STUDY OF THE MECHANISM OF ETHYLENE OXIDATION BY PALLADIUM(II) COMPLEXES CONTAINING NITRO AND/OR NITRATO LIGANDS IN CHLOROFORM

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Summary

Complexes of $Pd(NO_n)_{2-m}Cl_mL_2$ (where $n = 2, 3; m = 0, 1, 2; L = CH_3CN, CD_3CN$) were synthesized and their reactivities towards ethylene and propylene oxidation in a chloroform medium were investigated. The detailed mechanism of ethylene oxidation by dinitro- and mono-nitrato complexes of palladium in chloroform solutions was studied by IR and ¹H NMR spectroscopy. The structures and routes of decomposition of the intermediates to reaction end products are proposed.

Introduction

Selective oxidation of olefins catalyzed by palladium(II) compounds is now recognized to be a promising route for the synthesis of various oxygencontaining organic compounds. Of special interest are stoichiometric reactions involving olefin oxidation by palladium complexes containing oxygen transfer agents as ligands. Anions of nitrogen-containing acids (nitric and nitrous) are among such ligands.

Experiments with palladium nitro complexes labelled with heavy isotopes of oxygen [1, 2] have revealed the 'nitrite' oxygen transfer to the reaction products as a distinguishing feature of these reactions. There are also some indications [1, 2] that this process occurs in intermediate complexes that contain a cyclic structure composed of an olefin molecule, nitrite ligand and palladium atom.

Previous attempts to oxidize olefins by metal nitrate complexes have lacked success [3] and led to a premature conclusion about the impossibility

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of using nitrate ligands for oxygen transfer to olefin molecules. Our investigations have demonstrated that nitrate complexes of palladium are even more active towards ethylene oxidation than nitro complexes.

The $Pd(NO_n)_{2-m}Cl_mL_2$ (where n = 2, 3; m = 0, 1, 2; $L = CH_3CN$, CD_3CN) complexes soluble in organic solvents were synthesized to study the mechanism of interaction between olefins and oxygen-containing ligands of palladium complexes. The data on reactivities of such complexes towards ethylene and propylene oxidation in chloroform and acetic acid solutions have been already reported in [4].

The mechanism of ethylene oxidation by the $Pd(NO_2)ClL_2$ complex in chloroform has been studied by IR and ¹H NMR spectroscopy in [5], where kinetic and spectral evidence for formation of a number of organometallic intermediates is presented, and the structures and routes of decomposition of these intermediates have been suggested. In this paper we report the results of the mechanistic studies of ethylene oxidation by the $Pd(NO_3)ClL_2$ and $Pd(NO_2)_2L_2$ complexes in chloroform.

The transformation of nitrogen-containing anions during reaction with ethylene was studied by IR spectroscopy. Simultaneously, transformations of the ethylene molecule were recorded by ¹H NMR.

Experimental

In kinetic experiments, a volumetric static system having a shaking thermostatted reactor was used. Reaction products were identified via NMR and IR 'fingerprint' techniques. Quantitative analysis of the reaction products was made using a LHM-8MD chromatograph with a flame ionization detector on a column (2 m × 4 mm) filled with 15% 1,2,3-tris(β -cyanetoxy) propane on Polysorb at 373 - 423 K, with a carrier gas velocity of 50 ml min⁻¹.

In ¹H NMR experiments in order to decrease the intensities of signals not belonging to compounds formed from ethylene molecules, acetonitriled₃ (residual protium content 0.3%) was used as ligand L, and the reaction was carried out in deuterochloroform medium (residual protium content 0.5%). The concentration of palladium in solution was 2×10^{-2} M l⁻¹ in all experiments. As much as 5 mol of ethylene per palladium ion was introduced into the solutions of the Pd(NO_n)_{2-m}Cl_mL₂ complexes. NMR spectra were recorded using Bruker CXP-300 spectrometer with a magnetic field induction of 7 T. The temperature of the samples was continuously monitored with a precision of 1° by a BVT-1000 thermocouple. Chemical shifts of ¹H NMR signals were measured with respect to the internal reference hexamethyldisiloxane (HMDSO).

IR spectra were recorded using a Specord-75 IR spectrometer in a CaF_2 cell (0.5 mm thick).

