to the reversibility of the NO adsorption step. Under the conditions of our experiments (atmospheric pressure), when the net occupation of the surface by the reagents may be considerable, it is necessary to take into account the reversibility of the NO adsorption step. Indirectly, this is supported by the data presented in Fig. 1, where the reaction rates of NO and O2 with CO in an excess of reducer (Fig. 1a) and oxidizers (Fig. 1b) are contrasted.

From mechanism (I), it follows that with increase in the concentration of CO, the removal of oxygen from the surface to an increasing degree is realized in steps 4 and 6 (the reactions of oxygen with gas phase and adsorbed CO), the influence of the steps involving the recombinative desorption of NO with absorbed oxygen becoming less important. In this case the structure of the kinetic model of the reaction process for CO with NO approximates the structure of the kinetic model for the reaction between CO and O_2 (up to their complete coincidence, if the atomic nitrogen surface coverage is not great [1]). In this event, as is easy to show, the rates of the comparable processes satisfy the ratio

$$r_{\rm NO}/r_{\rm O_2} \cong k_1 C_{\rm NO}/2k_7 C_{\rm O_2}$$

(In the given case, as for other ratios of reagents, the desorption of oxygen may be disregarded due to its high endothermicity; its contribution to the kinetics of the process becomes noticeable at considerably higher temperatures than those used in the present study.) Hence, when $k_1 \approx k_7$, the reaction rates for CO with O_2 and NO have similar values for reactive mixtures having an excess of CO. This agrees with the experimental data (Fig. 1a). In contrast, with an excess of NO, the role of the NO desorption step may be significant, since the total rate of NO adsorption in this event is considerably less than the rate of step 1 in the forward direction. This can lead to a decrease in the reaction rate of CO with NO compared to that for CO with O_2 . We obtained precisely that result in experiments with an excess of oxiduzer (Fig. 1b). We also note that the introduction of the last path, the conversion of N_2O to N_2 (step 8), permits one to explain the dependence of the degree of conversion of NO to N_2O on temperature, indicated in Fig. 1.

The diverse influence of oxygen on the transformation rate of NO (accelerating, slowing, weak effect) also qualitatively agrees with mechanism (I) in its dependence on conditions of the process. In [1], it was found, using the numerical simulation of the kinetics of the reactions occurring in the $CO-NO-O_2$ system, that the speeding up of the transformation rate of NO by oxygen can occur at relatively high surface coverage by absorded CO (in the absence of O_2). In these conditions, introduction of the O_2 into the reaction mixture can lead to a growth in the free surface area of the catalyst available for adsorption of NO, as long as the surface concentration of O_2 does not become so great that reaction inhibition begins to predominate as a result of blocking of the surface by oxygen. On the whole, the dependence of the reaction rate on oxygen concentration describes a curve with a maximum. The data obtained, as well as results of [4], attest to the fact that the decrease of the nitrogen atom surface concentration, a result of the shift of the equilibrium of step 1 to the left with increasing oxygen atom concentration of CO with NO by oxygen.

With the aid of the kinetic model following from mechanism (I), one can obtain the conditions necessary for observing the enhancement of the reaction rate of CO with NO by oxygen. We examine the particular case $(k_2 = k_{-1} = 0)$ for which the atomic nitrogen surface concentration depends on the surface coverage by atomic oxygen in the following form:



Fig. 2. Dependence of the rates of reactions taking place in the CO + NO + O_2 system on oxygen concentration: 1) r_{N_2} ; 2) r_{N_2O} ; 3) r_{CO_2} [A) experiment, B) calculated]: a) 523 K; A) 4% NO + 1.5% CO; B) $C_{CO} = 7.5 \cdot 10^{-4}$, $C_{NO} = 2 \cdot 10^{-3}$; b) 573 K; A) 4% NO + 1.5% CO; B) $C_{CO} = 7.5 \cdot 10^{-4}$, $C_{NO} = 2 \cdot 10^{-3}$; c) 623 K; A) 8% CO + 1.5% NO; B) $C_{CO} = 2 \cdot 10^{-3}$; c) 623 K; A) 8% CO + 1.5% NO; B) $C_{CO} = 2 \cdot 10^{-3}$, $C_{NO} = 2 \cdot 10^{-3}$, $C_{NO} = 2 \cdot 10^{-3}$.

$$n = \frac{\sqrt{k_1 C_{\rm NO}/2k_3} (k_{-5} + k_6 x) (1 - x)}{k_5 C_{\rm CO} + (1 + \sqrt{k_1 C_{\rm NO}/2k_3}) (k_{-5} + k_6 x)}$$
(3)

