CATIONIC PD(II) COMPLEXES CATALYTICALLY ACTIVE IN THE OXIDATION OF OLEFINS: MECHANISMS OF THE FORMATION IN WATER–ACETONITRILE–CHLORIC ACID MEDIUM*

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The catalytic system Pd $(OAc)_2$–$HClO_4$–CH_3CN (AN)–H_2O of olefins oxidation was studied. Information about the ways of forming catalytic active cationic palladium complexes was detected. Analysis of the electron spectroscopy data shows the probability of existence complexes $[Pd(AN)(H_2O)_3]^{2+}$ (λmax = 360–365 nm), $[Pd(AN)_2(H_2O)_2]^{2+}$ (λmax = 335–345 nm) in catalytic system. The preparation method of stable and sufficient active catalytic system for obtaining reproducible kinetic data was designed.

Keywords: *oxidation of olefins, water – acetonitrile, complexes of palladium (II), the active catalyst.*

Introduction

Cationic complexes of Pd(II) and other transitional metals have been long drawing the attention of researchers as active and superelectrophilic catalysts and reagents of olefins and alkynes transformations [1–15]. In addition to the increased and specific reactivity towards olefins, palladium cationic complexes in aqueous organic media show also special "non-classical" kinetic behavior [1, 8, 12, 13] in olefins oxidation into carbonyl compounds. This behavior considerably differs from the regularities of palladium(II) anionic chloride complexes oxidation (Wacker oxidation) [16] in solutions. It was found [8] that acidic ligands HSO_4^-, NO_3^-, ClO_4^-, OAc^- do not affect the process rate in aqueous acetonitrile (and in other aqueous organic media) in the presence of strong acids. This fact, in turn, is the evidence of the participation of cationic Pd^{2+} complexes containing acetonitrile and water as ligands in the process.

The most successful form of a precursor for catalysts for aqueous organic media is $Pd_3(OAc)_6$ trimer forming cationic complexes in acidic media. Thus, $Pd(OAc)_2$–$HClO_4$–CH_3CN (AN)–H_2O system was studied in the oxidation of cyclohexene with *p*-benzoquinone at 25°C with an attempt of creating a kinetic model for the description of the obtained kinetic regularities within a certain standardized procedure of preparing contact solutions [12].

At the same time, the behavior of $Pd_3(OAc)_6$ trimer in organic media is very complex [17]. In methanol, substitution of bridging ligands μ_2–OAc by μ_2–OMe with preservation of the trimeric composition of palladium diacetate [18] is observed. Interaction with coordinating solvents (L) results

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in a number of transformations of the trimer with the formation of dimeric and mononuclear $Pd(OAc)_2(L)_2$ complexes with the solvent. The formation of palladium(II) cationic complexes with acetonitrile in acidic aqueous solutions [19] was studied. We showed previously that the electronic absorption spectra and the kinetic behavior of the catalytic system in the oxidation of olefins into *p*-benzoquinone are influenced by the time of $Pd_3(OAc)_6$–AN [14] system keeping.

In view of the above the purpose of this work was to establish the ways of forming a catalytic system that is active and reproducible in cyclohexene and ethylene oxidation and to reveal the dependence of the complexes state in solutions on H_2O, $HClO_4$ and palladium concentration and on the time of the active precursors formation by UV and NMR spectroscopy.

Experimental

The following reagents were used in the work: acetonitrile, CH_3CN, Lab-scan HPLC (SG) grade, CAS: 75-05-8, with the content of the main substance ≥ 99.9%; chloric acid, $HClO_4$, chemically pure, TU 6-09-2878-84, 11 M; lithium perchlorate anhydrous, $LiClO_4$, pure, TU 6-09-3360-73; ethylene, C_2H_4, GOST 25070-87; *p*-benzoquinone, $C_6H_4O_2$, 99% purity, mp = 116°C (additionally purified by sublimation); palladium dichloride, pure, TU 2625−048−00205067−2003.

Palladium diacetate trimer $Pd_3(CH_3COO)_6$ was obtained according to method [20] and identified by ^1H NMR [21]. An additional confirmation of the trimeric crystalline composition of the obtained product is its good solubility in organic solvents [17].

$[Pd(AN)_4](NO_3)_2$ complex was obtained by dissolving palladium dichloride in acetonitrile with the subsequent addition of silver nitrate in the quantity necessary to terminate silver chloride precipitation. A filtered solution with λ_{max} = 380–385 nm was used further for experiments.

Pd(II) perchlorate in a water solution was obtained by the technique [22] improved by us for obtaining reproducible results. A sample of palladium(II) chloride was dissolved in hydrochloric acid at 40 – 50°C. The obtained transparent brown solution was diluted 8−10-fold, and a 0.2 M sodium hydroxide solution was added to it dropwise at vigorous stirring until the neutralization (accompanied by the formation of a brown flake-like precipitate of palladium hydroxide) was complete. In the process the solution became colorless.[1] The precipitate was washed to remove chloride ions by multiple decantations and then dissolved with the addition of concentrated chloric acid and water in such quantities that the obtained solution had concentration $[H^+]$ = 1.2 M. The specified acidity is necessary to exclude the possibility of palladium(II) aquacomplex hydrolysis. Soon after the acid addition the precipitated hydroxide dissolved, and the solution became deep-brown again. After 24 h the color of the solution changed to yellow, and the UV spectra of the yellow solution coincided with the literature data for Pd(II) perchlorate [22] containing an ion. The cationic complex of palladium in

[1] If an excess of the alkali is added, the hydroxide precipitate starts dissolving, and the solution becomes brown.

the acidic water solutions of the perchlorate is in the form $Pd(H_2O)_4]^{2+}$. The quantity of the formed complex was determined by the quantity of palladium(II) in the solution with the use of calibration straight lines (UV spectra) at the transformation of palladium(II) into chloride $PdCl_4^{2-}$ complexes. The synthesis loss is about 15–20% of the initial quantity of palladium.