The procedure for $Pd(NO_n)_{2-m}Cl_mL_2$ synthesis and data from elemental analysis can be found elsewhere [4].

Results and discussion

Oxidation of ethylene and propylene by $Pd(NO_n)_{2-m}Cl_mL_2$ complexes in chloroform occurs to give mainly α -nitroolefin and a carbonyl compound (acetaldehyde or acetone). An analysis of the data listed in Table 1 indicates that the oxidation rate of ethylene is typically higher than that of propylene, and the composition of the resulting products depends upon the nature of ligands in the palladium complex. Mononitro and mononitrato complexes of palladium oxidize ethylene almost solely to acetaldehyde, while significant amounts of nitroolefin are produced upon decomposition of palladium complexes containing two oxo anions. For example, 50% nitroethylene is formed in the case of dinitro complex.

TABLE 1

Oxidation of ethylene and propylene by $Pd(NO_n)_{2-m}Cl_mL_2$ complexes in chloroform. $[Complex] = 5 \times 10^{-3} \text{ M l}^{-1}, P_{olefin} = 0.1 \text{ MPa}, T = 298 \text{ K}$

Complex	$ \begin{array}{c} W_{C_2H_4}^{a} \\ (M 1^{-1} \\ min^{-1} \\ \times 10^{3}) \end{array} $	$ \frac{W_{C_{3}H_{6}}^{a}}{(M l^{-1} min^{-1} X 10^{3})} $	<i>S</i> _{СН3} сно ^ь (%)
Pd(NO ₂)ClL ₂	0.75	0.34	96
$Pd(NO_2)_2L_2$	0.20	0.22	50
Pd(NO ₃)ClL ₂	0.81	0.58	97
$Pd(NO_3)(NO_2)L_2$	0.83	0.58	64
$Pd(NO_3)_2L_2$	1.10	0.66	76

 ${}^{a}W_{C_{2}H_{4}}, W_{C_{3}H_{6}}$ are initial rates of olefin oxidation. ${}^{b}S$ is the yield of acetaldehyde per reacted ethylene.

Study on the mechanism of ethylene oxidation by the $Pd(NO_3)ClL_2$ complex

IR spectroscopy data

In the IR solution spectra of the initial $Pd(NO_3)ClL_2$ complex in $CHCl_3$, absorption bands (a.b.) at 1264 (band m) and 1516 (band l) cm⁻¹ are observed (Table 2) within the range of vibration frequencies under study (1900 to 1200 cm⁻¹). These bands correspond respectively to $\nu_{\rm s}$ and $\nu_{\rm as}$ of a nitrate ligand in the palladium complex [6]. Treatment of the complex solution with ethylene changed the band intensities and led to the appearance of new bands whose intensities were dependent on the reaction time (Fig. 1). From an analysis of the changes in band intensities with reaction time, it was concluded that the intensities of some absorption band groups change in the same manner and thus can be attributed to the same compounds. The assignment of these absorption bands to certain compounds (Table 2) was made on the basis of literature data.

During the reaction, a rapid decrease in intensities of absorption bands attributed to the nitrate ligand and the appearance of bands corresponding

TABI Attrik CN) ₂	E 2 oution of abs complexes in (orption bands CHCl3 solution	observed in the s treated with eth	IR spectra of Pd(NC ylene	$(CH_3)_{2-m}Cl_m(CH_3)$
Line	Absorption	Attribution	Formula of	References	

