move away from the tricobalt face onto possibly another face of the cluster or to an edge-bridging position. However, our results show that the addition of $[Ph_3PAu]^+$ to derivatives of $[FeCo_3(CO)_{12}]^-$ is apparently very site specific. When the approach to the tricobalt face is blocked by a bulky ligand, the $[Ph_3PAu]^+$ cation will not react with the substituted anion. This may very well be a kinetic problem reflective of the centering of the electron density of the anion on the blocked tricobalt face.

We had also wanted to see if $[Ph_3PAuFeCo_3(CO)_{12}]$ was as labile to phosphine substitution as is the hydride compound $[HFeCo_3(CO)_{12}]$. Unfortunately, due to the electrophilic nature of the gold atom in the cluster, no conclusions can be drawn about the lability of the carbonyl ligands to phosphine substitution in the cluster since the phosphine first attacks at the gold atom rather than substitutes for a carbonyl. The isolation of the disubstituted compound, $[Ph_3PAuFeCo_3(CO)_{10}\{P(OMe)_3\}_2]$, seems to suggest a labilization of the carbon monoxide ligands toward phosphorus-ligand substitution. Perhaps ^{13}CO exchange studies would give a better indication of the lability of the carbonyl ligands in this cluster since a cationic gold carbonyl complex would not be particularly stable.

Finally, when a phosphorus ligand substitutes for a carbonyl ligand in the $[M_4(CO)_{12}]$ cluster family, or a metal fragment is added to an open face, the other carbonyl ligands are able to move away in order to relieve the steric congestion. This is in agreement with our observations from force field calculations that the $[M_4(CO)_{12}]$ family of clusters is relatively strain free.

Acknowledgment. This work is supported by the National Science Foundation under Grant CHE8216662. We thank Dr. S. Sherlock and the other members of our research group for their assistance.

Registry No. $[Et_4N][1]$, 110637-27-9; $[Co(CO)L_4][2]$, 110660-49-6; 3, 110661-32-0; $4{\cdot}C_7H_8$, 110613-97-3; $[Et_4N][FeCo_3(CO)_{12}]$, 53509-36-7; $[FeCo_3(CO)_{11}P(OMe)_3]^-$, 110613-95-1; Ph_3PAuNO_3, 14897-32-6; Co, 7440-48-4; Fe, 7439-89-6; Au, 7440-57-5.

Supplementary Material Available: For each of the four structures, listings of additional atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (33 pages); listings of observed and calculated structure factors for the four structures (49 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Catalysis, Novosibirsk 630090, USSR

Formation, Structure, and Reactivity of Palladium Superoxo Complexes

Eugeni P. Talsi, Vera P. Babenko, Alexandr A. Shubin, Victor D. Chinakov, Vyatcheslav M. Nekipelov, and Kirill I. Zamaraev*

Received September 9, 1986

Formation of palladium superoxo complexes in the reactions of palladium(II) acetate, propionate, trifluoroacetate, and bis(acetylacetonate) and palladium(0) tetrakis(triphenylphosphine) with hydrogen peroxide and potassium superoxide has been detected in solution by EPR. According to EPR parameters the superoxo complexes observed fall into two main types. The g factor of type I complexes is closer to an axial symmetrical one than that of type II complexes. For type I complexes, g_1 = 2.08–2.1, g_2 = 2.01, and g_3 = 2.001–2.002, and for type II complexes, g_1 = 2.075–2.085, g_2 = 2.027–2.04, and g_3 = 2.006–2.01. The EPR spectrum of type I complexes resulting from the interaction of H_2O_2 with $Pd(OAc)_2$ in $CHCl_3$ has a hyperfine structure indicating coupling to one Pd nucleus: A_1^{Pd} = 6.7 G, A_2^{Pd} = 3.0 G, and A_3^{Pd} = 4.5 G. Type I superoxo complexes appear to be characteristic of trimeric Pd species, formed by palladium(II) acetate and palladium(II) propionate in poorly coordinating solvents (chloroform and benzene), while type II superoxo complexes are characteristic of monomeric Pd species, formed by palladium(II) acetate and palladium(II) propionate in well-coordinating solvents (acetonitrile, dimethyl sulfoxide) and by palladium(II) trifluoroacetate, palladium(II) acetylacetonate, and palladium(0) tetrakis(triphenylphosphine) in poorly coordinating solvents. When prepared via interaction with KO_2 in the presence of 18-crown-6 ether, the type I superoxo complex initially formed in palladium(II) acetate and palladium(II) propionate systems rapidly transforms to the more stable type II complex, presumably due to the destruction of the trimeric Pd species by the 18-crown-6 ether. Type I superoxo complexes are more reactive than those of type II. Type I complexes formed by palladium(II) acetate and palladium(II) propionate easily oxidize simple olefins and CO, while type II complexes are inert with respect to these compounds. The type I superoxo complex of palladium(II) acetate oxidizes ethylene to ethylene oxide, 1 ± 0.1 mol of ethylene oxide being formed per 1 ± 0.3 mol of the superoxo complex decomposed. No other products have been detected with NMR for this reaction. The same superoxo complex oxidizes propylene to propylene oxide and acetone in a 1:2 ratio, again no other products being detected with NMR. The reaction rates demonstrate the first-order dependences on concentration of both the superoxo complexes and the olefins. The pseudo-first-order rate constants, determined for reactions of palladium(II) acetate type I complex with various alkenes at 300 K in $CHCl_3$ with a large excess of the alkenes (0.3 M) over the superoxo complex (0.005 M), are as follows: $10^3k = 2.3\ s^{-1}$ ($CH_2{=}CH_2$); 5.1 s^{-1} ($MeCH{=}CH_2$); 5.1 s^{-1} ($Me_2C{=}CH_2$); 1.2 s^{-1} ($Me_2C{=}CMe_2$). For the oxidation of CO by the same complex, the pseudo-first-order rate constants determined with a large excess of CO (concentration about 0.01 M, determined by solubility of CO at 1 atm) over the superoxo complex (3×10^{-4} M) at various temperatures are as follows: $10^3k = 9\ s^{-1}$ (266 K); 2 s^{-1} (258 K); 1 s^{-1} (238 K); 0.6 s^{-1} (226 K). Quantum-chemical calculations suggest that for the monomeric $Pd(acac)O_2$ complex η^2-coordination of the O_2^- ligand is energetically more advantageous than η^1-coordination. On this ground η^2-coordination can be assumed for relatively stable superoxo complexes of type II. g values for more reactive palladium superoxo complexes of type I are similar to those of cobalt superoxo complexes, which, according to X-ray data, have η^1-coordination. On this basis η^1-coordination of the O_2^- ligand can be assumed for palladium superoxo complexes of type I.