Electronic absorption spectra of the solutions were measured with the use of a Specord M-40 spectrophotometer in a closed quartz cuvette 0.5 cm thick at room temperature. ^{1}H NMR and ^{13}C NMR spectra were measured with the use of an AVANCE 600 spectrometer at operating frequencies 600 and 150 MHz, respectively. The signals of solvents: CD_3CN (1.93 ppm for ^{1}H and 1.28 ppm for ^{13}C); $CDCl_3$ (7.25 ppm for ^{1}H and 77.00 ppm for ^{13}C) were used as the standard. Measurements were performed at 30°C.

For measuring kinetic dependences a closed volumetric installation with a 100 ml reactor and a solution volume of 10 ml was used. Stirring was carried out with a magnetic mixer. The temperature of 30°C was maintained constant by means of a temperature-controlled box, in which the reactor, a burette and most connecting hoses were located.

Results and Discussion

In $Pd(OAc)_2$–AN–H_2O–ClO_4 system, the formation of Pd(II) complexes of various composition is possible. Therefore, it was necessary to reveal:

- possible transformations of $Pd_3(OAc)_6$ trimer in AN;
- the conditions of the existence of dicationic complexes of palladium in the absence of mono- and diacetate complexes in acidic media, namely: $Pd(OAc)^+$ and $Pd(OAc)_2$;
- the conditions of the termination of the hydrolysis of the cationic complexes of palladium;
- the existence of multinuclear complexes;
- the conditions of the formation of cationic complexes of assumed composition $[Pd(AN)_x(H_2O)_{4-x}]^{2+}$ with various values of *x*.

Interaction of $Pd_3(OAc)_6$ trimer with acetonitrile. Analysis of time changes in the UV spectra of $Pd_3(OAc)_6$ – AN solutions (Figure 1) showed that the absorption maximum at 393 nm is observed within the first 30 min after mixing, which conforms to $Pd_3(OAc)_6$ spectra in THF and chloroform [20]. However, the specified band practically disappears within one day. After 7 days there is a slight inflection in the range of 370 nm.

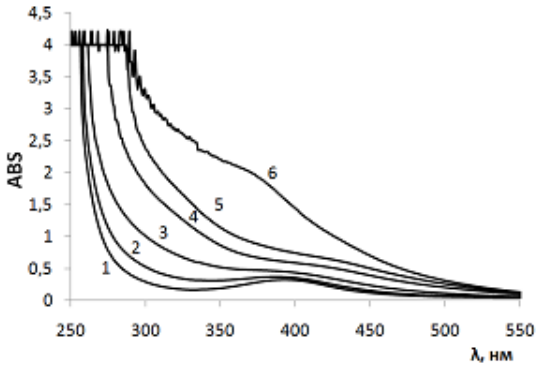

Figure 1. Time changes in the UV spectra of the system $Pd_3(OAc)_6$–AN ($[Pd(OAc)_2]$=0.005 mol/l: 3 min (1), 21 min (2), 45 min (3), 150 min (4), 1 day (5), 7 days (6).
[нм means nm]

Fuller information on the time transformations in the solution of the palladium diacetate trimer in acetonitrile was obtained by studying the ^1H and ^{13}C NMR spectra of a saturated solution of the palladium diacetate trimer in CD_3CN. The measurement of the ^1H NMR spectra was carried out for 6 h. Then ^1H and ^{13}C NMR spectra were periodically measured within two weeks.

The following signals were observed in the ^1H NMR spectrum measured immediately after the sample preparation:

1) A quintet of residual protons of acetonitrile at 1.93 ppm.

2) A signal of palladium acetate trimer at 1.89 ppm. The intensity of this signal constantly decreased subsequently, and it practically disappeared in two weeks.

3) A signal of acetic acid at 1.95 ppm, the intensity of which constantly increased in time.

4) Six signals of different intensity at 1.75; 1.83; 1.87; 1.88; 1.91 and 2.00 ppm, which are presumably related to the acetate ligands in the palladium complexes: their intensity decreased in time, but other signals, the intensity of which grew, appeared in the same area (1.6÷2.2 ppm).

5) A broad signal of an acidic proton of acetic acid at 8.88 ppm, the intensity of which increased in time, and it was shifted to the weak field (after two weeks: 9.29 ppm).

6) A broad signal at 0.75 ppm probably due to water coordinated by palladium, the intensity of which gradually decreased, and after 24 h it practically disappeared (it could be seen only at long accumulation with the number of impulses NS=160).

7) A broad signal at 2.13 ÷ 2.15 ppm, most likely, due to water, which undergoes exchange with the coordinated water and the acidic proton, the intensity of which also decreased in time, and it was practically not observed after 24 h even at long accumulation.

The presence of water in the solution can be explained by the presence of traces of water in the solvent. When the content of water no more than 0.1%, the number of moles of H_2O per mole of $[Pd]_\Sigma$ is approximately equal to 10.

8) A broad signal at 2.12 ppm was registered for the first time (at the number of impulses NS=64) 1.5 h after palladium acetate mixing with acetonitrile. The signal intensity reached a maximum within 24 h and kept at this level for two days. Then it began to decrease and almost disappeared after two weeks (long accumulation, the number of impulses NS=160). Presumably, this signal can be attributed to the bridging ligand μ-OH in the formed palladium complex, which then undergoes further transformations.