Differentiating n with respect to x, we obtain

$$\left(\frac{\partial n}{\partial x}\right)_{x=0} = \frac{\sqrt{k_1 C_{\rm NO}/2k_3} \left[b_5 C_{\rm CO} \left(k_6/k_{-5} - 1\right) - \left(1 + \sqrt{k_1 C_{\rm NO}/2k_3}\right)\right]}{\left[b_5 C_{\rm CO} + \left(1 + \sqrt{k_1 C_{\rm NO}/2k_3}\right)\right]^2}$$
(4)

where $b_5 = k_5/k_{-5}$, (the CO adsorption coefficient). In the region where x = 0, we have $\partial n/\partial x > (i.e., n \text{ grows with increasing } x)$ if the following inequality is satisfied:

$$b_5 C_{\rm CO}(k_6/k_{-5}-1) > 1 + \sqrt{k_1 C_{\rm NO}/2k_3}.$$
(5)

In this case, n acquires a maximum value for the following value of oxygen surface concentration:

$$x_{opt} = \frac{-\left[b_{5}C_{CO} + (1 + \sqrt{k_{1}C_{NO}/2k_{3}})\right]}{(1 + \sqrt{k_{1}C_{NO}/2k_{3}})(k_{6}/k_{-5})} + \frac{\sqrt{b_{5}C_{CO}\left[b_{5}C_{CO} + (1 + \sqrt{k_{1}C_{NO}/2k_{3}})(1 + k_{6}/k_{-5})\right]}}{(1 + \sqrt{k_{1}C_{NO}/2k_{3}})(k_{6}/k_{-5})}$$
(6)

(expression (6) is obtained from the complete expression for $\partial n/\partial x$ at $\partial n/\partial x = 0$).

If the given reagent concentrations (CO and NO) satisfy the inequality

$$x_{C_{O_2}=0} < x_{opt}$$

(7)

 $(x_{CO_2} = 0, \text{ the oxygen surface coverage in the absence of gas-phase oxygen) and (5), then the introduction of oxygen into the reaction mixture leads to a growth in n and, hence, to an increase in the conversion rate of NO. In the examined case <math>(k_2 = k_{-1} = 0)$, conditions (5) to (7) are not only necessary, but sufficient for speeding up to CO + NO reaction under the influence of oxygen. This is due to the fact that upon introduction of O_2 , the quantity x grows (the acceleration should be observable as long as x does not exceed the value of x_{opt}). Conditions (5)-(7) remain necessary for observing the accelerating effect when $k_2 \neq 0$, $k_{-1} \neq 0$, but will no longer be sufficient. Following (5) to (7), it is possible to conclude also that the manifestation of oxygen's accelerating influence is favored by an increase in CO concentration, a decrease in NO concentration, and a decrease in temperature (in the latter case the quantity b_5 increases, as does the ratio k_6/k_{-5} , since $E_6^a < E_{-5}^a$). This agrees with our experimental data (see Fig. 2A).

Finally, results of numerical modeling (Fig. 2B) are in qualitative agreement with experiment conveying well the tendencies of the changes of oxygen's influence on the formation of N_2 and N_2O with changes of temperature and reagent concentrations. We also note that in Fig. 2B, the calculated dependences correspond with low oxygen surface coverage (no higher than 2%), i.e., the hindering influence of oxygen in the given instance is associated not with oxygen's blocking of the surface, but with its influence on the degree of reversibility of the NO dissociative adsorption step.

On the whole, the results obtained in this study support the correctness of mechanism (I), which we proposed for the palladium catalyst. The given mechanism may obviously be used for the quantitative modeling of the kinetics of reactions taking place in the $CO-NO-O_2$ system. At the same time, it cannot be excluded that modeling of the reaction kinetics for a wide range of conditions will require additional mechanisms with other steps (the inclusion of the nondissociative adsorption of NO, for example). According for such a step (with the assumption that molecularly adsorbed NO is not reactive) allowed Druzhinin et al. [6] to obtain a good qualitative description of auto-oscillations observed experimentally in the reaction of CO with NO on platinum [7].

Under certain conditions, isocyanate structures can form on the surface of layered palladium catalysts [8]. In the opinion of Alikina et al. [8], they are not intermediate compounds in the reduction of NO by carbon monoxide. With oxygen, they may be destroyed according to the reaction 2NCO + $O_2 \rightarrow N_2$ + 2CO₂. The possibility of the formation of isocyanate structures and their destruction under the influence of oxygen ensues from our experimental data, for upon the introduction of oxygen into the reaction mixture at 523 K (Fig. 2A, a) an increase in the rate of formation of N_2 and CO_2 was observed at the beginning of he nonstationary portion of the reaction. At the same time, the stationary value of the reaction rate with a low concentration of oxygen ($C_{0_2}^{\circ} = 0.45 \cdot 10^{-4}$ M, Fig. 2A) was hardly distinguishable from the formation rate of N₂ and CO₂ in the absence of oxygen. This attests to the insignificant influence of isocyanate structures on the kinetics of the process under these conditions, i.e., in an excess of NO with respect to CO. It is also possible that for an excess of CO, the stationary rate of formation and destruction of isocyanate structures under the influence of oxygen will become commensurable with the rate of formation of nitrogen in the step involving the recombination of adsorbed atomic nitrogen [step 3 of mechanism (I)], which is evidenced by several differences between the experimentally found character of the dependence of r_{N_2} on C_{O_2} and that calculated using mechanism (I), (Fig. 2c).