Introduction

Superoxo complexes of transition metals are assumed to be key intermediates of many reactions of homogeneous catalytic oxidation.[1-4] The superoxo complexes of Ni(II), Zn(II), Co(II), Co(III), Fe(II), Fe(III), Ce(III), Cr(III), Ti(IV), Th(IV), Hf(IV), Zr(IV), Sn(IV), V(V), Nb(V), and Mo(VI) are known.[5-8] However, there are very few reliable quantitative data on their reactivity. The sole exception is oxidation of hindered phenols

(1) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.
(2) Nishinaga, A.; Tomita, H. *J. Mol. Catal.* **1980**, *7*, 179.
(3) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580.
(4) Corden, B. B.; Drago, R. S.; Perito, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2903.
(5) Afanasiev, I. B. *Usp. Khim.* **1979**, *48*, 977.
(6) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.
(7) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471.
(8) Shuvalov, V. F.; Moravskii, A. P.; Lebedev, Ya. S. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 877.

to quinones with cobalt–dioxygen complexes.[2-4] Coordination of O_2 to the cobalt(II) complexes that results in the formation of the superoxo complex was found to enhance the ability of dioxygen to abstract hydrogen atoms from hindered phenols.[2,3]

We have found recently complexes of the radical ion O_2^- with palladium compounds and have demonstrated its high reactivity toward the oxidation of simple alkenes to epoxides.[9-11]

In this work the mechanism of formation of palladium superoxo complexes, their structure, and their reactivity are discussed. In particular, oxidation of olefins and carbon monoxide by these complexes is considered.

Experimental Section

The solvents employed, namely benzene, chloroform, acetonitrile, dimethyl sulfoxide, and acetic acid, were purified by standard techniques.[12] Palladium complexes were prepared as described in the literature.[13-15] Palladium(II) acetate, palladium(II) propionate, palladium(II) trifluoroacetate,[13] palladium(II) bis(acetylacetonate),[14] and palladium(0) tetrakis(triphenylphosphine)[15] were used.

Palladium superoxo complexes were obtained by interaction of palladium compounds in organic solvents with hydrogen peroxide or potassium superoxide (KO_2).

(a) Preparation of Superoxo Complexes by Interaction of Palladium Compounds with H_2O_2. In water-miscible solvents such as CH_3CN, Me_2SO, and AcOH, superoxo complexes were obtained by adding 30% H_2O_2 (concentration 1 M) to a solution of the 0.05 M palladium complex directly in the EPR cell. EPR spectra were recorded 1–3 min after the reagents were mixed. The concentration of the superoxo complexes did not exceed 10^{-4} M, as follows from EPR data.

In water-immiscible solvents such as C_6H_6 and $CHCl_3$, superoxo complexes were prepared by agitating a solution of the palladium compound in organic solvent (3 mL; concentration 0.1 M) with 30% hydrogen peroxide (1 mL for 3–5 min). The brown organic layer, containing up to 10^{-2} M of superoxo complexes, as ascertained by EPR, was then separated. Solid samples, containing superoxo complexes as impurities of the initial palladium complex (up to 1% by weight), were obtained by removal of the solvent under vacuum after the separation of the organic layer. The superoxo complexes so obtained can be stored at room temperature for several months.

(b) Preparation of Superoxo Complexes by Interaction of $Pd(OAc)_2$ with KO_2. KO_2 was synthesized as described in the literature.[16] The specific magnetic susceptibility of KO_2 was 19 cgsu and was close to the literature value.[16] KO_2 was dissolved in organic solvents with the aid of 18-crown-6 ether prepared as described in the literature.[17]

The experiments were carried out as follows. KO_2 (2.8 mg, 0.04 mmol) and 18-crown-6 ether (11 mg, 0.04 mmol) were placed in a cylindric EPR glass cell of 5-mm diameter. Then 0.2 mL of a 0.1 M $Pd(OAc)_2$ solution was added at low temperature (243 K for chloroform and 273 K for benzene). The reagents were mixed, and the cell was quickly transferred into the EPR spectrometer, where the temperature was fixed within 1 K accuracy in the range 243–273 K.

(c) Kinetic Measurements. Recording of NMR and EPR Spectra. The kinetics of the interaction of superoxo complexes with reductants—alkenes (ethylene, propylene, isobutylene, and tetramethylethylene) and carbon monoxide—was monitored via the disappearance of the EPR line of superoxo complex in the presence of a large excess of the reductants. The concentration of alkenes in solution was determined from ^1H NMR spectra and that of CO from its solubility.[18a] The reaction products were analyzed chromatographically and from ^1H NMR spectra.

^1H NMR and EPR spectra were recorded on Bruker CXP-300 and ER-200D spectrometers, respectively. The concentration of paramagnetic centers was measured by EPR by comparing second integrals of EPR spectra of the sample of interest and of the reference, a $CuCl_2 \cdot 2H_2O$ crystal.

To measure the concentration of paramagnetic centers in $CHCl_3$ or C_6H_6 solutions or in solid samples, two tubes (diameters 1 mm), one tube with the sample to be examined and the other with the reference sample, were placed simultaneously into the center of the EPR spectrometer cavity. The concentration of paramagnetic centers in AcOH solutions was assessed by comparing EPR signal intensities of the sample under study and the reference one (in our case a $CHCl_3$ solution with the known concentration of the same paramagnetic centers). Measurements were made in a flat cell of a dual EPR cavity furnished with the spectrometer. Periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+}, which served as a side reference, was placed into the center of the second compartment of the dual cavity. The accuracy of the measurements of the concentration of PCs in $CHCl_3$ and C_6H_6 solutions and in solid samples was

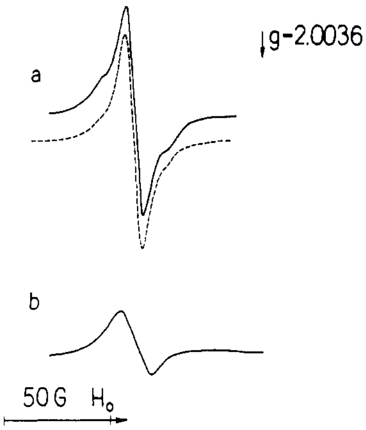


Figure 1. EPR spectra (T = 300 K) observed during the interaction of H_2O_2 with $Pd(OAc)_2$ in $CHCl_3$ (a) and AcOH (b). The dotted line corresponds to a simulated spectrum.