Line	Absorption band (cm ⁻¹)	Attribution	Formula of compound	References $(\nu \text{ in cm}^{-1})$
b g	1724 1372	ν (C=O) δ_{s} (CH ₃)	СН₃СНО	$CH_{3}CHO [7]$ $\nu(C=O) = 1724$ $\delta_{s}(CH_{3}) = 1375$
a	1730	ν(N=O)	∋Pd—N=O	Pd(II) nitroso complex, $\nu(N=O) = 1728, [8]$
с	1630	ν(N=O)	Pd ← CH ₂ − CH ₂ 0 N 0	organic nitrites [9] (a) cis $\nu(N=0) = 1625 - 1610$ (b) trans $\nu(N=0) = 1680 - 1650$
d	1552	$v_{as}(NO_2)$	Pd O ^{CH2} -CH2 J O ^{CH2} O	nitroalkanes R-NO ₂ [9] $\nu_{as}(NO_2) = 1570 - 1550$ $\nu_s(NO_2) = 1360 - 1320$
e	1480	ν(N=O)	>Pd <o-nno< td=""><td>metal nitritocomplexes [6] M—ONO ν(N=O) = 1460 - 1490</td></o-nno<>	metal nitritocomplexes [6] M—ONO ν (N=O) = 1460 - 1490
f k	1437 1319	$ \nu_{as}(NO_2) $ $ \nu_{s}(NO_2) $	>PdO	metal nitrocomplexes [6] $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ in the region 1470 - 1320
i h	1530 1346	$ $	CH2=CH-N	nitroolefins R-NO ₂ [9] $\nu_{as}(NO_2) = 1505 \cdot 1500$ $\nu_{s}(NO_2) = 1360 \cdot 1330$
l m	1516 1264	ν(N=O) ν(N=O)	Pd O-NO	metal nitrate complexes M—ONO ₂ [6], $\nu(N=0) = 1530 - 1480$ $\nu(N=0) = 1290 - 1250$
n o	1627 1272	$ \nu_{\rm as}({\rm NO}_2) $ $ \nu_{\rm s}({\rm NO}_2) $		organic nitrates R-ONO ₂ [7] $\nu_{as}(NO_2) = 1650 - 1620$ $\nu_s(NO_2) = 1300 - 1250$

to the reaction end product, namely acetaldehyde (v(C=O) = 1724 cm⁻¹ (band b) and $\delta_s(CH_3) = 1372 \text{ cm}^{-1}$ (band g) [7]), were detected. A series of bands, namely (e), (f), (k), (d), (n) and (o), on the basis of the initial increase followed by a subsequent decrease in their intensities with reaction time, appear to belong to intermediate compounds formed during the reaction (Fig. 2).



Fig. 1. IR spectra of the $Pd(NO_3)Cl(CH_3CN)_2$ complex in CHCl₃ solution treated with ethylene at 298 K. After exposure to ethylene: 2 min (1), 50 min (2), 300 min (3).



Fig. 2. The change of absorption band intensities in the IR spectrum of the $Pd(NO_3)ClL_2$ complex in CHCl₃ solution, treated with ethylene, with reaction time at 298 K (designations of absorption bands are given in Table 2).

Absorption bands at 1480 (e), 1437 (f) and 1319 (k) cm⁻¹ are attributed to two isomers of the product of reduction of the initial nitrato complex of palladium, that is, to the palladium nitro complex ($\nu_s = 1319$ cm⁻¹ and $\nu_{as} = 1437$ cm⁻¹) and nitrito complex ($\nu(N=O) = 1480$ cm⁻¹) which further react with ethylene to produce acetaldehyde and nitroethylene via the scheme suggested in [5].

As shown in [5], a 1552 cm⁻¹ band (d) belongs to an organometallic intermediate of the type Pd— CH_2 — CH_2 — NO_2 , which is formed as a result of olefin insertion into a Pd—N bond of palladium nitro complex and is decomposed to yield nitroethylene.

Absorption bands at 1627 cm⁻¹ (n) and 1272 cm⁻¹ (o), whose intensities also first increase and then decrease with reaction time, may be caused by vibrations of N=O bonds in an organonitrato compound [7]. The high lability of the latter, as well as the type of its decomposition products (acetaldehyde and a mixture of isomeric palladium complexes having NO_2 ligands), suggests that it is an organometallic compound containing a $Pd-CH_2-CH_2-ONO_2$ fragment.

$^{1}HNMR$ data

Treatment of the $Pd(NO_3)CIL_2$ complex in chloroform solution with ethylene gave rise to the appearance of several lines in the NMR spectra, the line intensity ratio being dependent on reaction time. An analysis of the changes in the integral intensities of the lines on reaction time and of ${}^{3}J(H-H)$ parameters of multiplet lines was made. As the result, groups of lines have been distinguished which may be attributed to the same compounds (see Table 3).