The same picture of changes similar to the proton spectra was observed in the ^{13}C NMR spectra: the intensity of the acetic acid signals increased, and the intensity of the signals of the trimer acetate groups decreased. Therefore, in all the complexes that are present in the solution the total quantity of acetate ligands decreases, which, in turn, indicates the possible coordination of acetonitrile by palladium. Unfortunately, in none of the carbon spectra registered during the two-week period was it possible to observe additional signals in the acetonitrile area (0 ÷ 4 ppm) confirming the coordination of acetonitrile with palladium. However, the existence of acetonitrile ligands cannot be excluded, because signals of carbon nuclei coordinated with CD_3CN should be observed in ^{13}C spectra as quintets (analogously to the ^{13}C signals of CD_3CN). Probably they were not accumulated because of the low concentration.

In general, the transformation of the cyclic trimer <u>in the absence of water and acid additives</u> can be explained by its gradual transformation into various palladium complexes, among which there can be both cyclic and linear complexes − the trimer, dimer or monomer containing acetate ligands (according to NMR spectra), and, perhaps, acetonitrile. In our opinion, water in the solution of $Pd_3(OAc)_6$ – AN that is present in a small quantity in the solvent can be also coordinated by palladium(II).

Determination of conditions of equilibrium achievement in $Pd(OAc)_2$ – AN – H_2O – $HClO_4$ – $LiClO_4$ system. Because the UV spectra of the catalytic system after introduction of water and acid, as well as the rate of ethylene oxidation, depend on the time of preliminary keeping the palladium diacetate solutions in acetonitrile, it was necessary to find out, how keeping the solutions before the addition of water and the acid affects the positions of the maxima in electronic absorption spectra 20 min after the addition of the acid, water and $LiClO_4$ and after long keeping of the acidic water-acetonitrile solutions.

It turned out that the UV spectra of the solutions obtained from two initial solutions (**IS**) of $Pd(OAc)_2$ – AN (freshly prepared **IS I** and **IS II** kept for 1 week), 20 min after the addition of the acid, water and $LiClO_4$ (systems **III** and **IV**, respectively) strongly differ. Thus, system **III** obtained from solution **I** is characterized by maxima at 275 and 345−350 nm (Figure 2, spectrum 1), and solution **IV** (from kept solution **II**) has a maximum at 360−365 nm (Figure 2, spectrum 6). At the same time the

state of the palladium complexes in systems **III** and **IV** after keeping for a week becomes identical, because one band at 305−310 nm (system **V**) is observed in the UV spectra of these solutions. Note that the system obtained on the basis of palladium(II) perchlorate (i.e., in the absence of acetate ligands, see below) also comes to the same final state.

In order to establish the influence of the time of keeping the initial solution on the state of the catalytic system we carried out an experiment, during which every day within a week after the preparation of initial solution $Pd_3(OAc)_6$ – AN (**I**) we prepared systems on its basis with the addition of water, the acid and $LiClO_4$ (to maintain constant ionic strength). The spectra of the obtained solutions are also presented in Figure 2. We observed the tendency of gradual change of the spectral bands of the studied solutions from state **III** to state **IV** as the initial solutions are used upon the transition from **IS I** to **IS II**. The band with a maximum at 275 nm disappears as the time of keeping the IS increases, and the band at 347 nm is shifted to the area of 360 nm (system **IV**).

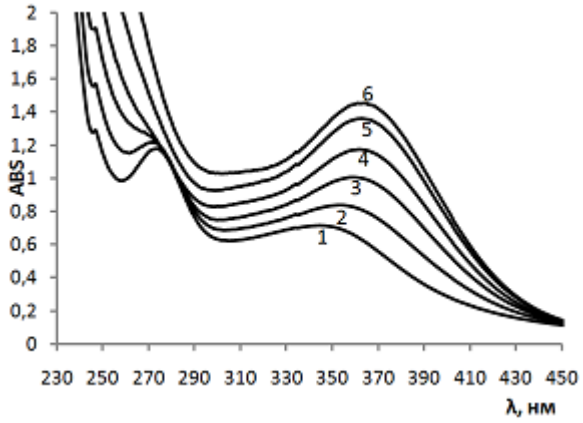

Figure 2. The influence of the time of preliminary keeping the initial solution **IS** on the spectra of catalytic system $Pd(OAc)_2$–AN–H_2O–$HClO_4$–$LiClO_4$ (**I**) ($[H^+]$ = 0.2 mol/l, I=0.5 M, $[H_2O]$ = 0.74 (mole fraction in the system AN–H_2O), $[Pd(OAc)_2]$=0.005 mol/l):
IS keeping time: freshly prepared (1), 1 day (2), 2 days (3), 3 days (4), 4 days (5), 6 days (6).
[нм means nm]

The next experiment was performed with the use of a solution of $Pd(OAc)_2$ – AN – H_2O – $HClO_4$ – $LiClO_4$ system obtained by preliminary keeping the IS for three days (spectrum 3 in Figure 2). This solution (let us denote it as solution **3**) was kept from 1 to 8 days before the measurement of the UV spectra. The electronic spectra of solution **3** are presented in Figure 3.