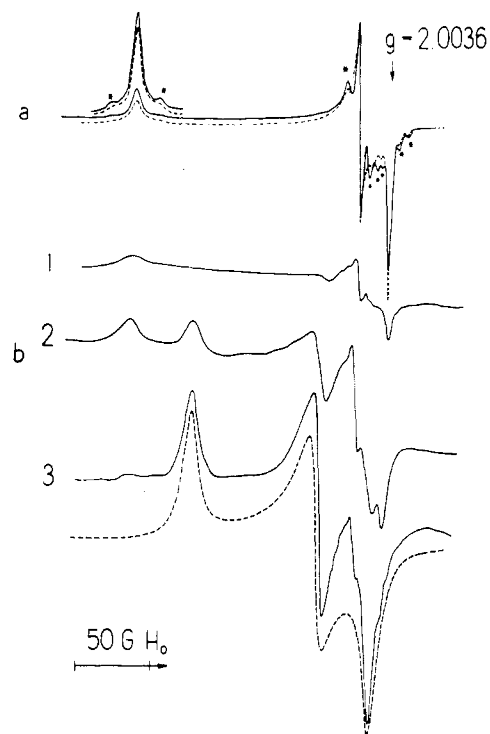


Figure 2. EPR spectra (T = 77 K) observed during the interaction of H_2O_2 with $Pd(OAc)_2$ in $CHCl_3$ (a) and in AcOH (b) at different concentrations of H_2O_2: (1) 0.5 M; (2) 2 M; (3) 6 M. Dotted lines correspond to simulated spectra. For parameters of simulated spectra, see Table I.

(9) Talsi, E. P.; Babenko, V. P.; Nekipelov, V. M.; Shubin, A. A. *React. Kinet. Catal. Lett.* **1986**, *31*, 209.
(10) Talsi, E. P.; Babenko, V. P.; Chinakov, V. D.; Nekipelov, V. M. *React. Kinet. Catal. Lett.* **1986**, *32*, 347.
(11) Talsi, E. P.; Babenko, V. P.; Likholobov, V. A.; Nekipelov, V. M.; Chinakov, V. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1768.
(12) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.
(13) Stephenson, T. A.; Morehouse, S. M.; S. M.; Powell, A. R.; Hefeer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.
(14) Grinberg, A. A.; Simonova, L. K. *Zh. Prikl. Khim. (Leningrad)* **1953**, *266*, 880.
(15) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 774.
(16) Malykhin, E. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1981**, *17*, 2402.
(17) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
(18) (a) Gjaldbaek, J. Chr.; Anderson, E. K. *Acta Chem. Scand.* **1954**, *8*, 1398. (b) Dalal, D. P.; Eaton, S. S.; Eaton, G. R. *J. Magn. Reson.* **1981**, *44*, 415.
(19) Zhidomirov, G. M.; Dobryakov, N. S.; Lebedev, Ya. S.; Shteinshneider, N. Ya.; Gubanov, N. I. *Interpretation of Complex EPR Spectra*; Nauka: Moscow, 1975.

Table I. EPR Parameters of Superoxo Complexes Resulting from the Interaction of Palladium Complexes with H_2O_2 and KO_2 in Various Solvents

complex	reagent	solvent	superoxide type	$g_0 \pm 0.001$	$g_1 \pm 0.001$	σ_1,[b] G	$g_2 \pm 0.001$	σ_2,[b] G	g_3 ■ 0.001	σ_3,[b] G
$Pd(OAc)_2$	H_2O_2	$CHCl_3$	I	2.041	2.1073	4	2.0134	1.2	2.001	1.2
	H_2O_2	AcOH	I	2.041	2.108		2.013		2.001	
			II		2.082	6	2.030	6	2.0068	6
	H_2O_2	CH_3CN	II	*a*	2.077		2.027		2.006	
	H_2O_2	Me_2SO	II	*a*	2.081		2.030		2.008	
	KO_2	$CHCl_3$	I	2.031	2.084		2.010		2.002	
			II	2.045	2.085		2.036		2.011	
	KO_2	C_6H_6	I	2.032	2.083	15	2.0125	8	2.0010	6
			II	2.044	2.085	12	2.041	11	2.013	10
$Pd(OPr)_2$	H_2O_2	$CHCl_3$	I	2.042	2.109		2.012		2.002	
	H_2O_2	CH_3CN	II	*a*	2.083		2.031		2.007	
$Pd(OOCCF_3)_2$	H_2O_2	$CHCl_3$	II		2.085		2.03		2.008	
$Pd(acac)_2$	H_2O_2	$CHCl_3$	II	2.037	2.0736	3	2.0337	3	2.0064	3
$Pd(PPh_3)_4$	H_2O_2	$CHCl_3$	II	2.038	2.082	15	2.0335	19	2.008	8

[a] Recording of the EPR spectra at room temperature was a failure because of a vigorous decomposition of H_2O_2. [b] σ_1, σ_2, and σ_3 are the main values of the line width tensor used for spectra simulation.

about 30%. But in AcOH solutions the accuracy may be worse, because of the cavity Q and "lens" effect of the differing dielectric constants of the sample (solution in acetic acid) and the reference (solution in chloroform).[18b] EPR spectra were simulated on a BESM-6 computer using the extended version of the Naya program described in the literature.[19] The calculation was made in the second order of perturbation theory relative to hyperfine interactions. Integration by the polar angle was carried out by using Simpson's method in steps of 2° and that by the azimuthal angle, in steps of 30′. An individual line was assumed to have a Lorentzian shape.

Results

1. Interaction of Palladium(II) Carboxylates with H_2O_2.[9] EPR spectra at 300 and 77 K observed during the interaction of $Pd(OAc)_2$ with H_2O_2 in $CHCl_3$ and in AcOH are shown in Figures 1 and 2. The concentration of paramagnetic centers (PCs) at 300 K in $CHCl_3$ (Figure 1a) was up to 10^{-2} M and in AcOH (Figure 1b) did not exceed 10^{-4} M. PCs in $CHCl_3$ and AcOH (T = 300 K) had close values of g factors, g_0 (see Table I). Side components of the EPR spectrum (Figure 1a) seem to be due to an unresolved hyperfine structure from a ^{105}Pd nucleus (nuclear spin $I = {}^5/_2$; natural abundance 22%). The dotted line (Figure 1a) corresponds to simulated spectrum. A theoretical spectrum was calculated as superposition of two spectra with relative intensities 0.78 and 0.22. The spectrum with relative intensity 0.22 was assumed to have hyperfine (hf) structure from ^{105}Pd (A_0 = 4 G), while the spectrum with relative intensity 0.78 was assumed to have none. The line width σ = 4 G.

The intensity of the EPR signals observed (T = 300 K) had a tendency to gradually decrease with time (the signal disappeared after several hours in $CHCl_3$ and after tens of minutes in AcOH).

