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Carbon monoxide oxidation by oxygen in water–acetonitrile solutions of palladium(II) bromide complexes in the presence of Co(II), Fe(II) and Mn(III) phthalocyaninates

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Objectives. *The objective of this paper was to compare acetylene oxidative dicarbonylation that leads to maleic anhydride with a side reaction of CO oxidation by oxygen in a $PdBr_2$–LiBr–H_2O–CH_3CN system and in the presence of insoluble (Co) and soluble (Co, Fe, and Mn) phthalocyaninates (PcM).*
Methods. *To study the oxidation of CO to CO_2, a kinetics method was used; UV and IR spectroscopy was used to determine the concentrations of initial and intermediate compounds.*
Results. *The kinetics of CO to CO_2 oxidation were investigated and the reactivity series of PcM in CO oxidation and maleic anhydride synthesis was characterized. A satisfactory correlation was observed between reaction rates and PcM concentration, as well as the nature of metal, in both processes. The IR measurements of concentrations of Pd(II) and Pd(I) intermediate carbonyl complexes, and CO_2 concentrations, have made it possible to hypothesize the mechanism of CO_2 generation. The effect of PcM concentration on the concentrations of Pd(II)(CO) in CO oxidation has been shown.*
Conclusions. *Based on the data regarding CO oxidation and acetylene oxidative dicarbonylation, certain conditions have been proposed to effectively produce double-labeled maleic anhydride with ^{13}C (from ^{13}CO).*

Keywords: *metal complex catalysis, palladium carbonyl complexes, maleic anhydride, carbon monoxide, carbon dioxide, transition metal phthalocyaninates.*

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Окисление монооксида углерода кислородом в водно-ацетонитрильных растворах бромидных комплексов палладия(II) в присутствии фталоцианинатов Co(II), Fe(II) и Mn(III)

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Цели. *Сравнение результатов изучения процесса окислительного дикарбонилирования ацетилена до малеинового ангидрида (МА) с закономерностями побочной реакции окисления СО кислородом в системе $PdBr_2$–LiBr–H_2O–ацетонитрил в присутствии нерастворимых (Со) и растворимых (Co, Fe и Mn) фталоцианинатов (PcM).*
Методы. *Использованы кинетический метод для изучения реакции окисления СО до CO_2 и УФ- и ИК-спектроскопия для контроля за концентрациями исходных и промежуточных соединений.*
Результаты. *Изучена кинетика образования CO_2. Установлены ряды активности PcM в реакции окисления СО и получения МА и показана удовлетворительная корреляция характера зависимостей скоростей R_{CO2} и R_{MA} от [PcM] и от природы металла в обоих процессах. По результатам измерения концентраций промежуточных карбонильных комплексов Pd(II) и Pd(I) и концентраций CO_2 в ходе процесса методом ИК-спектроскопии предложены гипотезы о механизме образования CO_2, а также установлено влияние [PcM] на концентрацию $[Pd^{II}](CO)$ в стационарных условиях в ходе каталитического процесса окисления СО.*
Заключение. *По результатам изучения модельной реакции окисления СО и закономерностей окислительного дикарбонилирования ацетилена предложены рекомендации по условиям эффективного процесса получения дважды ^{13}C-меченного малеинового ангидрида (из ^{13}CO).*

Ключевые слова: *металлокомплексный катализ, карбонильные комплексы палладия, малеиновый ангидрид, монооксид углерода, диоксид углерода, фталоцианинаты переходных металлов.*

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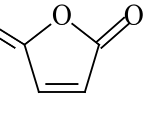
Introduction

Oxidative carbonylation processes, including those for alkynes, have been long known in the field of catalysis with metal complexes, and have been described in reviews [1–7] and monographs [8–10]. One of the most important oxidative carbonylation reactions for acetylene (and alkynes) is oxidative dicarbonylation that leads to maleic anhydride (MA):

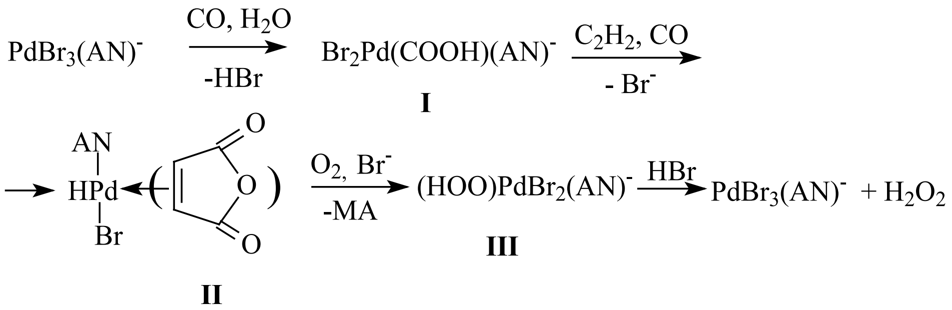
$C_2H_2 + 2CO + 1/2O_2$ =



(1)

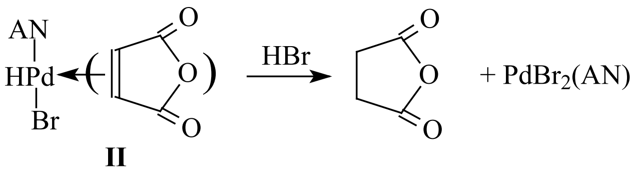
This reaction may be used to obtain MA labeled with ^{13}C for medical diagnostic purposes [11]. The reaction occurs efficiently in the catalytic system of $PdBr_2$–LiBr–acetonitrile (AN)–H_2O. To lower the partial pressure of oxygen, a second catalyst is used to activate O_2–metal phthalocyaninates (PcM) [12]. It has been shown that in the presence of the insoluble PcCo and soluble $(C_4H_9)_2SO_2N)_4$PcFe, the partial pressure of O_2 can be lowered to 0.05 bar in an acetonitrile–H_2O system.

A simplified scheme for the reaction mechanism (Scheme 1) shows the main steps of acetylene dicarbonylation that takes place, for example, in the presence of the $PdBr_3(AN)^-$ complex.



Scheme 1

Oxidation of hydride intermediates of type **II** (Scheme 1) with oxygen [13–21] or the oxygenyl complex $PcM(O_2)$ [12] results in the regeneration of Pd(II). The formation of H_2O_2 upon oxidation of CO has been noted in the papers [22, 23]. The synthesis of succinic anhydride (SA) is one of the side reactions (2) [24]:



(2)

Another side reaction (3) is CO to CO_2 oxidation via oxygen through Intermediate **I**:

$$\underset{\mathbf{I}}{Br_2Pd(COOH)(AN)^-} \xrightarrow[-CO_2]{} HPdBr_2(AN)^- \xrightarrow{O_2,\ HBr} PdBr_3(AN)^- + H_2O_2 \tag{3}$$

Depending on a solution's composition, Pd(0) complexes may be produced instead of hydride complexes; the former may also be oxidized by O_2 or oxygen complexes of PcM [14–16]. Optimization of MA synthesis in the $PdBr_2$–LiBr–PcM–AN–H_2O catalytic system requires an understanding of a simpler process – the side reaction of CO oxidation. The latter includes stages that are also involved in MA synthesis, namely the generation of Intermediate **I** and oxidation of palladium hydride complexes. In order to investigate the process of CO oxidation, we used kinetics, infrared (IR) spectroscopy, and ultraviolet (UV) spectroscopy.

The kinetics for the homogenous oxidation of CO were thoroughly studied for aqueous solutions of Pd(II) complexes with various oxidants: $CuCl_2$ [25–28], $CuCl_2$ + O_2 [29], Fe(III) [29–31], Fe(III) + O_2 [32], heteropolyacids [29, 33], para-quinones [35–37], and oxygen (in certain aqueous–organic solvents [23, 24]). However, for the catalytic system of $PdBr_2$–LiBr–PcM–AN–H_2O used in MA synthesis, the kinetics of CO oxidation were not studied.

Materials and Methods

The following reagents were used: $PdBr_2$ (*Pure*, TU-6-09-05-905-83), acetonitrile (HPLC grade, 99.9%, *Macron* GAS-75-05-8, Poland), tetrahydrofuran (99.95%). Prior to use, tetrahydrofuran (THF) was stored in the presence of NaOH and distilled in the presence of Na. Commercial cobalt phthalocyaninate was additionally purified by reprecipitation from sulfuric acid. Tetra-dibutylsulfamoyl derivatives of cobalt phthalocyaninate $[(C_4H_9)_2SO_2N)_4CoPc]$ and iron phthalocyaninate $[(C_4H_9)_2SO_2N)_4PcFe]$ (termed Pc*Co and Pc*Fe, respectively), and phthalocyaninate of manganese acetate PcMnOAc have also been used in this work.