TABLE 3

Characteristics of lines observed in ¹ H NMR spectra of solutions of $Pd(NO_3)Cl(CD_3CN)_2$ in CDCl ₃ treated with ethylene (chemical shifts are given with respect to HMDSO)

No. of	No. of	Line	δ	³ J(H—H)	Intensity
compound	lines	structure	(ppm)	(Hz)	ratio
I	1	quartet	9.73	2.8	1
	10	doublet	2.17	2.8	3
II ^a	2	triplet	9.56	3.5	1
	9	doublet	2.34	3 <i>.</i> 5	2
III	5	triplet	4.22	7.2	1
	12	triplet	1.88	7.2	1
	3	singlet	7.20		signal of residual CDCl ₃ protons
	4	singlet	5.34	-	signal of C ₂ H ₄ protons
IVb	6	triplet	4.3 - 4.05	6.3	1
	8	broad line	2.37 - 3.26	—	1
	11	singlet	2.00		signal of residual CD ₃ CN protons
VII	13	triplet	4.30	7.3	1
	14	triplet	1.61	7.3	1
VIII	15	doublet of doublets	6.55		1
	16	doublet of doublets	5.87		1
	17	doublet of doublets	7.12		1

^aLines are observed below 273 K; the multiplet structure is observed at 254 K.

^bNature of chemical shift variations for compound IV has been analyzed in detail elsewhere [5].



Fig. 3. Dependences of signal intensities in the ¹H NMR spectrum on time during ethylene oxidation by the $Pd(NO_3)Cl(CD_3CN)_2$ complex in $CDCl_3$ for compounds I, III, IV, VII, VIII at 283 K, and for compound II at 263 K.

The dependence of the intensities for various groups of lines on reaction time is shown in Fig. 3. The singlet with a chemical shift at 5.34 ppm, whose intensity tends to decrease during the reaction, corresponds to protons of the ethylene molecule. According to chemical shifts and multiplet structures, line groups I and VIII may be attributed to acetaldehyde and nitroethylene respectively (end products of the interaction between the initial palladium complex and ethylene). Line groups II, III, IV and VII, on the basis of the initial increase and subsequent decrease of their intensities with time, seem to belong to intermediates formed during the reaction. Note that an induction period was observed in the process of accumulation of the intermediate products II, III, and IV and end products I and VIII. The kinetic data given in Fig. 3 suggest that the following sequence of transformations occurs in the system under study:

$$C_{2}H_{4} \longrightarrow VII \longrightarrow \begin{cases} II, III, IV, \longrightarrow \\ CH_{3}CHO \end{cases} CH_{2}=CHNO_{2} \end{cases}$$

The group of signals III, consisting of two equally intense triplets, indicates the presence of two magnetically non-equivalent CH_2 groups in compound III. One of these groups may be bound with the electron-withdrawing NO_2 group, which is responsible for a downfield shift ($\delta = 4.22$ ppm). The other CH_2 group, whose signal is far broader than that at 4.22 ppm, appears to be bound with the palladium atom. Thus the structure $Pd-CH_2-CH_2NO_2$ can be suggested for compound III. The fact that the palladium nucleus has a quadrupole moment could account for the broadening of the triplet lines at 1.88 ppm as compared with the triplet at 4.22 ppm.

The group of lines II, consisting of a doublet and a triplet with an intensity ratio of 2:1, indicates the presence of the $X-CH_2-CH=O$ group in compound II. It should be noted that this compound is stable only at temperatures below 273 K, and rapidly transforms to I at higher temperatures. Such properties of compound II reveal its organometallic nature; most probably, it is a palladium complex having a Pd—CH₂—CHO fragment.

The signal group IV involves two lines of the same intensity, namely, a triplet at 4.05 - 4.30 ppm and a broad line at 2.37 - 3.26 ppm. From the fact that these lines have equal intensities which depend in the same manner upon reaction time, we suggest that they belong to the same compound. The similarity of the chemical shifts of downfield triplets of compounds III and IV suggests that both these triplets belong to X—CH₂—Y fragments with similar X and Y groups, *i.e.* compounds III and IV are likely to be structural isomers. Note that if this is true, then the broad line at 2.37 - 3.26 ppm should be treated as a noticeably broadened triplet. As is seen from Fig. 3, compound III is more stable kinetically than compound IV.