EPR spectra of frozen solutions of PCs (T = 77 K, Figure 2) are characterized by a 3-fold anisotropy of the g factor. EPR spectra of solid samples containing superoxo complexes are the same as the spectra in the frozen state of the solutions from which solid samples were isolated. An EPR signal of only one type is observed in $CHCl_3$ (Figure 2a). The average value of the g factor, $g_0' = {}^1/_3(g_1 + g_2 + g_3) = 2.040$, for this signal practically coincides with the value g_0 = 2.041 for the signal in liquid $CHCl_3$. This suggests the identity of PCs observed in liquid and frozen $CHCl_3$. In AcOH, along with this signal, there is also a signal of the second type, the relative intensity of which increases with increasing H_2O_2 concentration (Figure 2b, spectra 1–3). The second type of PCs is characterized by a considerably stronger deviation of the symmetry of the g factor from the axial symmetry (see Table I). Note that PCs of the second type are observed for only frozen solutions. For liquid solutions in AcOH at a large concentration of H_2O_2 ($[H_2O_2] \geq 6$ M), the EPR spectral parameters (e.g. g_0) are similar to those in $CHCl_3$ (Figure 1 and Table I). It seems likely that the stability of PCs of the second type in AcOH grows with decreasing temperature.

The interaction of $Pd(OAc)_2$ with H_2O_2 in acetonitrile and in dimethyl sulfoxide produces EPR spectra with parameters similar to those for spectrum 3 (Figure 2b; see Table I), that is, for spectra of PCs of the second type.

The EPR spectrum of the first type (T = 77 K, Figure 2a) is seen to have weak components, indicated by asterisks, which can be assigned to hf structure from one ^{105}Pd nucleus. In accordance with the natural abundance of palladium isotopes, a theoretical spectrum (dotted line, Figure 2a) was calculated as superposition of two spectra with relative integral intensities 0.78 and 0.22. In these simulations the spectrum with relative intensity 0.22 was assumed to have a hf structure from ^{105}Pd while the spectrum with relative intensity 0.78 was assumed to have none. Identical values of g_1, g_2, and g_3 taken from Table I were assumed for both spectra. The main values of the hf tensor for coupling to one ^{105}Pd nucleus for a spectrum with a lower integral intensity are A_1 = 6.7 G, A_2 = 3 G, A_3 = 4.5 G. It is seen that, in general, the theoretical spectrum is in good agreement with the experimental one. Some lack of agreement in minor details can be connected with effects of nuclear quadrupole interaction and nonparallelism of the axes of the **g** and **A** tensors, which were not considered in our calculations.

The presence of the hf structure from the ^{105}Pd isotope indicates that this PC of the first type is a palladium compound.

Note that substitution of palladium acetate by palladium propionate does not lead to noticeable changes of EPR parameters for both types of PCs. The interaction of H_2O_2 with palladium trifluoroacetate results in formation of PCs of only the second type (see Table I).

EPR parameters of the PCs observed are very similar to those of the O_2^- radicals in the coordination sphere of metal cations.[20,21] Therefore, it is reasonable to assume that these PCs are superoxo complexes of palladium. To provide direct support for this assumption, we made an attempt to prepare such complexes directly via substituting acetate ion in $Pd(OAc)_2$ by superoxide ion through the reaction of $Pd(OAc)_2$ with KO_2, where KO_2 served as a source of the O_2^- species.

2. Reaction of $Pd(OAc)_2$ with KO_2.[10] In this reaction at 273 K in $CHCl_3$ and C_6H_6, PCs with g_0 = 2.031 are initially formed. However, they are subsequently transformed to PCs with g_0 = 2.045 (see spectra in Figure 3A). The rate of the transformation increases with increasing temperature. The absolute concentration of PCs is ca. 10^{-3} M. PCs with g_0 = 2.045 are fairly stable and exist in solution for an hour at room temperature. The PCs observed are assumed to be O_2^-–palladium complexes, since EPR signals of free-radical O_2^- ions in KO_2 solutions are recorded only below 193 K due to a short of spin–lattice relaxation time.[22] The spectra of the PCs at T = 77 K are illustrated in Figure 3B. Immediately after interaction between $Pd(OAc)_2$ and KO_2, a PC of type I is formed that is characterized by a relatively small difference between g_2 and g_3 (see Table I). Subsequently this PC of type I transforms to a PC of type II characterized by a relatively large difference between g_2 and g_3. Note that the values g_0' =

(20) Lunsford, J. H. *Catal. Rev.* **1973**, *8*, 135.
(21) Basolo, F.; Jones, R. D.; Summerville, D. A. *Chem. Rev.* **1979**, *79*, 139.
(22) Ozawa, T.; Hanaka, A.; Yamamoto, H. *FEBS Lett.* **1977**, *74*, 99.

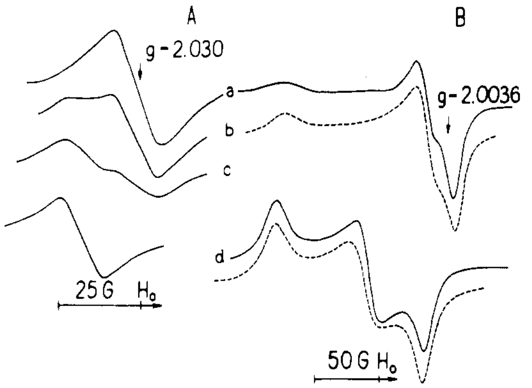


Figure 3. EPR spectra of (A) liquid solutions (T = 273 K) and (B) frozen solutions (T = 77 K) during the reaction of $Pd(OAc)_2$ with KO_2 in $CHCl_3$. Spectra were registered 5 (a), 10 (b), 25 (c), and 120 min (d) after the beginning of the reaction. Dotted lines correspond to simulated spectra. Their parameters are given in Table I.

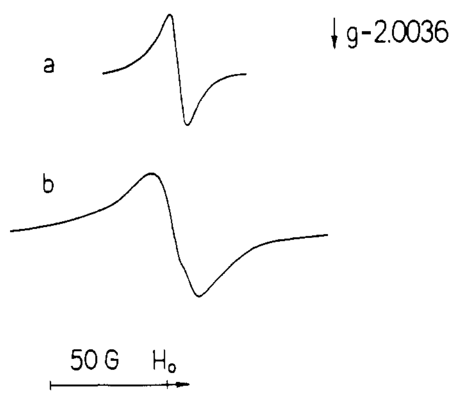


Figure 4. EPR spectra (T = 300 K) observed during reaction of H_2O_2 with Pd complexes in $CHCl_3$: (a) $Pd(acac)_2$; (b) $Pd(PPh_3)_4$.

$^1/_3(g_1 + g_2 + g_3)$, which are equal to 2.032 for a PC of type I and to 2.044 for a PC of type II, coincide with the corresponding values of g_0 measured at 273 K (see Table I). This indicates that in frozen solutions, the same PCs of types I and II are present as in liquid solutions. No signal from the anion radical O_2^- in a free (i.e. noncoordinated to palladium atom) state has been observed at 77 K.