CO oxidation was studied at 40 °C in a gas flow reactor with complete mixing. A magnetic stirrer was used to mix the solution. The flow of the incoming gas was measured using a rheometer. The flow of the outgoing gas was measured with a Mariotte vessel or by introducing an inert gas (nitrogen or helium) into the gas reaction mixture. The CO oxidation rate ($\boldsymbol{R}_{CO2}$) was calculated using the stationary areas of the curves of CO_2 accumulation.

In the first step, all components of the catalytic system were loaded into the reactor prior to execution of the experiment (Method A). Then the loading sequence was changed; this was necessary because of the low CO oxidation rate. To elevate the CO_2 portion in the outgoing gas flow ($[CO_2] \approx 2–9$ vol %), the initial gas mixture was put through the reactor at a low speed (3–6 mL/min while the contact solution volume was 5 mL). It is not possible to rapidly fill up the reactor with the gas mixture after reagent loading when working with low speeds of gas flow. This is why a technique was developed whereby PcM was loaded into the reactor first then the reactor was filled up with the gas mixture; 2.5 mL of the solvent was added with a syringe; and then stirring was turned on. Contact solutions containing $PdBr_2$, LiBr and AN (THF) were prepared separately. The experiment started with the introduction of 2.5 mL of the contact solution into the reactor. The loading of the solvent and contact solution was controlled by weighing the syringes (Method B). The behavior of carbonyl complexes during CO oxidation was studied in a closed reactor, while loading the reagents according to Method B. The ratio of LiBr and $PdBr_2$ concentrations is termed α. The composition of the gas mixture and purity of the individual gases were determined by gas adsorption chromatography using an LKHM-8MD chromatograph. Separation of the gases occurred in two sequential packed columns, each 3 m in length. The first column was packed with AG-3 activated charcoal (with a separation temperature of 128 °C), the second column was packed with a 13X molecular sieve (with a separation temperature of 25 °C). The following conditions were used: detector (katharometer) temperature of 160 °C, detector current 70 mA, argon as a carrier gas (1.5 L/h). The concentration of water in the contact solution was determined by gas adsorption chromatography using an LKHM-8MD chromatograph. The following conditions were used: packed column, 3 m in length, 3 mm in diameter, and packed with sorbent Polisorb-1; a separation temperature of 170 °C; evaporator temperature of 200 °C; a detector (katharometer) temperature of 180 °C; detector current 120 mA; helium as a carrier gas (1.2 L/h). Concentrations of MA and SA in the contact solution were determined by gas-liquid chromatography according to the aforementioned method [12, 24].

The IR spectroscopy of contact solutions was performed using a *Specord* M-82 spectrophotometer. For analysis, a portion of the contact solution was taken out of the reactor with a syringe and then it was loaded into 0.25 mm cuvettes, with NaCl windows. Ultraviolet (UV) and visible spectra were recorded using the *Specord* M-40 spectrophotometer, in 1 mm, or 0.1 mm, or 0.01 mm quartz cuvettes.

Results and Discussion

Oxidation of CO using oxygen

It had earlier been shown that the rate of CO oxidation in the catalytic system of $PdBr_2$–LiBr–AN–H_2O was much lower than in the systems of $PdBr_2$–LiBr–THF or $PdBr_2$–LiBr–1,4-dioxane [22]. Because of this to evaluate the experimental setup and analyze low concentrations of CO_2, and to find the conditions for the reaction to occur at a considerable rate, the preliminary experiments in this work were carried out in THF and in the mixture of THF and AN, in a flow reactor. The results of these experiments, with varying concentrations of LiBr and water, as well as temperature, are shown in Table 1.

The preliminary data demonstrate that the rate of CO oxidation in the catalytic system increases with the growth in water concentration (Table 1, exp. 1–3). A partial replacement of tetrahydrofuran with acetonitrile leads to a lower rate of CO_2 production (Table 1, exp. 4, 5). When THF was absent in a $PdBr_2$–LiBr–AN solution, it was impossible to detect CO_2 (Table 1, exp. 6). It is worth mentioning that Experiments 6 and 7 were performed in two stages: first, the gas mixture was put through the $PdBr_2$–LiBr–AN solution, and second, $PcCo_{solid}$ was added into the reactor and the reaction was performed for 1–1.5 h. The addition of $PcCo_{solid}$ into the contact solution in Experiment 6 did not lead to the production of CO_2. A small amount of CO_2 was detected in the $PdBr_2$–LiBr–AN contact solution in Experiment 7, which was carried out at 40 °C, with a lower LiBr concentration (0.025 M) and in a closed reactor.

A change in color was observed in the solution before CO_2 was detected. After contact with CO, an orange color cleared up and went on to become greenish. The greenish color could be due to the reduced forms of palladium. By the 60th minute of the reaction, 0.067 mmol CO_2 was detected, which is ~25% of the $PdBr_2$ amount. Therefore, in Experiment 7, CO_2 production occurs due to the reduction of $PdBr_2$ in the absence of $PcCo_{solid}$, potentially through reaction (4):

$$PdBr_2 + CO + H_2O \rightarrow Pd^0 + CO_2 + 2HBr. \quad (4)$$

The introduction of $PcCo_{solid}$ in the 60th minute of the reaction resulted in a higher rate of CO_2 production (Fig. 1). The initial rate of this process, in the presence of $PcCo_{solid}$, was 0.17 (M/h). The lower rate of CO_2 production towards the end of the reaction was due to the lower reagent concentration or the higher product concentration, in the closed reactor.

The next experimental series was carried out in a gas flow reactor at 40°C, with $\alpha = [LiBr]/[PdBr_2] = 0.5$. All the components of the catalytic system ($PdBr_2$, LiBr, AN, $PcCo_{solid}$, and water) were loaded into the reactor prior to the reaction. The unsubstituted $PcCo_{solid}$ almost did not dissolve in the contact solution; this is why the process took place in a three-phase catalytic system.

The contact solution's volume and amount of $PcCo_{solid}$ were varied, and the conditions that allowed the kinetic reaction to occur were found.

During the first stage, the process was investigated at $[PdBr_2] = 0.05$ M, $[LiBr] = 0.025$ M ($\alpha = 0.5$). The catalytic system would become unstable at lower values of α. The reaction rate had a weak maximum of CO concentration in the gas phase (at O_2 concentration of ~50 vol %) and almost did not depend on $[O_2]$ in the 20–70% range (at a CO concentration of 30 vol %).

Table 1. Results of preliminary experiments*

Exp.	Concentration, M		Temperature, °C	Solvent	Initial gas composition, vol %		$\boldsymbol{R}_{CO2}$, M/h
	LiBr	H_2O			CO	O_2	
1	0.050	0.5–0.8	30	THF	34.3	53.3	0.170
2	0.050	0.6	30	THF	55.3	38.1	0.100
3	0.050	0.3	30	THF	46.3	51.6	0.010
4	0.050	0.6	30	THF + AN	35.7	60.5	0.038
5	0.050	0.9	30	THF + AN	46.5	51.8	0.034
6**	0.050	0.9	30	AN	44.4	52.8	0
7**	0.025	0.9	40	AN	42.0	56.4	0.170

* Conditions: $[PdBr_2]$ = 0.05 M; Experiment 7 was performed in a closed reactor and the duration of the experiments was 2 hours with a contact solution volume of 5 mL.