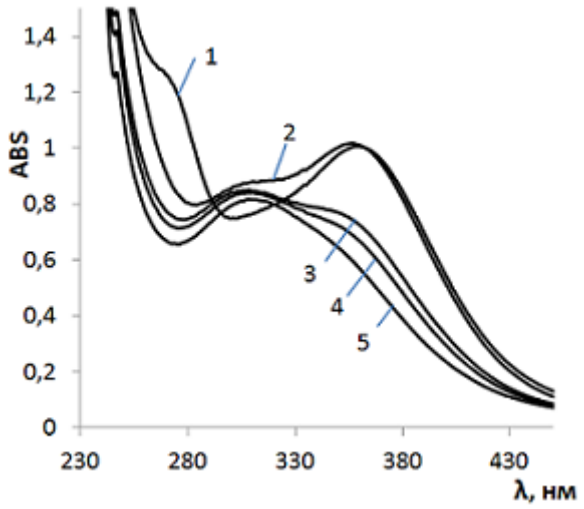

Figure 3. Influence of the time of keeping solution **3** of $Pd(OAc)_2$–AN–H_2O–$HClO_4$–$LiClO_4$ system ($[H^+]$=0.2 M, I=0.5 M, $[H_2O]$ = 0.74 (mole fraction), $[Pd(OAc)_2]$=0.005 M):
(1) 20 min, **(2)** 1 day, **(3)** 5 days, **(4)** 6 days, **(5)** 8 days.
[нм means nm]

It can be seen from Figure 3 that the band at 275 nm disappears the second day, and a maximum at 305 nm appears. The latter slightly decreases in the next days, while the band at 360 nm monotonously decreases and completely passes into a state with a maximum in the range of 305–307 nm.

The system $Pd(OAc)_2$–CH_3CN–$HClO_4$–H_2O was studied by NMR. A solution of $Pd_3(OAc)_6$ in $CDCl_3$ [5 mg (0.029 M) of palladium diacetate in 0.75 ml of chloroform] with the addition of 30 μl of CH_3CN (0.71 M) (MeCN : Pd molar ratio was 25 : 1) was prepared. Then 10 μl of 65% $HClO_4$ (0.145 M) in water (0.396 M) was added. It was found from the ^1H and ^{13}C NMR spectra that the palladium acetate trimer does not interact with acetonitrile in chloroform within a week. After the addition of the acid and water white flakes appeared in the whole volume of the solution, and after an hour the yellow-brown solution became colorless. The first registered ^1H NMR spectrum (5 min after the acid addition) showed essential changes:

(a) The signals of the acetate groups of the palladium acetate trimer, of the hydroxo-complex trimer and of the impurity disappeared (see [18] about the composition of palladium acetate in chloroform), and the intensity of the acetic acid signal (2.05 ppm) increased, which indicates decomposition of the structure of the palladium cluster.

(b) The intensity of the signal of free acetonitrile (1.97 ppm) decreased, and broad signals at 2.27; 2.35; 2.37 and 2.74 ppm appeared in the spectrum, as well as a narrower signal at 2.65 ppm (Figure 4).

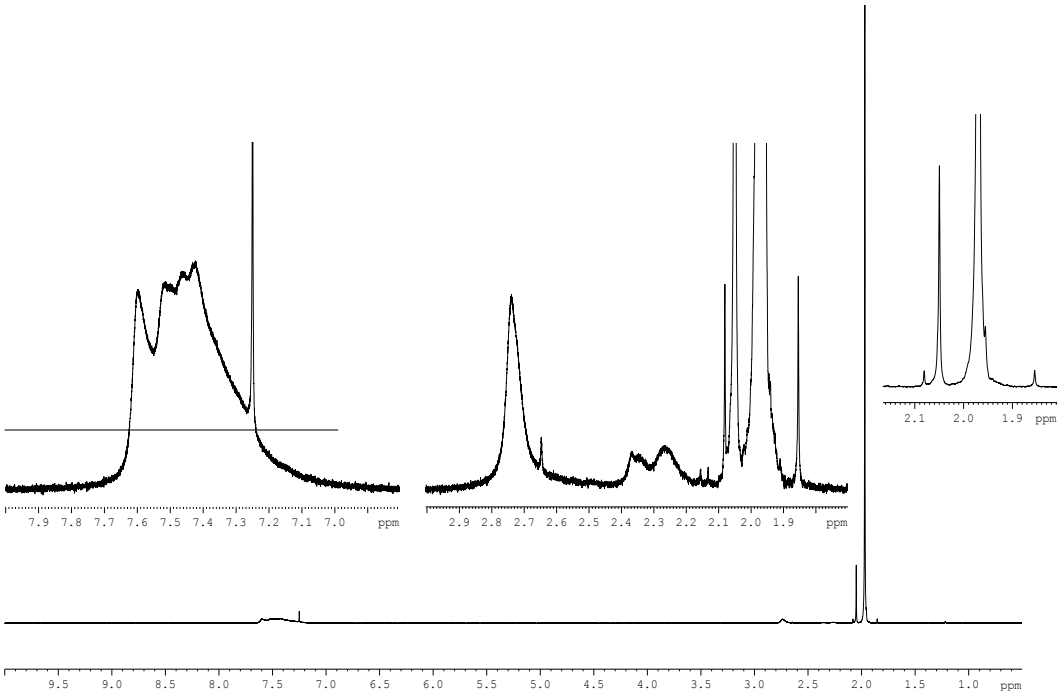

Figure 4. ^{1}H NMR spectrum 5 min after the addition of $HClO_4$ (65% aqueous solution) to the solution of a mixture of $Pd(OAc)_2$ and CH_3CN in $CDCl_3$:
$[Pd(OAc)_2]$=0.029 M, $[CH_3CN]$=0.71 M, $[HClO_4]$=0.145 M.