Thus, the interaction of $Pd(OAc)_2$ with O_2^- results in the formation of the two types of PCs, just as in the case of the interaction of $Pd(OAc)_2$ with H_2O_2. This observation lends further support for the previous conclusion that palladium superoxo complexes result from the interaction of $Pd(OAc)_2$ with H_2O_2. However, EPR parameters of the PCs formed in reaction involving H_2O_2 and KO_2 are notably different, especially for the PCs of the first type. This effect suggests different structures for superoxo complexes formed in reactions with H_2O_2 and KO_2, and this will be discussed in more detail below.

3. Reaction of $Pd(acac)_2$ and $Pd(PPh_3)_4$ with H_2O_2. The formation of PCs was also observed during the interaction of $Pd(acac)_2$ or $Pd(PPh_3)_4$ with H_2O_2. The EPR spectra obtained are shown in Figures 4 and 5. The concentration of PCs at 300 K was ca. 10^{-4} M. The intensity of the signals at 300 K gradually fell with time. The signal disappeared after several hours for $Pd(PPh_3)_4$ and after several minutes for $Pd(acac)_2$. The EPR spectra at 77 K (see Figure 5 and Table I) are characterized by g values similar to those of superoxo complexes of type II arising from the interactions of $Pd(OAc)_2$ with KO_2 and H_2O_2. Quite probably, the PCs observed are also superoxo complexes of palladium. Note that the EPR spectrum (Figure 5a) has additional lines indicated by asterisks, which can be attributed to hf structure from the ^{105}Pd isotope.

Thus the PC of type II formed upon interaction of $Pd(acac)_2$ with H_2O_2 is a palladium compound. However, because of a rather poor resolution of the observed hf lines, it is difficult to say whether

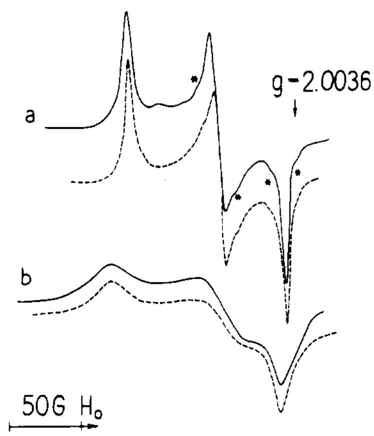


Figure 5. EPR spectra (T = 77 K) observed during the reaction of H_2O_2 with Pd complexes in $CHCl_3$: (a) $Pd(acac)_2$; (b) $Pd(PPh_3)_4$. Dotted lines correspond to simulated spectra (see Table I).

hf interaction takes place with one or several ^{105}Pd nuclei. A theoretical spectrum (dotted line, Figure 5a) was calculated as a superposition of two spectra with relative integral intensities 0.78 and 0.22. The spectrum with relative intensity 0.22 was assumed to have a hf structure to one ^{105}Pd nucleus (A_1, A_2, A_3 = 4 G). It is seen that the theoretical spectrum is in good agreement with an experimental one.

The values of hf splitting (A_1, A_2, A_3 = 4 G) are of the same order as those of the superoxo complexes of the first type (A_1 = 6.7 G, A_2 = 3 G, A_3 = 4.5 G) and are more typical for the situation where the unpaired electron is localized mainly on a ligand rather than on the palladium atom. Unfortunately, there are no data on hf coupling to ^{105}Pd for paramagnetic complexes of Pd(I) and Pd(III), where one should expect the unpaired electron to be mainly localized on the palladium atom. However, the above assumption is supported by the data for other metals. In fact, for superoxo complexes of cobalt A = 10–20 G, while for non-oxygenated parent cobalt compounds A = 80–100 G,[21] for superoxo complexes of vanadium(V) A_0 = 5.0 G,[23] and for paramagnetic vanadium(IV) complexes A_0 = 90–100 G.[24]

Thus, interactions of palladium carboxylates as well as of $Pd(acac)_2$ and $Pd(PPh_3)_4$ with H_2O_2 and KO_2 produce two types of PCs. On the basis of their EPR parameters those PCs are suggested to be superoxo complexes. To elucidate a possible role of such complexes in the oxidation of organic compounds, we have studied their reactivity.

4. Reactivity of Palladium Superoxo Complexes. Superoxo complexes of type I resulting from the interaction of H_2O_2 with $Pd(OAc)_2$ and $Pd(OPr)_2$ in $CHCl_3$ and C_6H_6 in the absence of alkenes and CO are rather stable. For example, in chloroform, these complexes decomposed not more than 10% at 300 K in an hour. When separated in the solid state together with palladium acetate or propionate (1% of PCs relative to $Pd(OAc)_2$ and $Pd(OPr_2)$) from chloroform, the complex could be stored at room temperature for several months. Owing to this relatively high stability of the superoxo complexes, resulting from the interaction of $Pd(OAc)_2$ and $Pd(OPr)_2$ with H_2O_2, it was possible to obtain reliable kinetic data on their reactivity.

A high reactivity toward linear alkenes and carbon monoxide was revealed for superoxo complexes of type I. In contrast to this, those of type II were found inert with respect to these compounds. Superoxo complexes of type I resulting from the interaction of $Pd(OAc)_2$ with KO_2 are unstable and transform to superoxo complexes of type II even at low temperatures. For this reason the reactions of superoxo complexes of the type I prepared via KO_2 with alkenes and carbon monoxide were carried out at low temperatures (273–253 K). The reaction products were analyzed by using chromatographic and NMR methods.

(23) Bains, M. S.; Arthur, J. C.; Hinojosa, J. *J. Am. Chem. Soc.* **1969**, *91*, 4673.
(24) Kivelson, D.; Lee, S. K. *J. Chem. Phys.* **1964**, *41*, 1896.

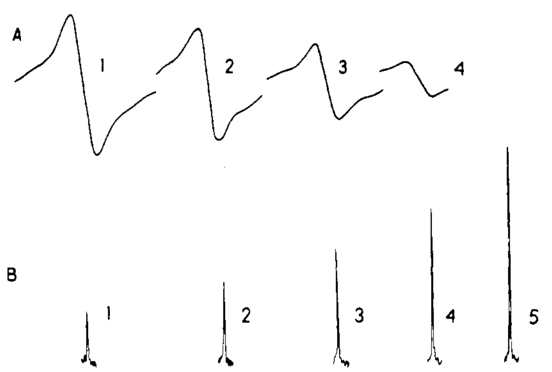


Figure 6. Kinetics of the reaction between the type I superoxo complex of $Pd(OAc)_2$ with ethylene in $CHCl_3$: (A) EPR spectra of the superoxo complex I ($g = 2.041$): 5 (1), 12 (2), 25 (3), and 48 min (4) after the beginning of the reaction; (B) ^1H NMR signal of ethylene oxide: 7 (1), 14 (2), 21 (3), 40 (4), and 600 min (5) after the beginning of the reaction. The initial concentration of the superoxo complex is 10^{-3} M; that of ethylene is 0.15 M.