** Experiments with addition of $PcCo_{solid}$ into the contact solution.

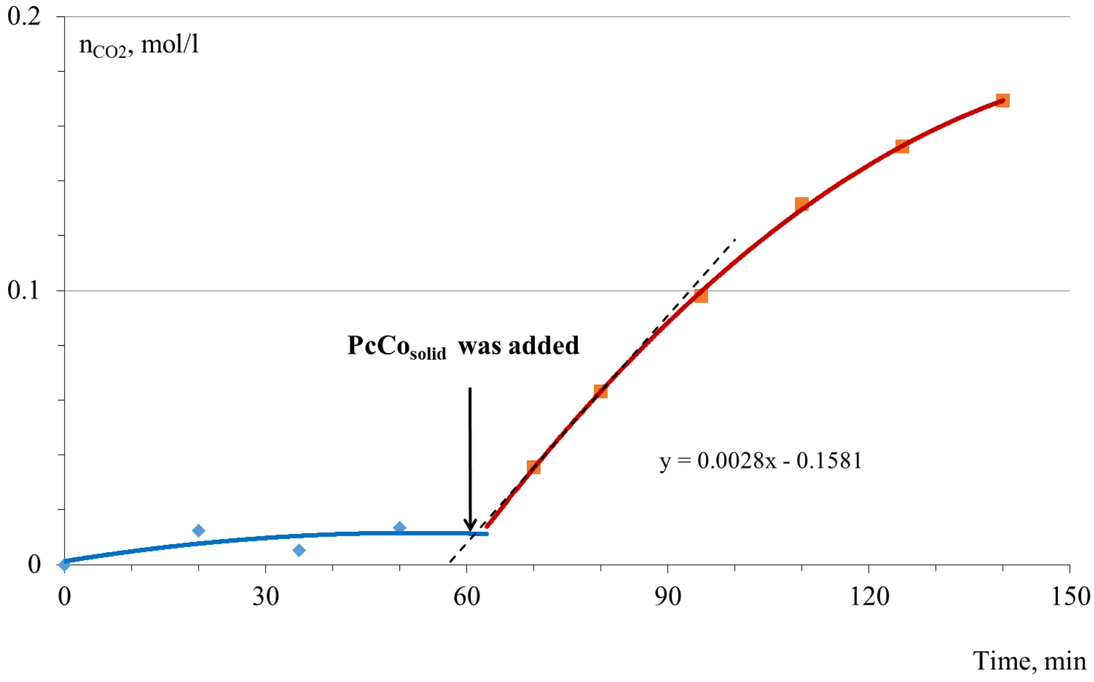


Fig. 1. CO_2 production in Experiment 7. Conditions: $[PdBr_2]$ = 0.05 M, [LiBr] = 0.025 M, $[PcCo_{solid}]$ = 0.025 M, and closed reactor.

The independence of $\boldsymbol{R}_{CO2}$ from $[O_2]$ may be due to the complete coverage of $PcCo_{solid}$ surface by oxygen in this concentration range, and also due to the participation of $PcCo(O_2)$ complexes in the rapid stage of oxidation of palladium hydride complexes, beyond the limiting stage of the process. The reaction rate is a linear function of water concentration in the 0–1.6 M range (Fig. 2).

The effect of the amount of PcM on the rate of CO oxidation was studied at lower concentrations of the components: $[PdBr_2]$ = 0.025 M, [LiBr] = 0.0125 M (Method B) (Fig. 3). The concentration of water in the contact solution was 0.5–0.7 M. Figure 3 shows that only in the case of $PcCo_{solid}$, $\boldsymbol{R}_{CO2}$ is a linear function of the amount (concentration) of PcM. The $\boldsymbol{R}_{CO2}$ curves for soluble PcM are saturation curves.

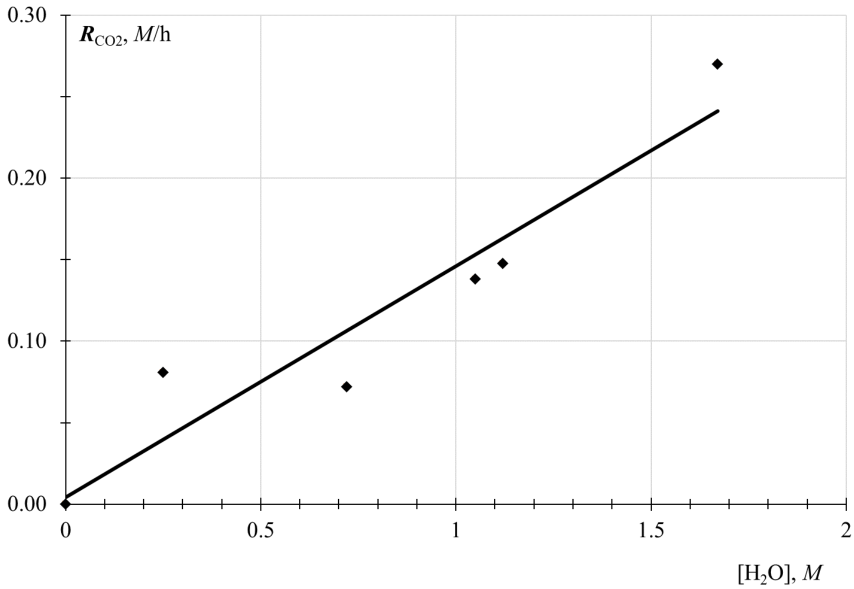


Fig. 2. Dependence of R_{CO2} on H_2O concentration.
Conditions: [$PdBr_2$] = 0.05 M, [LiBr] = 0.025 M. Method A.

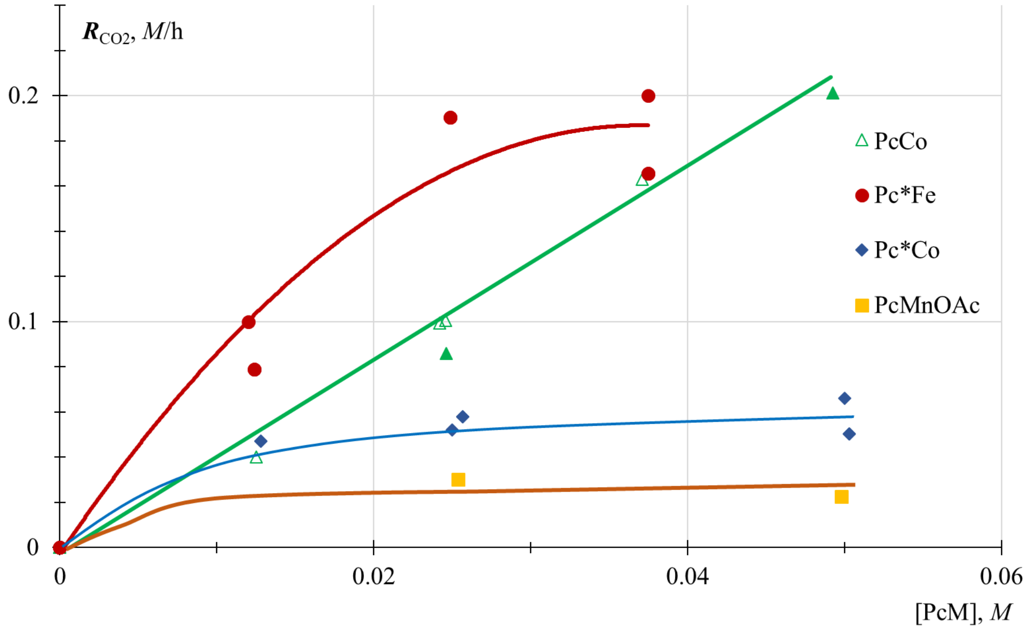


Fig. 3. Dependence of R_{CO2} on amount of $PcCo_{solid}$ and Pc*Co, Pc*Fe concentrations.
Conditions: [$PdBr_2$] = 0.025 M, [LiBr] = 0.0125 M, [H_2O] = 0.5–0.7 M,
a contact solution volume of 5 ml (closed dots), and contact solution volume of 10 ml (open dots).

Interaction between components of the catalytic system during CO oxidation and MA synthesis

To study the mechanisms of component interaction, $PdBr_2$–LiBr–$PcCo_{solid}$–AN and $PdBr_2$–LiBr–$PcCo_{solid}$–adiponitrile (ADN) systems were used. The choice of ADN was due to its well-known use as a solvent in MA synthesis [12]. In addition, ADN allows us to study the behavior of $PcCo_{solid}$ in a solution via spectral methods, because $PcCo_{solid}$ is insoluble in acetonitrile, but its solubility in adiponitrile is approximately 0.001 M, if the solution is incubated with the solid substance for 24 hours at 25 ºC.

a) According to data in [38], in the $PdBr_2$–LiBr–AN system, palladium bromide is mainly found in the form of $[PdBr_2(AN)]_2$ complex (even when α = 2), and in the form of small amounts of anionic complexes $PdBr_3(AN)^-$ (λ_{max} = 273 nm), $PdBr_4^{2-}$ (λ_{max} = 253 and 343 nm), $Pd_2Br_6^{2-}$, and cationic bromide-acetonitrile complexes of palladium. The equilibrium constant of dimeric neutral complex formation, 5.7×10^5 M^{-1}, is approximately 10^3 times higher than all other equilibrium constants, and the concentration of the sum of cationic complexes is 3–4% of $[Pd]_\Sigma$. The predominant formation of $PdBr_4^{2-}$ complex is only observed when $\alpha > 200$ [38].