Within an hour seven ^{1}H NMR spectra were registered. During this time, changes of signals by the chemical shifts, by the intensity ratios and by the signals width were observed in the field of 2.1÷3.0 ppm. The measurements were performed periodically within 20 days. A complex superposition of the signals of chloric acid and water was observed in the field of 7.0 ÷ 7.7 ppm. Besides, the chemical shifts and intensity ratios of these signals also changed over time. The obtained data indicate continuous exchange processes occurring for a long time in the studied system ($Pd(OAc)_2$–$CDCl_3$–CH_3CN–H_2O–$HClO_4$).

Five days after the addition of chloric acid (accumulation during 16 h, NS = 7627) a ^{13}C NMR spectrum was registered, in which, in addition to the signals of acetic acid and acetonitrile, broad signals in the acetonitrile area 0.8 ÷ 4 ppm (methyl groups) and 115÷126 ppm (CN groups) were observed, as well as broad signals of the acetate groups in the range of 18 ÷ 30 ppm (methyl groups) and 175÷183 ppm (carbonyl groups) (Figure 5).

On the basis of ^{1}H and ^{13}C NMR it is possible to assume that the solution containing $Pd(OAc)_2$–$CDCl_3$–CH_3CN–H_2O–$HClO_4$ contains various palladium complexes, which undergo a complex exchange interaction and contain both acetate and acetonitrile ligands. It will be shown below that the acetate ligands do not remain in more acidic solutions at high concentration of acetonitrile.

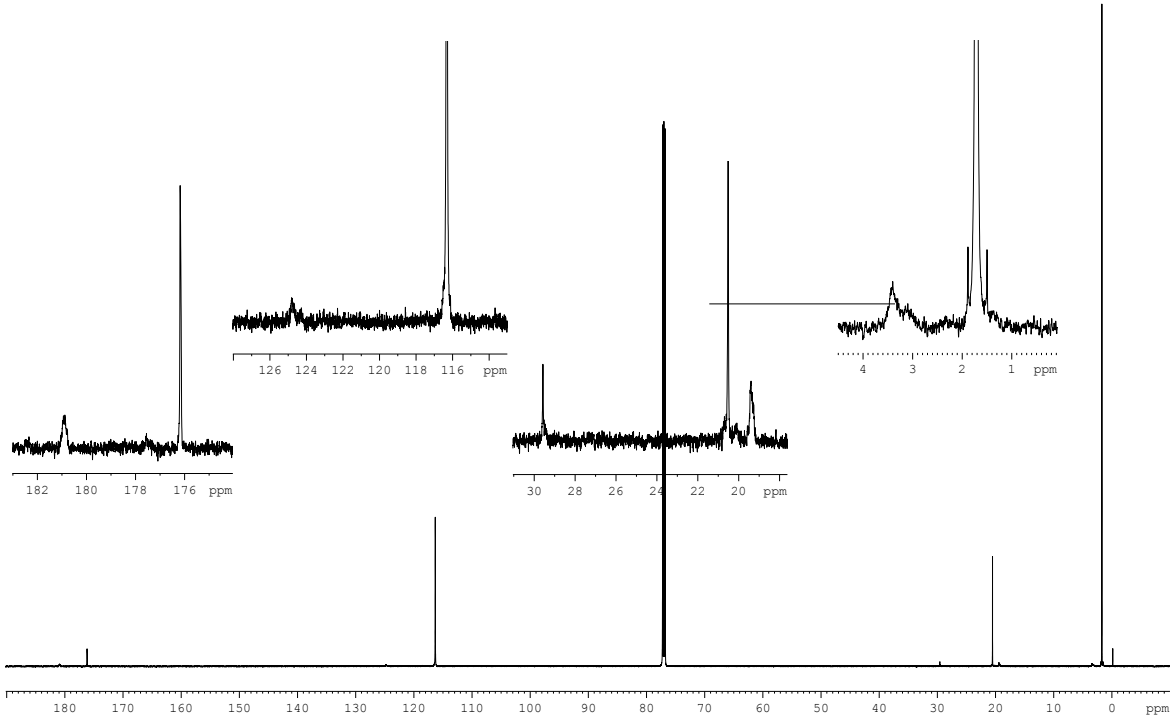

Figure 5. ^{13}C NMR spectrum 5 days after the acid addition to the solution of a mixture of $Pd(OAc)_2$ and CH_3CN in $CDCl_3$: $[Pd(OAc)_2]$=0.029 M, $[CH_3CN]$=0.71 M, $[HClO_4]$=0.145 M.

Comparison of the properties of the solutions obtained on the basis of $Pd(ClO_4)_2$ and $Pd(OAc)_2$. Comparison of the UV spectra of systems Pd^{2+}–AN – H_2O – $HClO_4$ – $LiClO_4$ based on palladium perchlorate and diacetate followed by kinetic studies was performed at constant ionic strength of the solutions (I=1.0 M), which was supported by the introduction of $LiClO_4$ at various times of keeping the solutions. It can be seen from the UV spectra (Figure 6) that these systems come after a time to some identical final state with a characteristic absorption band in the range of 305–310 nm.