(a) Reactions with Alkenes. Addition of alkenes to a solution of superoxo complexes of type I in chloroform, formed in the reaction of $Pd(OAc)_2$ or $Pd(OPr)_2$ with H_2O_2, resulted in a rapid decrease in concentrations of the superoxo complex, which was monitored by the fall of its EPR signal intensity.

The detailed kinetic studies were carried out for $Pd(OAc)_2$ system. The initial concentration of the superoxo complex was 0.005 M and the concentration of alkene was 0.3 M. The rate of the signal disappearance showed a first-order dependence on alkene concentration. With excess of alkene the disappearance obeyed pseudo-first-order kinetics with respect to superoxo complex up to conversion of 90%. The first-order rate constants, determined for various alkenes at 300 K, are as follows: $10^3k = 2.3\ s^{-1}$ ($CH_2{=}CH_2$); 5.1 s^{-1} ($MeCH{=}CH_2$); 5.1 s^{-1} ($Me_2C{=}CH_2$); 1.2 s^{-1} ($Me_2C{=}CMe_2$).

As shown by ^1H NMR data, the stoichiometric reaction of the palladium superoxo complex with excess ethylene yields only ethylene oxide (singlet 2.68 ppm). In agreement with this conclusion addition of the ethylene oxide, independently synthesized as in ref 25, to the reaction solution enhances the signal intensity at 2.68 ppm. We have compared the initial concentration of the superoxo complex with the concentration of the resulting ethylene oxide and the decomposition rate of the superoxo complex with the formation rate of ethylene oxide. For this purpose superoxo complex I, separated as solid preparation mixed with $Pd(OAc)_2$, was used. Using the EPR method, we have succeeded in determining the superoxo complex I concentration in a fresh solid preparation (1.2% relative to $Pd(OAc)_2$) to an accuracy of not worse than 30%. An 11-mg sample of this solid preparation had been placed into the ^1H NMR cell, diameter 5 mm, which was then filled with 0.5 mL $CHCl_3$ and plugged with a rubber stopper. Then the constancy of the intensity of an EPR spectrum of the superoxo complex in this cell (concentration 10^{-3} M) was monitored for 10 min. Such a procedure made it possible to preclude the possibility of the decomposition of part of the superoxo complex prior to the reaction. Ethylene (concentration 0.15 M, as ascertained by NMR) in $CHCl_3$ was then injected, the cell was shaken up, and NMR and EPR spectra were recorded at various moments of time after the reaction beginning. The spectra so obtained are shown in Figure 6. The observed rate constants of the superoxo complex decomposition ($k = (5.2 \pm 0.6) \times 10^{-4}\ s^{-1}$) and ethylene oxide formation ($k = (5.8 \pm 0.6) \times 10^{-4}\ s^{-1}$), found from data in Figure 6, are practically the same. The final concentration of ethylene oxide (10^{-3} M) determined from a ^1H NMR spectrum coincides within the accuracy of the NMR (10%) and EPR (30%) measurements with that of the superoxo complex. No products other than ethylene oxide have been detected with NMR in the solution after the end of the reaction. Thus ethylene oxide seems to be the only product of the reaction, 1 ± 0.1 mol of ethylene oxide being formed per 1 ± 0.3 mol of the superoxo complex decomposed.

The stoichiometric reaction of the palladium superoxo complex with excess propylene occurs to give propylene oxide (the multiplets at 2.99, 2.75, and 2.35 ppm and the doublet at 1.32 ppm[26]) and acetone (the singlet at 2.16 ppm) in a 1:2 ratio.

End products of interactions of the superoxo complex with other alkenes have not been analyzed.

The following peculiarities of the process of alkene oxidation by the palladium superoxo complex of type I resulting from interaction of H_2O_2 with $Pd(OAc)_2$ in $CHCl_3$ should be mentioned. First, the superoxo complex oxidizes alkenes to epoxides, in contrast to Pd–OOR peroxo complexes, which are reported to oxidize alkenes predominantly to ketones.[27] Second, the rate of ethylene oxide formation during the oxidation of ethylene by the superoxo complex is $\sim 10^3$ times greater than the rate of oxidation by such well-known epoxidating reagents as peroxyacids.[28] Furthermore, whereas the rate of the alkene oxidation by peroxyacids increases markedly when the number of methyl substituents near the double bond are increased,[28] the rates of oxidation by the palladium superoxo complex of four alkenes studied here are similar.

As follows from ^1H NMR data, ethylene oxide is also formed upon ethylene interaction with the superoxo complexes of type I, resulting from the reaction of KO_2 with $Pd(OAc)_2$ in $CHCl_3$. The reaction was carried out at low temperature (263 K) to avoid a rapid transformation of the superoxo complex of type I to an unreactive complex of type II.

(b) Reaction with CO. To study this reaction, superoxo complex I, prepared by using H_2O_2 and isolated as a solid preparation in mixture with $Pd(OAc)_2$, was dissolved in $CHCl_3$ saturated with carbon monoxide. Because of its high rate, the reaction was carried out at low temperatures within the range 226–266 K. The initial concentration of the superoxide was 3×10^{-4} M, as ascertained by EPR. The concentration of CO was determined by CO solubility. The solubility of CO in $CHCl_3$ was assessed at 298 K (the Bunsen coefficient $\alpha = 0.168$).[18a] At the CO pressure p = 1 atm used in our experiments, such a value of α corresponds to a 0.01 M concentration of CO in $CHCl_3$. According to the results of other work,[29,30] the solubility of simple gases in nonpolar solvents changes rather slowly with temperature. For example, in the region from 248 to 298 K it typically changes by not more than 20%. The pseudo-first-order rate constants for the decay of the superoxo complex in the presence of CO, determined for various temperatures, are as follows: $10^3k = 9\ s^{-1}$ (266 K); 2 s^{-1} (258 K); 1 s^{-1} (238 K); 0.6 s^{-1} (226 K). Note that during the reaction, no formation of metallic palladium was observed; in other words, $Pd(OAc)_2$ was not reduced to a noticeable extent with carbon monoxide.

Superoxo complexes of type I, resulting from the interaction of KO_2 with $Pd(OAc)_2$, were also found to oxidize CO to CO_2.