Palladium bromide was shown to dissolve in nitriles in the absence of bromide anions. For example, $PdBr_2$ solubility at 25 °C is 0.021 M in acetonitrile and 0.07 M in adiponitrile. The UV spectroscopy analysis of $PdBr_2$ solution in AN without LiBr showed that the spectrum contained intensive absorption bands at 273, 208 and 218 nm, and a significantly less intensive band at 322 nm (Fig. 4).

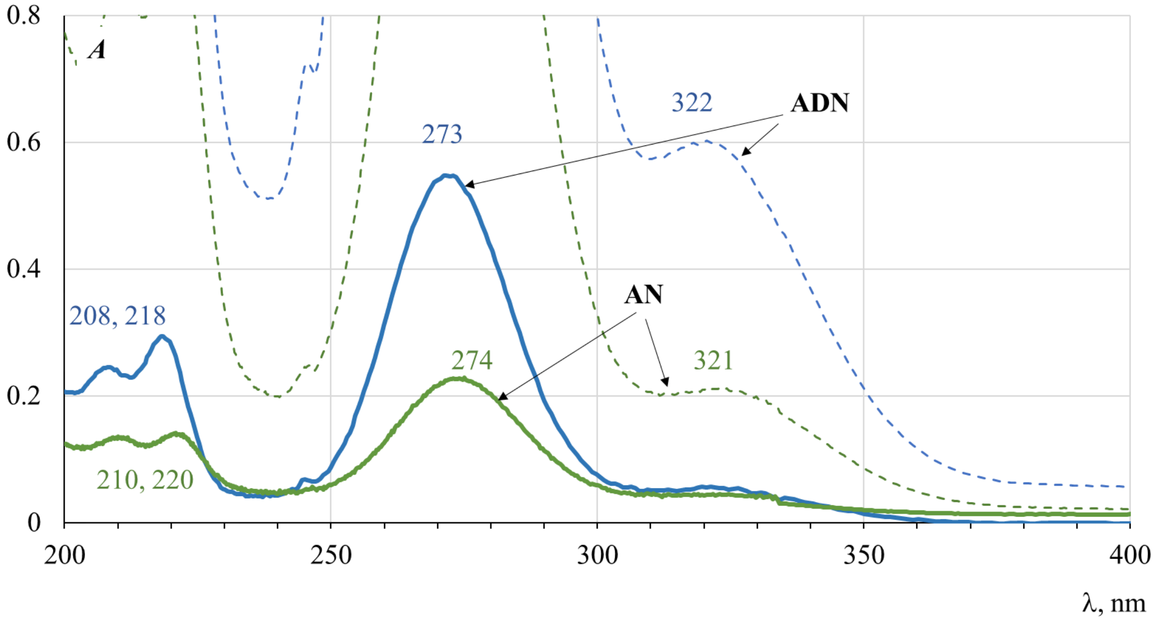


Fig. 4. UV spectra of $PdBr_2$–AN and $PdBr_2$–ADN solutions, in 0.01 mm cuvettes (solid line) and 0.1 mm cuvettes (dashed line).

The dilution of the $PdBr_2$ solution in AN with AN showed (Fig. 5) that, in accordance with the Beer–Lambert law, the absorbance was a linear function of palladium bromide concentration, at 208, 218, 273, and 322 nm, thus suggesting that there was just one predominant form of Pd(II) complex in the solution during the range of concentrations analyzed. When $\alpha = 2$ [38], the predominant form is the dimer $[PdBr_2(AN)]_2$ that has bromide bridges. In the absence of lithium bromide, this form seems even more likely to exist.

Replacement of the solvent with adiponitrile did not lead to considerable changes in the spectrum of palladium bromide.

A shift of all absorption bands by 1–2 nm was observed, which agrees with the idea that the solvent is incorporated into the coordination sphere of the palladium complex. Similarly, absorbance was a linear function of the concentration upon dilution of $PdBr_2$ in adiponitrile at 210, 221, and 274 nm.

Slow evaporation of the saturated (at 25 ºC) $PdBr_2$ solution in AN for 48 hours produced dark-brown crystals. X-ray crystallography[1] showed that these crystals were formed by monomeric complexes of *trans*-$PdBr_2(AN)_2$ that were described previously [39]. Dissolution of the crystals in acetonitrile resulted in the emergence of absorption bands at 208, 218, 273, and 322 nm in the UV spectrum, which is characteristic for a more soluble dimeric complex.

In order to explain the exceptional stability of bromide dimeric complexes upon addition of LiBr, and to interpret the absorption bands observed, one can use the following experimental technique [40] that is employed for palladium chloride complexes $[PdCl_2(AN)]_2$. It has been shown that the addition of excess LiCl to a $PdCl_2$ solution ($[LiCl]/[PdCl_2] < 4$) leads to a higher absorption intensity at 208 and 333 nm, whereas absorption intensity at 244 nm does not change. This fact, according to the

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[1] The analysis was performed by F.M. Dolgushin (D.Sc. in Chemistry) – a Senior Research Fellow at the Laboratory of X-Ray Crystallography, A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

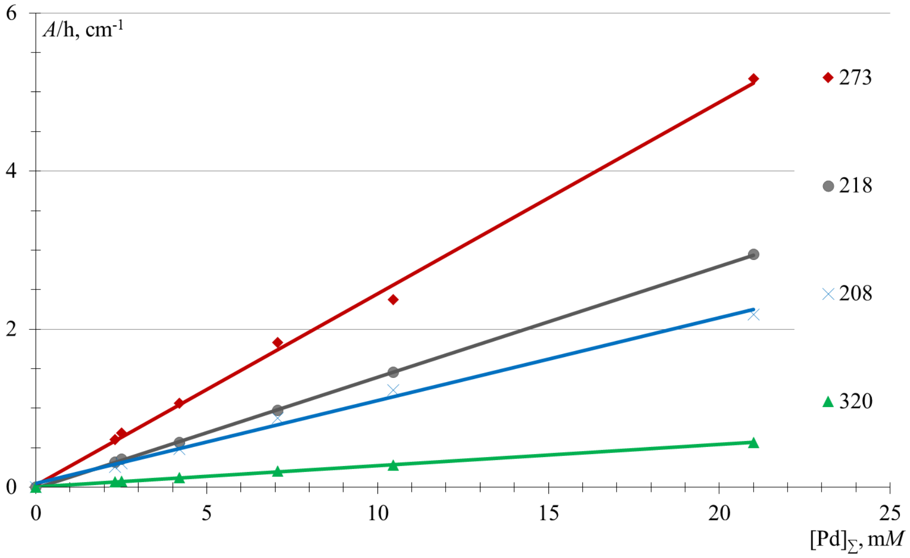

Fig. 5. Change in absorption intensity (the ratio of A to cuvette path length) upon variation of $PdBr_2$ concentration in AN.

authors of [40], agrees with the presence of terminal and bridging Cl^- ligands in the dimeric complex, and with the unchanged concentration of bridge complexes at low Cl^- concentrations. A further increase in Cl^- concentrations causes the disintegration of dimeric complexes and the formation of monomeric complexes.

In this work, similar experiments were carried out, with solutions containing 0.106 mM $PdBr_2$ and 0.08, 0.16, 0.21, and 0.42 mM LiBr. The addition of LiBr led to a higher absorption intensity at 208 and 218 nm, while absorption intensity at 273 nm remained unchanged. An additional absorption band was detected at 235 nm.

b) Cobalt phthalocyaninate $PcCo_{solid}$, dissolved in ADN, had a characteristic absorption band at λ_{max} = 668 nm, with a clear oscillating satellite at λ_{max} = 605 nm. Lithium bromide increased the solubility of $PcCo_{solid}$ in nitriles and shifted the absorption band into the range of longer wavelengths (for ADN, λ_{max} = 664 and 599 nm). In acetonitrile containing 0.1 and 0.2 mmol LiBr, cobalt phthalocyaninate had a major absorption band at 661 nm and a satellite at 598 nm.

c) The experiments with the soluble Pc*Co $[CoPc(SO_2N(C_4H_9)_2)_4]$ showed that this phthalocyaninate, when in acetonitrile, is an associate with a half-width value of 1530±20 cm^{-1} for the main absorption band at λ_{max} = 661 nm. The mixing of equivalent volumes of PcCo (0.001 M) and $PdBr_2$ (0.004 M) solutions in AN led to an almost two-fold decrease in optical density, in the absorbance range of Pc*Co and $PdBr_2$, without significant shifts in the absorption band of Pc*Co (Fig. 6). Similar results were observed for ADN solutions. Therefore, in the case of the soluble phthalocyaninate, no noticeable interaction was detected between the two components of the catalytic system.