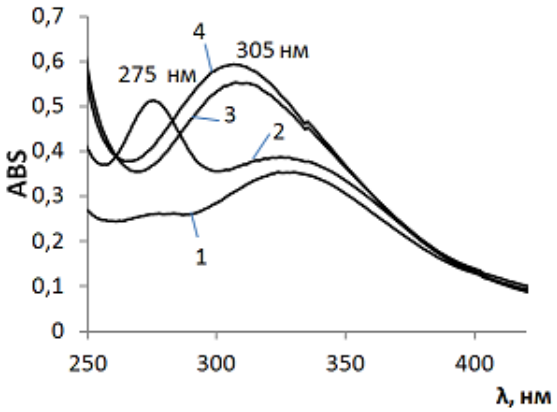

Figure 6. UV spectra of systems Pd(II)–AN–H_2O–$HClO_4$–$LiClO_4$ depending on keeping time ($[Pd]_\Sigma$ = 0.005 M, I = 1.0 M, $[H^+]$ = 0.2 M, $[H_2O]$ = 0.74 (mole fraction)):
Perchlorate system: $[Pd(H_2O)_4]^{2+}$ **(1)**, 20 min, $[Pd(H_2O)_4]^{2+}$, 1 week **(3)**;
Acetate system: $Pd(OAc)_2$, 20 min **(2)**, $Pd(OAc)_2$, 1 week **(4)**.
[нм means nm]

The difference between the freshly prepared solutions on the basis of palladium(II) diacetate and perchlorate consists in the presence of an intensive maximum at 275 nm for the acetate system and a very weak inflection in this area, for the perchlorate one. In order to determine the nature of the maximum at 275 nm the following experiments were made.

1. The addition of acetic acid (0.016 M) or sodium acetate (0.016 M) into the perchlorate system Pd^{2+}–AN–H_2O–$HClO_4$–$LiClO_4$ ($[Pd]_\Sigma$=0.004 M, I=1.0 M, $[H^+]$=0.5 M) did not result in changes in the spectrum. Most likely, this indicates the irreversible substitution of the acetate ligand in acidic media at dissolution of $Pd_3(OAc)_6$ trimer in the solutions with higher concentration of acetonitrile (more than 7 M).
2. The addition of acetonitrile into the aqueous solution of palladium perchlorate ($[Pd(H_2O)_4]^{2+}$ – H_2O – $HClO_4$) at $[H^+]$=0.2 M led to the emergence of a noticeable maximum at λ = 275–280 nm (Figure 7) disappearing over time.

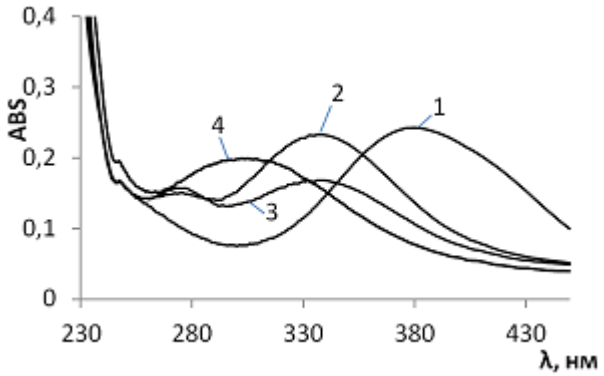

Figure 7. UV spectra of perchlorate system $[Pd(H_2O)_4]^{2+}$–H_2O–$HClO_4$ after one day depending on concentration AN ($[Pd^{2+}]$ = 0.005 M, I = 0.5 M, $[H^+]$ = 0.2 M): [AN] = 0 M **(1)**, [AN] = 3.7 M (mole fraction 0.11) **(2)**, [AN] = 7.5 M (mole fraction 0.26 **(3)**, [AN] = 7.5 M (mole fraction 0.26) **(4)**. [нм means nm]

The total of the results presented in Figures 6 and 7 suggests that the maximum in the UV spectra at λ = 275 nm in acidic media is not due to the Pd(II) complex with acetate ligands. The equality of ethylene oxidation rates in the perchlorate and acetate systems also indicates the small contribution of the complex containing the acetate ligands to the reaction rate, even if the complex is present in the solution.

Influence of $HClO_4$ concentration on the spectra of $Pd(OAc)_2$ – AN – H_2O – $HClO_4$ – $LiClO_4$ system. $LiClO_4$, H_2O and the acid were added to the initial $Pd(OAc)_2$ – AN solution immediately after the preparation. Spectra were measured 20 min after mixing the components. It follows from the spectra in Figure 8 that the increase in the acid concentration affects the intensity of the band at 275 nm. The band at 275 nm is practically absent at the acid concentration of 1.0 M, and the obtained spectrum of this solution coincides with the spectrum of the system based on palladium(II) perchlorate

(spectrum 1 in Figure 6). This explains the coincidence of the kinetic dependences of ethylene oxidation when using a mixture of palladium(II) acetate and perchlorate in an acidic medium as an initial solution for the catalytic mixture.

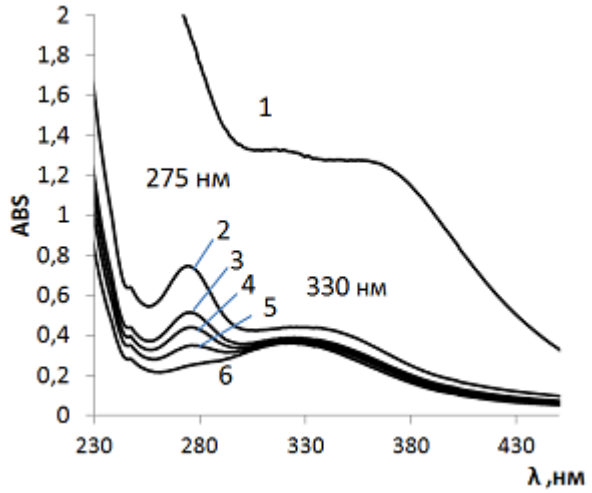

Figure 8. UV spectra depending on the acid concentration in $Pd(OAc)_2$–AN–H_2O–$HClO_4$–$LiClO_4$ system ($[Pd(OAc)_2]$=0.005 M, I=1.0 M; $[H_2O]$ = 0.74 (mole fraction)):$[H^+]$=0 M (**1**), $[H^+]$=0.1 M **(2)**, $[H^+]$=0.2 M (**3**), $[H^+]$=0.3 M (**4**), $[H^+]$=0.5 M (**5**), $[H^+]$=1.0 M (**6**). [нм means nm]