Discussion

1. Structure of Palladium Superoxo Complexes. As follows from EPR parameters (see Table I), all the superoxo complexes observed fall into two types. The complexes of type I have spectra with the **g** tensor closer to an axial symmetrical one (g_1 = 2.08–2.1, g_2 = 2.01, g_3 = 2.001–2.002; i.e. $g_1 - g_2 \gg g_2 - g_3$). The complexes of type II have spectra with a more pronounced 3-fold anisotropy of the **g** tensor (g_1 = 2.075–2.085, g_2 = 2.027–2.04, g_3 = 2.006–2.01; i.e. $g_1 - g_2 \approx g_2 - g_3$).

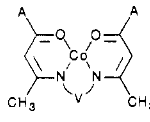
Note that stable superoxo complexes of type I are formed only when H_2O_2 reacts with $Pd(OAc)_2$ or $Pd(OPr)_2$ in poorly coordinating solvents. In all other cases either superoxo complexes

(25) Rejchsfeld, V. O.; Ruben, V. L.; Saratov, I. E. *Laboratory Methods on Technology of General Organic Synthesis*; Khimia: Moscow, 1966.

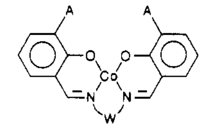
(26) Ionin, B. I.; Ershov, B. A. *NMR Spectroscopy in Organic Chemistry*; Khimia: Moscow, 1969.
(27) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047.
(28) Swern, D. *J. Am. Chem. Soc.* **1947**, *69*, 1692.
(29) Reeves, L. W.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1957**, *79*, 1313.
(30) Kretschmer, G. B.; Nowakowska, J.; Wiebe, R. *Ind. Eng. Chem.* **1946**, *38*, 506.

Table II. EPR Parameters for Superoxo Complexes of Cobalt[21]

compd	solvent	g_1	g_2	g_3	A_1^{Co}, G	A_2^{Co}, G	A_3^{Co}, G
$Co(salen)O_2$	CH_2Cl_2	2.089	1.998	1.998	25.1	18.1	18.1
$Co(acacen)(py)O_2$	toluene	2.08	1.998	1.998	19.3	16	16
$Co(benacen)(py)O_2$[a]	py	2.084	1.999	1.999	19.4	10.3	10.3
$Co(saldpt)O_2$	toluene/CH_2Cl_2	2.085	2.007	2.000	22.7	13.3	13.5
$Co(3\text{-}MeOsalMedapp)O_2$	toluene/CH_2Cl_2	2.097	2.009	2.000	23.6	14.3	13.1



compd	V	A
Co(acacen)	$-(CH_2)_2-$	CH_3
Co(benacen)	$-(CH_2)_2-$	C_6H_5



compd	W	A
Co(salen)	$-(CH_2)_2-$	H
Co(saldpt)	$-(CH_2)_3\text{-NH-}(CH_2)_3-$	H
Co(3-MeOsalMedapp)	$-(CH_2)_3\text{-PCH-}(CH_2)_3-$	CH_3O

[a] There are X-ray data for this compound.[38]

of type II are formed or, as in reactions involving KO_2, there occurs a fast transformation of initially formed superoxo complexes of type I to more stable complexes of type II.

What is the difference between the H_2O_2 + $Pd(OAc)_2$ and H_2O_2 + $Pd(OPr)_2$ systems in $CHCl_3$ and all other systems studied in this work? It is known that in poorly coordinating solvents $Pd(OAc)_2$ and $Pd(OPr)_2$ have trimeric structures, namely $Pd_3(OAc)_6$ and $Pd_3(OPr)_6$.[13] Binding of palladium atoms in trimers occurs by acetate bridges. Each palladium atom is surrounded by four oxygen atoms that lie in the same plane.[31]

In contrast to $Pd(OAc)_2$ and $Pd(OPr)_2$, other palladium complexes studied in this work ($Pd(OOCCF_3)_2$, $Pd(acac)_2$, and $Pd(PPh_3)_4$) are known to have monomeric structures in poorly coordinating solvents.[13,14,32] Thus one may assume that superoxo complexes of type I are characteristic of trimeric and those of type II are characteristic of monomeric palladium species.

The assumption made is in conformity also with the observation of only complexes II (Table I) in well coordinating solvents such as CH_3CN and Me_2SO that will dissociate the $Pd_3(OAc)_6$ trimers.[13] The formation of superoxo complexes II with an increasing amount of H_2O_2 solution in water added to AcOH can also be accounted for by the dissociation of $Pd_3(OAc)_6$ polymers.

As seen from Table I, there exists a distinct difference in EPR parameters for superoxo complexes formed in the presence of KO_2 and H_2O_2. Note also a lower stability of complexes of type I, prepared by interacting KO_2 with $Pd(OAc)_2$ in $CHCl_3$ as compared to those prepared by interacting H_2O_2 with $Pd(OAc)_2$ and $Pd(OPr)_2$ in the same solvent. In fact, in the former case complexes of type I transform to complexes of type II over 2 h even at low temperatures (273 K), whereas, in the latter case, complexes of type I are stable for several hours at room temperature. These differences can be attributed to the different compositions of palladium carboxylates in the absence and presence of the crown ether, which is added together with KO_2. During dissolution of KO_2 with crown ether in $CHCl_3$, a trimeric structure typical of palladium carboxylates can be distorted as a result of their interaction with the crown ether. Note that the addition of the crown ether to a solution of the superoxo complex of type I, produced by interaction of H_2O_2 with $Pd(OAc)_2$, also leads to a rapid transformation of complex I to complex II.

Thus, the interaction of H_2O_2 and KO_2 with palladium complexes gives rise to the two types of superoxo complexes. The structure of type I seems to be stabilized better by trimeric palladium complexes and the structure of the type II better by monomeric palladium complexes.

As suggested by numerous experimental data and theoretical calculations, variations of EPR parameters for O_2^- ion coordinated to metal atoms are determined primarily by variations of the oxidation state of metal atoms and of the way, η^1, or η^2, in which the O_2^- ligand is coordinated to metal atoms.[20,21,33-35]

Thus, substantial differences in the EPR parameters of the type I and type II superoxo complexes can be explained either by different oxidation states of palladium or by different O_2^- ligand coordination to the palladium atom. The first explanation seems to us rather improbable due to the following reason. When obtained via the reactions of KO_2 with $Pd(OAc)_2$, the less stable superoxo complex of type I transforms quantitatively to more stable superoxo complex of type II (see Figure 3). This transformation cannot be associated with oxidation or reduction of $Pd^{II}O_2^-$ species to $Pd^{III}O_2^-$ or $Pd^{I}O_2^-$ species since both species must either be diamagnetic or possess an even number of unpaired electrons and thus have an EPR spectrum substantially different from that observed for the PCs of type II. Ascription of the type II superoxo complex to $Pd^{IV}O_2^-$ species also seems improbable, since for $M^{IV}O_2^-$ complexes (where M is a metal) the values of g_1 typically fall within the range g_1 = 2.02–2.03, which is substantially different from the value g_1 = 2.05–2.1 typical for $M^{II}O_2^-$ complexes.[8,20,21,35]