LITERATURE CITED

- Yu. I. Pyatnitskii, M. G. Martsenyuk-Kukharuk, S. N. Orlik, and V. A. Ostapyuk, "On the reaction mechanism for CO win NO on palladium catalysts," Teor. Eksp. Khim., <u>23</u>, No. 4, 484-489 (1987).
- 2. G. P. Korneichuk, V. A. Ostapyuk, and N. A. Boldyreva, "A gradientless reactor with individual or combined inputs of reaction mixture constituents to a layer of a granular catalyst," Katal. Katal., 22, 77-79 (1984).
- 3. S. I. Spivak, L. S. Mamykina, S. N. Orlik, et al., "Kinetic model of the oxidation of CO on a Pd-containing catalyst," Dokl. Akad. Nauk SSSR, <u>276</u>, No. 6, 1427-1430 (1984).
- 4. V. L. Kuchaev, "Mechanism of the reaction of carbon monoxide with nitrogen oxide on platinum in the absence and presence of oxygen," Abstracts of reports of the Fourth All-Union Conference on the Mechanisms of Catalytic Reactions, No. 2, Moscow, (1986), pp. 298-302.

- 5. G. I. Golodets, Heterogenous Catalytic Reactions with the Participation of Molecular Oxygen [in Russian], Naukova Dumka, Kiev (1977).
- 6. D. L. Druzhinin, A. N. Ivanova, and G. A. Furman, "Modeling of auto-oscillations in reactions of CO with NO on platinum," Preprint Acad. Sci. USSR, Institute of Chemical Physics, Chernogolovka (1985).
- W. Aldhoch, H.-G. Lintz, and T. Wesker, "Oscillationen der Reaktionsgeschwindigkeit bei der Reaktion von NO mit CO an Platin im Knudsengebiet," Surf. Sci., <u>103</u>, No. 2/3, 576-585 (1981).
- 8. G. M. Alikina, A. A. Davydov, I. S. Sazonova, and V. V. Popovskii, "Influence of the composition of the reaction mixture NO + CO + O_2 on the catalytic properties and state of the surface of layered noble metals. 1. Pt/γ -Al₂O₃," Kinet. Katal., <u>28</u>, No. 2, 428-426 (1987).

NH-TAUTOMERISM EFFECTS AND ISOCYCLIC SUBSTITUTION IN ALKYLPORPHYRINS AND THEIR CHEMICAL DIMERS

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A study has been made of the absorption spectra, circular dichroism in a magnetic field (MCD), and polarized fluorescence of individual NH-tautomers of free-base porphyrins with asymmetric substitution. The four-orbital model of Gouterman and the perimeter model of Michl have been used in demonstrating that, in spite of the basic differences in type of electronic spectra of the two NH-tautomers of each compound, their absorption spectra in the visible region are described by a system of two linear oscillators X and Y. The fluorescence polarization spectra of the tautomers in the region of band III are extremely sensitive to changes in the side substituents in the isocycle. From an analysis of the sign sequence of electronic bands in the MCD spectra, it has been established that these compounds may be classed as "hard" chromophores with identical type of orbital splitting for the HOMO (b_1 and b_2) and LUMO (c_1 and c_2) in the two tautomers of one and the same compound. A specific role has been found for the keto group in the isocycle, as manifested in inversion of the sign sequence of electronic bands in the MCD spectra.

A characteristic feature of free-base porphyrins is NH-tautomerism, which is related to displacement of mobile protons from one pair of N atoms to another in the center of the macroring. For symmetric porphyrins, the migration of NH-protons in the ground state is manifested in NMR spectra [1]; at low temperatures (77° to 4.2°K) with selective excitation, the NH-tautomerism is of a photoinduced type and can be detected by optical methods [2]. It should be noted that, in the free bases of symmetric porphyrins, NH-tautomerism does not lead to any changes in the frequencies or intensities of electronic transitions in the visible region of the spectrum; i.e., the electronic absorption and fluorescence spectra of individual tautomers in these compounds are identical.

However, in porphyrins with asymmetric substitution (cyclopentaneoporphyrins and their chemical dimers, compounds with a cyclopentanone ring, tetraalkylporphyrins), pairwise displacement of protons leads to basic differences in the electronic spectra of the two tautomers of one and the same compound [3, 4]. The spectral separation of the S_0-S_1 transitions (Q_0^X band) may be as much as 380 cm⁻¹, and for the S_0-S_2 transitions (Q_0^Y band) as much as 800 cm⁻¹, so that the presence of the two tautomers in solutions can be detected on the basis of their electronic spectra, even at room temperature. Moreover, the absorption spectra of the two

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