Intermediate products II, III and IV have also been observed in the process of ethylene oxidation by $Pd(NO_2)ClL_2$ in chloroform, and their chemical nature has been discussed in [5].

The character of intensity variation as a function of reaction time for the group of lines VII in the NMR spectra is similar to that for the absorption bands at 1627 and 1272 cm⁻¹ in the IR spectra. Thus, we may conclude that both these NMR lines and IR bands belong to the same compound VII. As suggested by its ¹H NMR spectrum consisting of two triplets of the same intensity, this compound contains two magnetically non-equivalent CH₂ groups. One CH₂ group may be bound with a nitrato group, which causes a downfield shift of its signal ($\delta = 4.30$ ppm). The other CH₂ group seems to be bound with a palladium atom which leads to the broadening of the triplet at 1.61 ppm, in comparison with that at 4.30 ppm. The similarities in the chemical shifts of both the well-resolved downfield triplets and poorlyresolved upfield lines for compounds III, IV and VII suggest that these compounds have similar structures.

Reaction mechanism

Based on the analysis of ¹H NMR and IR data and on the results of our previous study on the mechanism of interaction between the $Pd(NO_2)ClL_2$ complex and ethylene [5], we propose the following scheme for ethylene interaction with Pd(II) nitrato complex (see Scheme 1).

In the first reaction step, as in the case of $Pd(NO_2)ClL_2$ [5], displacement of an acetonitrile molecule and formation of a π -ethylene complex of palladium take place. Insertion of the coordinated ethylene into a Pd-O bond leads to the formation of an organopalladium compound VIII. Decomposition of complex VII by β -hydride shift results in the formation of acetaldehyde as well as nitro and nitrito complexes of palladium. The latter are also involved in reaction with ethylene (see [5] for more detail). While insertion of the coordinated olefin into a Pd-O bond of the nitrito complex leads to the formation of acetaldehyde through organometallic intermediates IV and II, insertion of ethylene into a Pd-N bond of the nitro complex produces complex III, which decomposes to give nitroethylene.



Scheme 1.

Mechanism of ethylene oxidation by the $Pd(NO_2)_2L_2$ complex in $CHCl_3$

A characteristic feature of ethylene reactions with palladium complexes containing two NO_n (n = 2, 3) ligands is the formation of quite large amounts of nitroolefin, along with acetaldehyde (Table 1). For example, the dinitrite complex of palladium oxidizes ethylene to produce 50% nitroethylene, while in the case of mononitro and mononitrato complexes only some 3 - 5% of nitroethylene (per reacted ethylene) are formed.

IR spectroscopy data

In IR spectra of the initial $Pd(NO_2)_2L_2$ complex in chloroform solutions within the range of vibration frequencies under study, absorption bands were observed at 1437 cm⁻¹ (f) and 1319 cm⁻¹ (k), attributed to ν_{as} and ν_s of the coordinated nitro group bound with a palladium atom via the nitrogen atom (Table 2). An absorption band at 1480 cm⁻¹ (e) corres-

ponding to the $\nu(N=O)$ of the nitro ligand bound with palladium atom via an oxygen atom was not observed. Moreover, in the initial spectrum there are absorption bands at 1730 cm⁻¹ (a) attributed to $\nu(N=O)$ of the palladium nitroso complex [8] and at 1516 cm⁻¹ (l) and 1264 cm⁻¹ (m) corresponding to ν_{as} and ν_{s} of the ONO₂ group of the palladium nitrato complex, respectively.

Thus we may conclude that in solution an intramolecular redox rearrangement of two nitro ligands into nitroso- and nitrato groups occurs, with the following equilibrium:



Similar intermolecular disproportionation reactions are well known for cobalt [10] and ruthenium [11] nitro complexes.

Treatment of the solution of $Pd(NO_2)_2L_2$ with ethylene affected the intensities of the initial lines in the IR spectra and led to the appearance of new bands whose intensities depend upon reaction time (Fig. 4). The band assignments were made on the basis of available literature data (Table 2). Bands whose intensities change in the same manner are attributed to the same compounds. The dependence of IR band intensities on reaction time is shown in Fig. 5. An analysis of the data obtained indicates that as the result of the reaction, the intensities of bands corresponding to the palladium nitro complex decrease, whereas those of bands corresponding to the end products, namely, acetaldehyde and nitroethylene, are enhanced. The presence of an



Fig. 4. IR spectra of the $Pd(NO_2)_2(CH_3CN)_2$ complex in $CHCl_3$ solution, treated with ethylene at 298 K. After exposure to ethylene: 7 min (1); 35 min (2); 90 min (3).