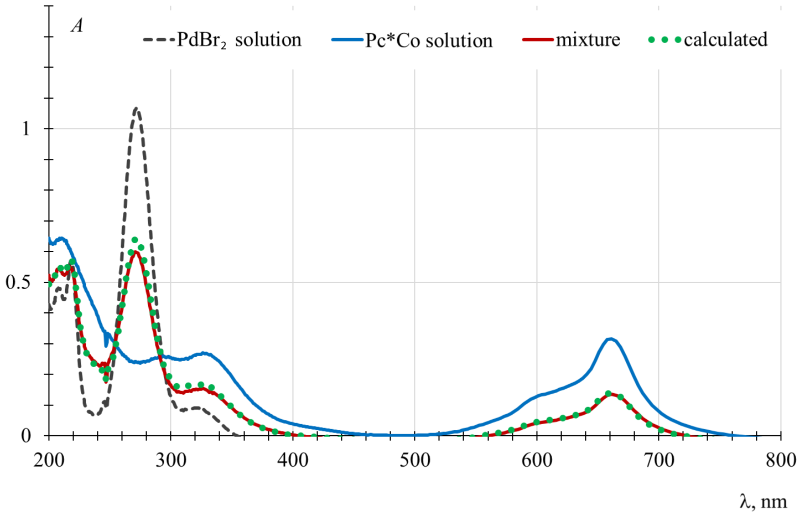

Fig. 6. Calculated and experimental data for solutions obtained by mixing of equal volumes of $PdBr_2$–AN (0.004 M) and Pc*Co–AN (0.001 M).

d) The introduction of LiBr into the Pc*Co solution in AN led to a 1.25 times higher optical density, and a decrease in the half-width of the band at 661 nm to 790 cm^{-1}. The addition of LiBr to the mixture of Pc*Co and $PdBr_2$ in AN resulted in a 1.4 times higher D_{661}, with a decrease in the half-width of the band from 1290±20 to 776 cm^{-1}. This means that bromide ions destroy the Pc*Co associates, both in the presence and in the absence of $PdBr_2$. One of the reasons for the disintegration of associates might be the oxidation of Pc*Co into Pc*Co^{III}Br by the dissolved oxygen.

IR studies of carbonyl complexes of Pd(II) and Pd(I) in various systems

The IR spectra for a number of carbonyl complexes of Pd(II) [41, 42] and Pd(I) [42–45], as well as structures of some complexes [41, 42, 45–49], has already been described. In order to investigate the possible intermediates of CO oxidation, the contact solutions were analyzed using IR spectroscopy. The absence of intensive absorption bands in the 1600–2200 and 2320–2400 cm^{-1} ranges in acetonitrile permitted the investigation of carbonyl complexes of palladium and CO_2 content (absorption band at 2341 cm^{-1}) in the contact solution.

CO oxidation was performed in a closed reactor. The components of the catalytic system ($[PdBr_2]$ = 0.025 M, [LiBr] = 0.05 M) were loaded into the reactor according to Method B. Introduction of the contact solution into the reactor led to CO absorption and the formation of a carbonyl complex with an absorption band at 2121 cm^{-1}, which is characteristic for carbonyl complexes of Pd(II) [41, 42, 45]. At low water concentrations (less than 0.1 M), the amount (mol) of CO absorbed in the $PdBr_2$–LiBr–AN–H_2O system ($\alpha = 2$) was almost equal to the amount of $PdBr_2$. It agrees with the formation of carbonyl complexes, where for each palladium atom there is one CO molecule. The intensities of the absorption band at 2121 cm^{-1}, observed in experiments with different $PdBr_2$ concentrations, were used in order to determine the extinction coefficient for the carbonyl complex of Pd(II). Carbon dioxide is quite soluble in the contact solution. The extinction coefficient for the dissolved CO_2 was determined using the intensities at 2341 cm^{-1}, for solutions where CO_2 concentration did not exceed 0.02 M.

An increase in water concentration in the solution of $PdBr_2$–LiBr–AN up to 0.4 M led to a decrease in the intensity at 2121 cm^{-1} (Pd(II) carbonyl complex) and appearance of absorption bands at 2341 cm^{-1} (CO_2), 1908 cm^{-1}, and 1966 cm^{-1}. Other absorption bands in the contact solution were not detected.

The existing data on the structures of $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ complexes with different cations (Pr_4N^+ [44], NBu_4^+ [46], NH_4^+ [47], PBu_4^+ [48]), as well as the IR spectral data for solutions of the following complexes: $(Pr_4N)[Pd_2(\mu\text{-}CO)_2Br_4]$ [42] and $Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ [43], have been analyzed. Based on this information, it can be assumed that the absorption bands at 1906 cm^{-1} and 1966 cm^{-1} might be associated with the carbonyl complexes of Pd(I). The first band is more intensive and might be associated with asymmetrical oscillations of the CO bridge, whereas the second band, which is less intensive, might appear due to symmetrical oscillations of the CO bridge [48]. The extinction coefficient for the carbonyl complex of Pd(I) was determined by the intensity of the 1906 cm^{-1} band. To do so, the mass balance of the catalyst (assuming that carbonyl complexes of Pd(0) have a low concentration [45]) was taken into account, and formation of a dimeric carbonyl complex of palladium(I) was also taken into account. The resulting extinction coefficients for carbonyl complexes of Pd(II), Pd(I) and CO_2 are 850, 980, and 425 M^{-1} cm^{-1}.

It is important to note that when the 1906 and 1966 cm^{-1} bands were assigned to the carbonyl bromide complexes of Pd(I), the following data was taken into account. In THF solutions of palladium bromide complexes that are obtained through replacement of Cl^- by Br^- in Pd(I) dimeric complexes, or through reduction of $PdBr_4^{2-}$ by CO, a band at 1908 cm^{-1} is observed (CO bridge) in the mixture of Pd(I) and Pd(0) dimeric complexes, and a band at 2106 cm^{-1} is observed (terminal CO) in Pd(0) complexes [45].

CO_2 concentration in the gas phase was determined by chromatography. During the experiment's first 3 to 5 hours, the temperature was 40 °C, and for the remaining 40 to 50 hours the temperature was 25±3 °C.

A. $PdBr_2$–LiBr–AN–H_2O in CO atmosphere

In this series of experiments, the stoichiometric oxidation of CO by bromide complexes of palladium(II) in an AN–H_2O system was investigated, in solutions containing $[PdBr_2]$ = 0.025 M and [LiBr] = 0.05 M ($\alpha = 2$). After the first introduction of water ($[H_2O]$ = 0.41±0.02 M), a small amount of CO_2 appeared in the solution, and the concentration of Pd(II) carbonyl complex decreased insignificantly throughout the 20 hours (Fig. 7). After the addition of more water ($[H_2O]$ = 0.70±0.02 M), a higher rate of CO_2 production and a dramatic drop in the concentration of Pd(II) carbonyl complex were observed, while a Pd(I) complex was formed. The latter's concentration decreased as the experiment continued for 50–70 hours, due to the participation of the compound in CO_2 production, and, potentially, in formation of palladium(0) complexes with CO bridges and terminal CO groups, as described previously [45]. The total amount of CO_2 corresponds to 60% conversion of palladium. Metallic palladium was not detected even after the addition of the second portion of water.