If the conclusion about the absence of the complexes containing acetate ligands in the acidic medium is true, the influence of $[H^+]$ on the value of optical density of the band λ_{max}=275–280 nm could be explained by the decomposition of hydroxocomplexes of assumed composition $[Pd(OH)(AN)_x(H_2O)_{3-x}]^+$ in the range 0.5–1.0 M $HClO_4$ or by catalytic acceleration of the ligands substitution in the coordination sphere of Pd(II) by the acid: the band at 275 nm disappears over time even at concentration $[H^+]$ = 0.2 (Figure 6). Experiments with an addition of water in palladium(II) nitrate solution in AN at $[H^+]$ = 1.0 M result to the emergence of an absorption band at 275 nm as well as the addition of AN into $Pd(ClO_4)_2$ solution in water at $[H^+]$ = 1.0 M. Therefore, the explanation of the acid influence by the acceleration of ligands substitution or *cis-trans* isomerization of $[Pd(AN)_2(H_2O)_2]^{2+}$ complexes is more plausible.

Test for the conformity to Beer–Lambert–Bouguer law. Our attention was engaged by the fact that $Pd(OAc)_2$–AN–H_2O–$HClO_4$–$LiClO_4$ system at various times of **IS** keeping (from 1 to 7 days) showed a linear dependence of absorption intensity on palladium concentration in the range 2.5–10 mmol/l ($[H^+]$= 0.2 M, I=0.5 M, $[H_2O]$ =0.74 (mole fraction)) at λ = 273 nm and λ = 344 nm. Similar linear dependences are observed also after keeping the solutions for a week. Deviations from linearity do not exceed 5%. These results can be interpreted as the absence of polynuclear palladium complexes under the observed conditions.

Let us discuss the processes occurring at various stages of the catalytic system formation on the basis of the obtained results.

1. At the first stage (solutions in acetonitrile without addition of H^+ and H_2O) a very slow transformation of $Pd_3(OAc)_6$ cluster is observed. Presumably, a mixture of neutral $Pd_n(OAc)_{2n}(AN)_x$ complexes [23] is formed, and they result in a continuous band in the range 200–400 nm without distinct absorption maxima (Figure 1). The ^1H and ^{13}C NMR spectra of $Pd_3(OAc)_6$ – CD_3CN system showed that the gradual substitution of μ-OAc ligands results in the formation of CH_3COOH, probably due to H_2O impurity in the solvent.

2. We assume that the decomposition of the cyclic trimer (and of products of its transformation in the reaction with acetonitrile) at the addition of $HClO_4$ and H_2O is followed by complete substitution of the acetate ligands at high concentrations of AN and the acid. The cyclic trimer is decomposed also in chloroform in $Pd_3(OAc)_6$–$CDCl_3$–CH_3CN system after the addition of $HClO_4$ and H_2O. However, this results in the formation of palladium complexes having both acetate and acetonitrile ligands, which undergo exchange (according to ^1H and ^{13}C NMR spectra). The incomplete substitution of the acetate ligands can be caused not only by the low concentration of the acid (0.14 5M) and acetonitrile (0.71 M), but also by the chloroform medium, in which palladium acetate behaves in a special way.

Judging by the data obtained for water solutions [19], the band at 360–365 nm can be assigned to $[Pd(AN)(H_2O)_3]^{2+}$ complex. According to the data of work [19] the band at 335–345 nm (Figure 2, 7, 8, system III) can be due to a diacetonitrile complex of composition $[Pd(AN)_2(H_2O)_2]^{2+}$. Judging by the dynamics of transformations in the studied systems, the transition of the *trans* isomers into possible *cis* isomers of the dinitrile complex is a very slow process, which was also noted by the author of [19]. Probably, the band at 275 nm is also due to one of the isomers of the diacetonitrile complexes. The maximum at 380–385 nm in the spectrum obtained in $Pd(AN)_4(NO_3)_2$ system in acetonitrile is not found in the spectra of the water and water-acetonitrile systems. The band with λ_{max} = 305–310 nm in system **V**, into which all the solutions are transformed at long keeping, can be assigned to $[Pd(AN)_3(H_2O)]^{2+}$ complex.

Standardized technique for preparing the catalytic system

- The initial solution is prepared by dissolving 0.0114 g of $Pd(OAc)_2$ in 10 ml of AN ($[Pd(OAc)_2]$=0.005 M) and kept for a week.
- Before the oxidation a solution of AN–H_2O–$LiClO_4$–$C_6H_4O_2$(Q) (8 ml) is placed into a reactor under the atmosphere of ethylene. (V_{AN}/V_{H2O} = 5:3, $[LiClO_4]$=0.3 M, [Q]=0.2 M).
- The catalytic solution obtained by mixing 1 ml of the initial precursor $Pd(OAc)_2$–AN ($[Pd^{2+}]$ = 0.005 M), 1 ml of water and 0.192 ml of 65% $HClO_4$ is kept for 10 min and then added into the reactor by means of a syringe.