Fig. 5. Dependence of absorption band intensities in IR spectra of the $Pd(NO_2)_2L_2$ complex in CHCl₃ solution treated with ethylene, on reaction time at 298 K (designations of absorption bands are given in Table 2).

induction period during the formation of nitroethylene should be noted. An absorption band at 1552 cm^{-1} whose intensity first increases and then decreases with the reaction time, seems to belong to an intermediate organometallic compound of the Pd-CH₂-CH₂-NO₂ type, whose decomposition yields finally the Pd(0) compound and nitroethylene.

¹H NMR data

Treatment of the $Pd(NO_2)_2L_2$ complex in deuterochloroform solution with ethylene gave rise to the appearance of several lines in the NMR spectra, whose relative intensities were dependent upon the time after addition of ethylene. The character of variations with reaction time of the integral intensities of the lines observed was analyzed in the same manner as for the complex $Pd(NO_3)Cl(CD_3CN)_2$ discussed above. The usage of 3J (H-H) parameters of multiplet lines allowed attribution of the groups of lines whose intensities varied in the same manner to the same compounds. As found, in the process of ethylene oxidation by $Pd(NO_2)_2L_2$ the lines of compounds I, III, IV and VIII, reported previously for $Pd(NO_2)ClL_2$ complexes [5], appeared in the spectrum (see Table 3). Dependences of intensities of the corresponding groups of lines in the NMR spectra on reaction time are illustrated in Fig. 6. Note that the maximum rate of the growth in intensity of the lines attributed to nitroethylene, nearly coincides in time with the maximum on the curve of concentration variations of compound III during the reaction.

This experimental observation provides additional support for the attribution of the line group III to an organometallic intermediate of the $Pd-CH_2-CH_2-NO_2$ type.

Thus, IR and NMR spectroscopic data obtained allow us to propose the following sequence of transformations in the C_2H_4 -Pd(NO₂)₂L₂-CHCl₃ system.

IR and NMR spectroscopic studies of interactions of ethylene with $Pd(NO_2)(NO_3)L_2$ and $Pd(NO_3)_2L_2$ provide evidence that a successive reduction of NO_n ligands takes place, and that the transformations of NO_n ligands in these systems can be described by Schemes 1 and 2.



Fig. 6. Dependence of line intensities in ¹H NMR spectrum on time during ethylene oxidation by the $Pd(NO_2)_2L_2$ complex in $CDCl_3$ solution at 276 K.



Conclusions

Results of this communication, as well as those reported earlier [4, 5], show that the rates of ethylene and propylene oxidation by Pd(II) nitro and nitrato complexes, as well as the composition of the resulting products, depend upon the nature of the oxidant ligands employed, the type of their binding to the palladium atom, the number of such ligands in the complex, and the nature of the solvent and the olefin.

The oxidation process seems to proceed via the following key steps:

(1) Olefin coordination to palladium:



(2) Transformation of the complex formed to give a σ -palladiumorganic compound via insertion of coordinated olefin into a palladiumoxygen or palladium-nitrogen bond:



(3) Decomposition of the latter into the reaction products via a β -hydride transfer:



A number of intermediates have been elucidated for steps 2 and 3 via ¹H NMR and IR spectroscopies.

It should be noted that in chloroform medium the oxidation of ethylene by Pd complexes, where a nitrogen-containing ligand is bound with the central atom through an oxygen atom (nitrito and nitrato complexes), leads to the formation of acetaldehyde. If palladium complexes contain the same ligand but are bound with the metal atom through a nitrogen atom (nitro complexes), then the main product of olefin oxidation is a nitroolefin.

Differences in reactivities of the complexes with different ways of coordination of nitrogen-containing ligands become even more marked in acetic acid solution. In this case, a new reaction route leading to glycol monoacetates, for nitro and nitrato complexes with palladium-oxygen bonds, appears. The results of a study on the mechanism of glycol monoacetate formation will be reported later.

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