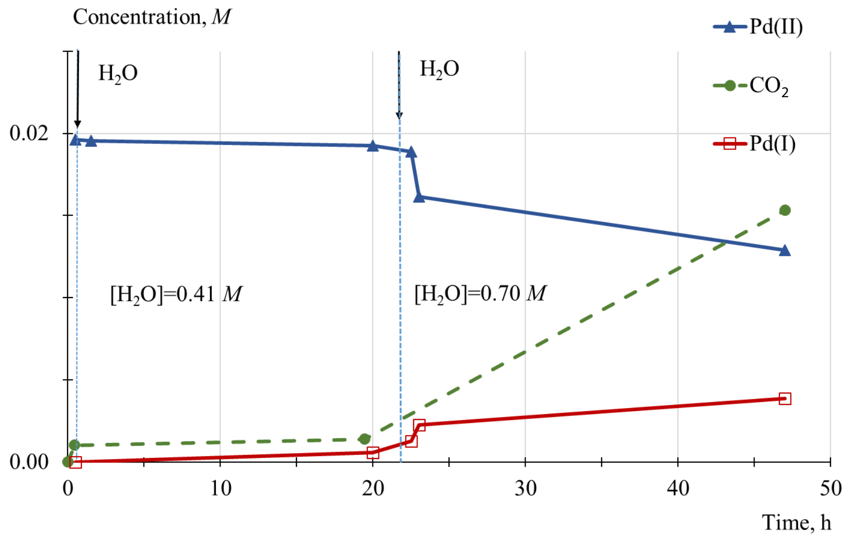

Fig. 7. Changes in concentrations of CO_2 and carbonyl complexes of Pd(II) and Pd(I) during stoichiometric CO oxidation. Conditions: $[PdBr_2]$ = 0.025 M, [LiBr] = 0.05 M.

The first stage of the process may be represented by reactions (5–9), with carbonyl bromide acetonitrile complex of Pd(II) that is formed upon interaction of CO with the dimeric complex.

Reactions (9) and (10) illustrate two mechanisms for the formation of a Pd(I) carbonyl complex. The reversibility of the reaction (10) may lead to the disproportionation of $Pd_2(CO)_2(AN)Br_2$. The processes that take place after 20 hours and the addition of extra water (5–9) result in a higher rate of CO_2 production, and the emergence of a second possible CO oxidation – reaction (11), which is followed by the participation of hydride intermediates in reactions (8) and (9).

B. $PdBr_2$–LiBr–AN–H_2O in CO/O_2 atmosphere

The same catalytic system and the same method were used to perform experiments with a mixture of gases, CO+O_2 (1:1) (Fig. 8). During the first 20 hours, the rate of CO_2 production was much higher than in the absence of oxygen (Fig. 7). The consumption rate for Pd(II) carbonyl complex was higher, too, but only the addition of extra water triggered the catalytic process, resulting in dramatically faster CO oxidation, while the concentration of Pd(II) carbonyl complex only decreased by 25%. By hour number 40 of the experiment, the catalyst turnover number was only 2.4.

It is important to note that in these conditions, the formation of a Pd(I) carbonyl complex was not observed. It is likely that the intermediates, which formed in reactions (7) and (8), as well as the hydride complexes in reaction (11), were oxidized by oxygen [13–21].

According to the data, hydrogen peroxide is not degraded in the system studied and may participate in the oxidation of all forms of the reduced palladium, including hydride complexes.

Mechanisms with direct involvement of palladium hydroperoxide complexes in forming reaction products can be found among the oxidation mechanisms of unsaturated substances [50]. In the case of CO, such a mechanism may be represented by reactions (15) and (16).

$$Pd_2Br_4(AN)_2 + CO + AN \rightarrow Pd(CO)(AN)Br_2 + PdBr_2(AN)_2 \quad (5)$$

$$Pd(CO)(AN)Br_2 + H_2O \leftrightarrow Br(AN)Pd(COOH) + HBr \quad (6)$$

$$Br(AN)Pd(COOH) + CO \rightarrow HPd(CO)(AN)Br + CO_2 \quad (7)$$

$$HPd(CO)(AN)Br \rightarrow Pd(CO)(AN) + HBr \quad (8)$$

$$HPd(CO)(AN)Br + Pd(CO)(AN)Br_2 \rightarrow HBr + Pd_2(CO)_2(AN)_2Br_2 \quad (9)$$

$$Pd(CO)(AN) + Pd(CO)(AN)Br_2 \leftrightarrow Pd_2(CO)_2\ (AN)_2Br_2 \quad (10)$$

$$Pd_2(CO)_2(AN)_2Br_2 + H_2O = HPd(CO)(AN)Br + HPd(AN)Br + CO_2 \quad (11)$$

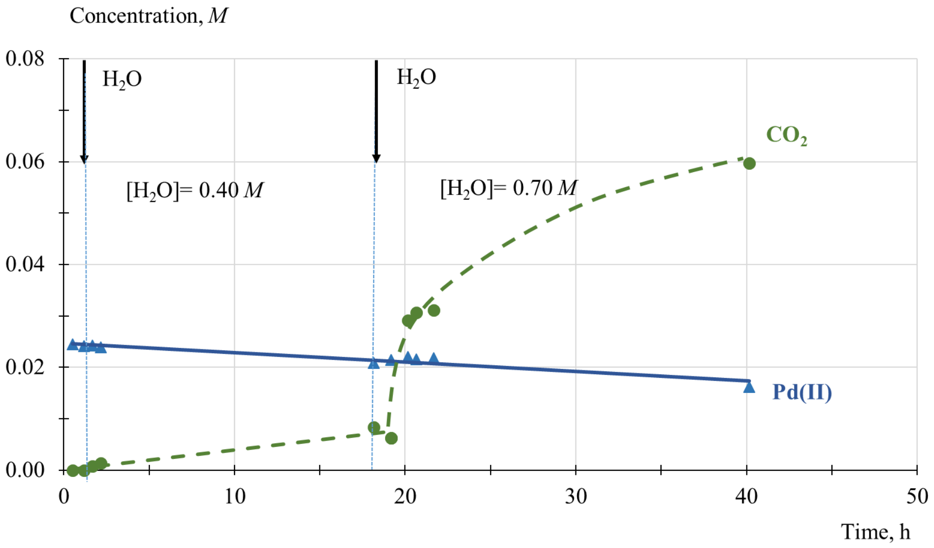

Fig. 8. Changes in concentrations of CO_2 and Pd(II) carbonyl complexes during CO oxidation using oxygen. Conditions: $[PdBr_2]$ = 0.025 M, [LiBr] = 0.05 M.

$$HPd(CO)(AN)Br + O_2 \rightarrow HOOPd(CO)(AN)Br \text{ (slow)} \quad (12)$$

$$HOOPd(CO)(AN)Br + HBr \rightarrow H_2O_2 + Pd(CO)(AN)Br_2 \quad (13)$$

$$Pd(CO)(AN) + O_2 \rightarrow Pd(CO)(AN)(O_2) \xrightarrow{2HBr} Pd(CO)(AN)Br_2 + H_2O_2 \quad (14)$$

$$HOOPd(CO)(AN)Br + CO \rightarrow HOOCOPd(CO)(AN)Br \quad (15)$$

$$HOOCOPd(CO)(AN)Br + HBr \rightarrow CO_2 + Pd(CO)(AN)Br_2 + H_2O. \quad (16)$$

C. $PdBr_2$–LiBr–AN–H_2O–$PcCo_{solid}$

The same catalytic system was used to perform experiments with added $PcCo_{solid}$ ($[PcCo_{solid}]$ = 0.025 M) (Fig. 9). During the first 25 hours, the reaction was performed only with CO, then 20 mL O_2 (~35%) was added into the reactor. No changes were detected in the composition of products and intermediates during the first 5 hours without the addition water. The production of 13% CO_2 was observed, compared to the used palladium, potentially due to oxygen admixtures in CO and a small amount of oxygen on the surface of $PcCo_{solid}$.

After 5 hours, water was added ($[H_2O]$ = 0.55±0.02 M) and the formation of CO_2 was observed; the amount of the latter did not exceed the stoichiometric amount of Pd. The rate was not much higher than in the absence of $PcCo_{solid}$. A decrease in the concentration of Pd(II) carbonyl complex and an increase in the concentration of Pd(I) carbonyl complex were detected. Adding oxygen made the process almost quasi-stationary: concentrations of carbonyl complexes changed from 0.019 M to 0.0154 M for Pd(II), and from 0.0054 M to 0.0073 M for Pd(I). The rate of CO_2 formation increased significantly, and in the first 2 hours after the introduction of oxygen, it was 0.019 M/h. The catalyst turnover number was 4.3.