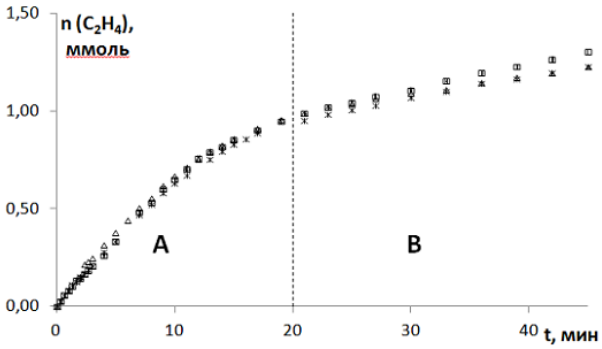

Figure 9. Kinetic dependencies of ethylene absorption with the use of catalytic system $Pd(OAc)_2$–AN–H_2O–$HClO_4$–$LiClO_4$:
$[Pd(OAc)_2]$=0.0005 M, I=0.5 M; H_2O=0.74 (mole fraction).
[ммоль means mmol; мин means min]

Five reproducible kinetic dependences of ethylene oxidation by *p*-quinone were measured with this catalytic solution (Figure 9). The kinetic curves have two regions, which were previously found and described by the kinetic model when studying cyclohexene oxidation [12]. The reaction rate is well reproduced in the initial region with an average error no more than 3% for 5 parallel experiments. The second region starts forming when 1 mmol of ethylene is consumed, which corresponds to a half of the stoichiometric quantity. At the same time the difference in the rates increases and reaches 10%.

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References:

1. Matveev K.I., Shitova N.B., Zhizhina E.G. // Kinetika i kataliz (Kinetics and Catalysis). 1976. V. 17. № 4. P. 893–902. (in Russ.)
2. Sen A., Lai Ta-Wang // J. Amer. Chem. Soc. 1981.V. 103. P. 4627–4629.
3. Sen A., Lai Ta-Wang // Organometallics. 1982. V. 1. P. 415–417.
4. Lai Ta-Wang, Sen A. // Organometallics. 1984. V. 3. P. 866–870.
5. Hegedus L.S., Mulbern T.A., Asada H. // J. Amer. Chem. Soc. 1986. V. 108. P. 6224–6228.
6. Tsuji J., Minato M. // Tetrahedron Lett. 1987. V. 28. № 32. P. 3683–3686.
7. Backvall J.-E., Hopkins R.B. // Tetrahedron Lett. 1988. V. 29. № 23. P. 2885–2888.
8. Miller D.G. Wayner D.D.M. // J. Org. Chem. 1990. V. 55. P. 2924–2927.
9. Hahn C., Morvillo P., Vitagliano A. // Eur. J. Inorg. Chem. 2001. № 2. P. 419–429.
10. Cucciolito M., D'Amora A., Vitagliano A. // Organometallics. 2005. V. 24. P. 3359–3361.
11. Cochran B.M., Michael F.E. // J. Amer. Chem. Soc. 2008. V. 130. P. 2786–2792.
12. Bruk L.G., Temkin O.N., Abdullaeva A.S., Timashova E.A., Bukina E.Yu., Odincov K.YU., Oshanina I.V. // Kinetika i kataliz (Kinetics and Catalysis). 2010. V. 51. № 5. P. 702–714. (in Russ.)
13. Zakharova D.S., Chertkova O.A., Chelkin A.A., Bruk L.G., Temkin O.N. // Izvestiya RAN . Seriya Khim. (Russian Chemistry Bulletin). 2013. № 3. P. 843–853. (in Russ.)
14. Zakharova D.S., Semenyako A.N., Chertkova O.A., Frolkova A.V., Kacman E.A., Bruk L.G., Temkin O.N. // Tonkie khimicheskie tekhnologii (Fine Chemical Technologies). 2015. V. 10. № 3. P. 77–84. (in Russ.)
15. Temkin O. N. // Kinetika i kataliz (Kinetics and Catalysis). 2014. Vol. 55. № 2. P. 181–221. (in Russ.)
16. Moiseev I.I. π-Kompleksy olefinov v zhidkofaznom okislenii (π-Complexes of olefins in liquid-phase oxidation). M.: Nauka Publ., 1970. 270 p. (in Russ.)
17. Mulagaleev R.F., Kirik S.D., Golovnyov N.N. // J. Siberian Federal University. Chemistry 3. 2008. № 1. P. 249–259. (in Russ.)
18. Nosova V.M., Ustynyuk Y.A., Bruk L.G.,Temkin O.N., Kisin A.V., Storozhenko P.A. // Inorg. Chem. 2011. V. 50(19). P. 9300–9310.
19. Hellquist B., Elding L.I., Ducommun Y. // Inorg. Chem. 1988. V. 27. P. 3620–3623.
20. Zagorodnikov V.P., Ryabov A.D., Yacimirskij A.K. // Kinetika i kataliz (Kinetics and Catalysis). 1981. V. XXII. № 1. P. 131–138. (in Russ.)
21. Stolyarov I.P., Demina L.I., Cherkashina N.V. // Zhurnal neorganicheskoy khimii (Russian Journal of Inorganic Chemistry). 2011. V. 56. № 10. P. 1611–1616. (in Russ.)
22. Nabivanets B.I., Kalabina L.V. // Zhurnal neorganicheskoy khimii (Russian Journal of Inorganic Chemistry). 1970. V. 15. № 6. P. 1595–1600. (in Russ.)
23. Biryukov A.A. The complexation of divalent palladium with some inorganic ligands in aqueous solutions) : abstract of the PhD dissertation. Moscow: MGU, 1965. (in Russ.)