Oxidation in the presence of $PcCo_{solid}$, as illustrated in Fig. 9, agrees with the results of Experiment 16 in the flow system as shown in Fig. 1. Since oxidation of CO using oxygen leads to the production of hydrogen peroxide, it was interesting to check if it was possible for CO to be oxidized by peroxide in the same system and in the same conditions (in the absence of O_2). After introducing the first portion of H_2O_2 (0.30 mmol, 0.07 M) at $[H_2O]$ = 0.53±0.02 M, the CO_2 concentration reached 0.04 M after 20 hours. The concentration of Pd(II) carbonyl complex decreased from 0.025 M to 0.0167 M, and the concentration of Pd(I) carbonyl complex increased from 0 to 0.012 M. After introducing the second portion of H_2O_2 (0.15 mmol, 0.04 M) and a simultaneous increase in water concentration to 0.82±0.03 M, the CO_2 concentration reached 0.054–0.059 M. By the 45th hour of the reaction, concentrations of carbonyl complexes became almost equal, around 0.01–0.012 M. As mentioned earlier, hydrogen peroxide may partake in the oxidation of hydride complexes of palladium for HPd(CO)Br type, $[Pd^0](CO)$ complexes, and also can be directly involved in CO_2 production through the HOOPd(CO)Br intermediate, according to reactions (15) and (16). There is no doubt that it is possible to form a hydroperoxide intermediate through reaction (17).

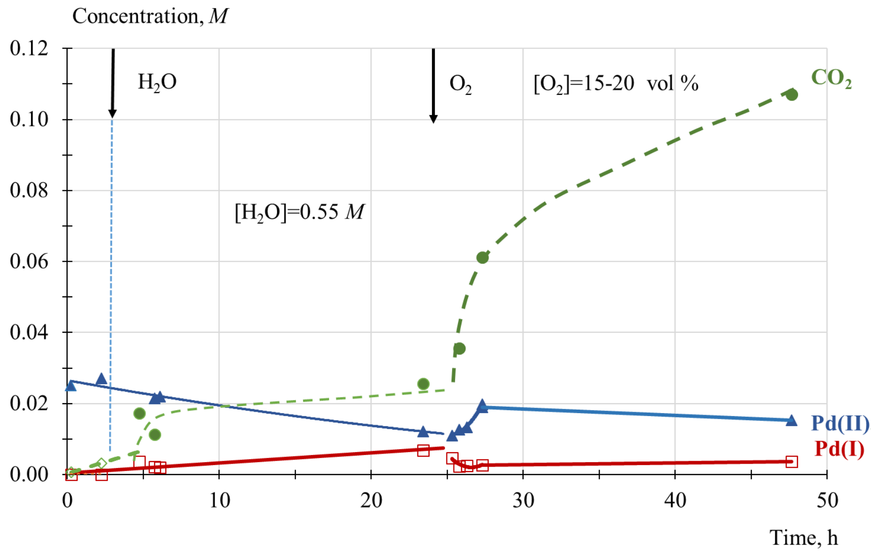

Fig. 9. Effect of $PcCo_{solid}$ on CO oxidation. Conditions: $[PdBr_2]$ = 0.025 M, [LiBr] = 0.05 M, $[PcCo_{solid}]$ = 0.025 M.

$$Pd(CO)(AN)Br_2 + H_2O_2 \rightarrow HOOPd(CO)(AN)Br + HBr \quad (17)$$

The oxidation of Pd(I) carbonyl complex by hydrogen peroxide does not appear to occur, because its concentration increases monotonously during the process.

Comparison of PcM activity in oxidation of CO and MA synthesis

The study of acetylene oxidative dicarbonylation in the presence of phthalocyaninates of different metals (Co, Fe, and Mn) showed that the production rate and MA selectivity by CO, as well as the share of MA in the total of anhydrides in solutions of PcMnOAc, were lower than in the presence of $PcCo_{solid}$ and Pc*Fe (Table 2).

A comparison between CO oxidation kinetics, and the existing kinetics data [12] for oxidative dicarbonylation of acetylene to MA, shows that kinetics are determined by the nature of PcM and do not depend on the type of process. For example, in the case of $PcCo_{solid}$, the rates for both processes increase linearly when its concentration in a solution increases. "Saturation" curves with the substituted Pc*Fe are observed for both processes as well. One of the reasons for the reaction rates to decrease at elevated concentrations of soluble PcM might be the formation of associates in the solution, as well as possible binding of $PdBr_2$ by metal phthalocyaninates (see below).

When the rates of CO_2 and MA production are compared it is necessary to take into account the differences in study conditions. Despite this, the reactivity series of PcM at [PcM] = 0.05 M are identical.

For $\boldsymbol{R}_{MA}$: $PcCo_{solid}$ > Pc*Fe > Pc*Co >> PcMnOAc.

For $\boldsymbol{R}_{CO2}$: $PcCo_{solid}$ > Pc*Fe > Pc*Co >> PcMnOAc.

The low activity of PcMnOAc complexes may be explained, according to theoretical calculations

Table 2. Synthesis of maleic anhydride (MA) and succinic anhydride (SA) via acetylene dicarbonylation reaction

Exp.	PcM	[PcM], M	α	$[O_2]_{exit}$,%	***R***, M/h		MA selectivity, %	
					MA	SA	MA + SA	CO
8	–	–	2	10	0.12	0.36	25.0	27.8
9	$PcCo_{solid}$	0.05	2	10	0.60	0.020	96.8	~ 100
10	Pc*Fe	0.04	2	10	0.39	0.01	97.5	82.6
11	Pc*Co	0.02	2	10	0.38	0.19	79.8	90.5
12	Pc*Co	0.05	2	20	0.43	0.01	97.3	85.0
13	PcMn(OAc)	0.025	1	15	0.08	0.03	72.7	28.0
14	$PcCo_{solid}$	0.05	1	22	0.58	0.054	91.4	83.4

*Conditions: $[PdBr_2]$ = 0.05 M, $[H_2O]$ = 0.1–0.2 M, T=40 °C.

(method DFT)[2], by the greater stability of superoxide manganese complexes, in comparison with $PcCoO_2$ and $PcFeO_2$. Whereas for PcFe and PcCo the changes in the Gibbs energy upon formation of $PcFeO_2$ and $PcCoO_2$ are similar, –0.6 and 0.2 kcal/mol, the ΔG^0_{298} is –6.7 kcal/mol upon formation of $PcMn(OAc)O_2$. This indicates that the connection between oxygen and manganese is too strong, which may be manifested through elevated activation barriers of oxidation stages for hydride complexes and Pd(0) complexes. A comparative quantum chemical analysis was performed for unsubstituted phthalocyaninate complexes PcFe, PcCo, and PcMn(OAc) to understand whether they could partake in the re-oxidation of Pd(0) and hydride complexes of Pd(II). The calculations suggest that for $PcFeO_2$, $PcCoO_2$, and $PcMn(OAc)O_2$ complexes, the mechanisms of interaction with $Pd(CO)_2(AN)_2{}^0$ (used as an example) are quite similar. During the first stage, an intermediate with the M–O–O–[Pd] fragment is formed. Then, the O atom (closest to Pd) is protonated. Finally, the O–O bond is destroyed, leading to the formation of oxo complexes of metal phthalocyaninates and $Pd(CO)_2(OH)Br$. Reduction of the intermediate oxo phthalocyaninate PcMn(OAc)=O by carbon oxide in PcMn(OAc) also has a very high barrier, 20 kcal/mol.

The differences between PcMn(OAc) and other PcM were observed in experiments where the effect of PcM concentration on the concentration of Pd(II) carbonyl complex was analyzed (Fig. 10). The system contained $[PdBr_2]$ = 0.025 M, [LiBr] = 0.0125 M (α = 0.5), $[H_2O]$ = 0.5–0.7 M, and CO/O_2 = 1:1. Pc*Co, Pc*Fe, and $PcCo_{solid}$ were found to decrease the $[Pd^{II}](CO)$ concentration almost to the same extent, as their own concentrations increased. The same effect was observed in the presence of PcMn(OAc), but the decrease in $[Pd^{II}](CO)$ concentration was less dramatic and led to a slightly higher concentration at high [PcM], which agreed with the lower oxidation rate of CO.

In order to explain certain peculiarities in Fig. 10, it is necessary to note that these experiments were carried out at α = $[LiBr]/[Pd]_\Sigma$ = 0.5, like the experiments that demonstrated high rates of CO oxidation (Figs. 1 and 3), and in contrast with the experiments at α = 2 (Fig. 9), at the same palladium concentration, $[Pd]_\Sigma$ = 0.025 M. For example, the initial rate of CO_2 production is 0.17 M/h in Fig. 1, but for $PcCo_{solid}$ and Pc*Fe, the rate is 0.1 and 0.15 M/h, respectively (Fig. 3). When α = 2 (Fig. 9), the initial rate, depending on the reaction time, 2.4 or 3.9 hours, at the same PcM concentrations, $[PcCo_{solid}]$ = 0.025 M, is 0.004 or 0.009 M/h.

It is necessary to note that at higher oxidation rates (Fig. 3), at α = 0.5, the concentration of Pd(II) carbonyl complex (Fig. 10) is 5 times lower than at α = 2 (Fig. 9), at the same PcM concentration, 0.025 M.

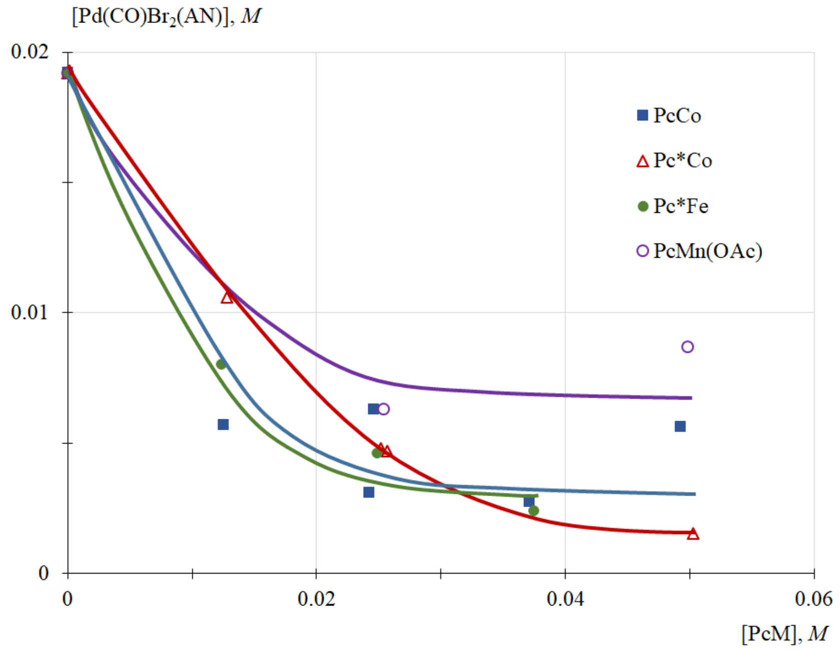

Fig. 10. Effect of PcM nature and concentration on $[Pd(CO)Br_2AN]$ concentration in the contact solution after two hours.

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[2] R.S. Shamsiev, O.L. Kaliya and others; unpublished data. The paper by R.S. Shamsiev, which contains the results of the quantum chemical calculations was submitted to the *Russian Chemical Bulletin* in 2019.

Therefore, at lower [LiBr] concentrations, the rates for the following processes increase: CO oxidation; formation and transformation of intermediates, including Pd(II) regeneration. At the same time, the concentration of Pd(II) carbonyl complexes decreases. A logical explanation for this trend is that Co/Fe/Mn phthalocyaninates, while accelerating CO oxidation (up to [PcM] = 0.03 M), not only participate in the oxidation of intermediates – complexes of Pd(0), [Pd]–H and Pd(I), but also in CO_2 formation (directly), i.e. in a new direction of CO oxidation. For example, the formation of an intermediate complex upon interaction between $PcM(O_2)$ and Pd(II) carbonyl complex could facilitate a nucleophilic attack by H_2O on the carbonyl, due to the higher electrophilicity of the C atom and a lower concentration of $[Pd^{II}](CO)$ (see Scheme 2):

$$\mathrm{PcMO{-}OPd(CO)Br_2(AN)} \xrightarrow[\text{-HBr}]{H_2O} \mathrm{PcMO{-}OPd(COOH)Br(AN)} \xrightarrow[\text{-CO}_2,\ \text{-AN}]{CO}$$

$$\longrightarrow \mathrm{PcMO{-}OPd(CO)(H)Br} \xrightarrow{AN} \mathrm{PcM{=}O} + \mathrm{Pd(CO)(OH)Br(AN)}$$

Scheme 2

The quantum chemical modeling (see Footnote 2) confirms that PcM–O–O–[Pd] (Scheme 2) and PcM–[Pd] complexes may be formed. This creates grounds for the second hypothesis, at least for the soluble PcM: binding of the initial Pd(II) complexes by metal phthalocyaninates or their oxygenyl complexes $PcMO_2$ decreases the concentration of those complexes that form Pd(II) carbonyl complexes.

Summary

The importance of transition metal phthalocyaninates in the catalysis of maleic anhydride synthesis has been demonstrated. For example, under comparable conditions, with $\alpha = [LiBr]/[PdBr_2] = 2$, $P_{O2} = 0.1$ bar, $[CO]/[C_2H_2] = 2$, and in the absence of $PcCo_{solid}$, the rate of MA synthesis is 0.12 M/h, while selectivity is 25% by MA. In the presence of $[PcCo_{solid}] = 0.05$ M, in the same conditions, $\boldsymbol{R}_{MA} = 0.60$ M/h, while selectivity is 96.8% (Table 2). The major advantage of phthalocyaninate catalysts is that they boost the selectivity of MA synthesis, at low amounts of oxygen in the gas mixture, $P_{O2} \geq 0.05$ bar. It is particularly important for syntheses that involve acetylene. For instance, in the presence of $PcCo_{solid}$, at $P_{O2} = 0.05$ bar (6.5 vol % of O_2), MA synthesis occurs with a rate of $\boldsymbol{R}_{MA} = 0.35$ M/h and selectivity of 91%.

PcM complexes also boost the rate of the side (model) reaction of CO oxidation into CO_2 (Fig. 3). For example, at $\alpha = 0.5$ and $P_{O2} = 0.38$ bar, the rate of CO oxidation in the absence of PcM is 0.013 M/h, and in the presence of 0.025 M $PcCo_{solid}$ the rate is 0.17 M/h, i.e. it is 13 times higher.

A comparison of two processes, CO_2 synthesis and MA synthesis, in the presence of PcM has made it possible to determine the reactivity series for Co(II), Fe(II) and Mn(III) phthalocyaninates, soluble or insoluble in acetonitrile. The reactivity series were similar for both processes. Based on the results of the present study, the following recommendations may be given to optimize MA synthesis, accelerate the reaction and boost the selectivity, as well as to improve the stability of the catalytic system:

(1) to catalyze the synthesis of maleic anhydride, it is recommended to use $PcCo_{solid}$ and the soluble Pc*Fe, at concentrations of 0.3–0.4 M;

(2) the concentration of LiBr should be in the following range: $[LiBr]/[PdBr_2] = 0.5–2.0$. This would provide the catalytic system with stability, a high oxidation rate and a low rate of CO_2 production (rate of ^{13}CO consumption in the synthesis of diagnostic molecules);

(3) water concentration should not exceed 0.1–0.2 M in order to slow down the side reaction – production of CO_2.

Conclusions

1. Based on the study of the kinetics of CO oxidation using oxygen, and oxidative dicarbonylation of acetylene into maleic anhydride, and based on the comparison of the reactivity series of metal phthalocyaninates in both reactions in the same catalytic system, it has been shown that CO oxidation is indeed a suitable model for acetylene oxidative dicarbonylation.

2. The kinetics of CO_2 production were analyzed. The PcM reactivity series, for CO oxidation and MA synthesis, was determined. It has been shown that there is a satisfactory correlation between the rates ($\boldsymbol{R}_{CO2}$ and $\boldsymbol{R}_{MA}$) and [PcM], as well as the nature of the metal in phthalocyaninate complexes for both processes.

3. Analyses of Pd(II) complexes dissolved in acetonitrile and adiponitrile were performed, using electron spectroscopy in UV and visible ranges. The important role of the dimeric $[PdBr_2(AN)]_2$ complexes in CO oxidation were demonstrated.

4. The concentrations of intermediate carbonyl complexes of Pd(II) and Pd(I), as well as CO_2

concentrations were measured throughout the course of the reaction, using IR spectroscopy. Based on this data, the mechanism of CO_2 formation was hypothesized. Also, the effect of [PcM] on $[Pd^{II}](CO)$ concentration in stationary conditions during the catalytic oxidation of CO was determined.

5. Improvements to conditions of maleic anhydride synthesis have been suggested for the effective synthesis of maleic anhydride double-labeled with ^{13}C.

Acknowledgments

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The authors declare no conflicts of interest.

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