Thus the difference in EPR parameters and reactivity of the two types of superoxo complexes observed most probably should be attributed to different types of O_2^- coordination to the metal atom in trimeric and monomeric palladium species. Two types of coordination, η^1 and η^2, have been suggested for the superoxo complexes of other metals.[21,34] From quantum-chemical calculations for the $Pd(acac)O_2$ complexes,[36] it follows that η^2 coordination is 72 kJ/mol more advantageous than η^1 coordination. The calculations were made by a modified semiempirical CNDO method.[37]

Equilibrium geometries and relative energies of PdO_2 fragment for η^1 and η^2 coordination of O_2^- ligand in $Pd(acac)O_2$ are

coord	R_{PdO^1}, Å	R_{PdO^2}, Å	$R_{O^1O^2}$, Å	rel energy, kJ/mol
η^2	1.781	1.781	1.509	0
η^1	1.571	1.548	1.574	72

For coordination η^2 the $Pd(acac)O_2$ complex is planar; for coordination η^1 the planes in which O_2^- and $Pd(acac)^+$ are lying are perpendicular. We would remind the reader that in the case of $Pd(acac)_2$, superoxo complexes II (Table I) are formed.

On the basis of these data, we have assumed η^2 coordination of the O_2^- ligand to occur for the palladium superoxo complexes II observed in this work.

(31) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658.
(32) Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186.
(33) Boca, R. *Coord. Chem. Rev.* **1983**, *50*, 1.
(34) Berdnikov, V. M.; Schastnev, P. V.; Merkulov, A. A.; Balaev, A. V.; Bazhin, N. M.; Gatilov, Yu. V. *Zh. Strukt. Khim.* **1973**, *14*, 634.
(35) Shubin, B. E.; Shvets, V. A.; Saveleva, G. A.; Popova, H. M.; Kazansky, V. B. *Kinet. Katal.* **1982**, *23*, 1153.
(36) Filatov, M. Yu.; Gritsenko, O. V.; Zhidomirov, G. M., private communication.
(37) Filatov, M. Yu.; Gritsenko, O. V.; Zhidomirov, G. M. *Theor. Chim. Acta*, in press.
(38) Rodley, G. A.; Robinson, W. T. *Nature (London)* **1972**, *235*, 438.

EPR parameters of superoxo complexes I are similar to those of cobalt superoxo complexes, which according to X-ray data have coordination η^1 (see Tables I and II). Thus it can be expected that η^1 coordination of O_2^- ligand occurs in the case of palladium superoxo complexes I.

As indicated above, superoxo complexes of type I presumably are formed upon coordination of the O_2^- ligand to trimeric palladium species. Stabilization in this case of the η^1 structure rather than of the otherwise more favorable η^2 structure can be, e.g., due to the fact that η^1 coordination of O_2^- causes a lesser distortion of the trimeric structure than η^2 coordination. Additional support for the validity of attribution of superoxo complexes I and II to superoxo complexes with different coordination of O_2^- (η^1 and η^2) comes from data on their reactivities. In fact, palladium superoxo complexes I (presumably η^1 coordination) oxidize *simple* olefins and CO, whereas superoxo-complexes II (η^2 coordination) are inert toward these compounds. The high reactivity seems to be more probable for η^1 coordination of O_2^-. For example, superoxo complexes of cobalt[39] and vanadium[1] (η^1 coordination) were reported to oxidize olefins. At the same time, our special experiments have shown that titanium superoxo complexes (most probably η^2 coordination[34]) are inert toward simple olefins and CO. The preparation procedure for titanium superoxo complexes in benzene (concentration 10^{-3} M) and their reactivity examination were similar to those for palladium superoxo complexes (see Experimental Section). Tetrakis(1-butanolato)titanium was used as starting compound. EPR parameters of the superoxo complexes obtained ($g_1 = 2.026$, $g_2 = 2.009$, and $g_3 = 2.003$) are close to literature values.[34]

Other PCs that in principle may be formed upon interaction of Pd(II) and Pd(0) complexes with H_2O_2 or KO_2 are compounds of Pd(III) and Pd(I). However the g factors for the PCs observed in this work are quite different from g factors that are typical for compounds of Pd(III) and Pd(I). In particular, the largest of the g factors, $g_1 = 2.08$–2.11, for our PCs is notably smaller than the values $g_1 = 2.4$–3 that are typical for Pd(I) and Pd(III).[40,41] On this ground the assignment of the observed EPR spectra to Pd(III) or Pd(I) complexes with diamagnetic ligands (including peroxo complexes of the $Pd^{III}O_2^{2-}$ and dioxygen complexes of the Pd^IO_2 types) seems much less probable than their assignment to superoxo complexes of Pd(II). Both g and the A values of PCs are indeed quite similar to those reported before for the O_2^- anion coordinated to metal atoms.[20,21,23] The chemistry of both the formation and the decomposition of the PCs also agrees with their being O_2^- species (see the discussion below). Thus the observed PCs of both types, I and II, should be assigned to superoxo complexes of palladium, the difference in the g values and reactivity of the superoxo complexes of types I and II resulting from different coordination, η^1 and η^2, of the O_2^- ligand to palladium complexes.

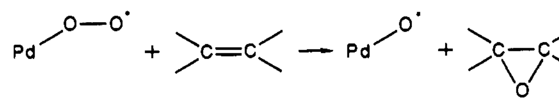
2. Possible Mechanism of Formation of Palladium Superoxo Complexes. In the case of the interaction of $Pd(OAc)_2$ with KO_2, the superoxo complex can be formed directly via the substitution of acetate ion by superoxide ion

$$Pd(OAc)_2 + KO_2 \rightarrow Pd(OAc)O_2 + KOAc \qquad (1)$$

The formation of superoxo complexes during the reaction of $Pd(OAc)_2$ with H_2O_2 seems to be due to the catalytic decomposition of H_2O_2 in the presence of palladium compounds.[42] One may suppose that $HO_2^•$ radicals formed during the decomposition of H_2O_2 interact with $Pd_3(OAc)_6$ trimers by substituting one of the acetate ions by the superoxide ion:

$$Pd_3(OAc)_6 + HO_2^• \rightarrow Pd_3(OAc)_5O_2 + HOAc \qquad (2)$$

3. Mechanism of the Oxidation of Alkenes and Carbon Monoxide by Palladium Superoxo Complexes. As has been mentioned, numerous superoxo complexes of transition metals are known at present. However, all of these complexes either are unreactive toward alkenes and CO or there are no quantitative data available on their reactivity toward these compounds. Note also that the free (noncoordinated) superoxide ion, obtained on dissolution of KO_2, is inert with respect to unsubstituted alkenes.[43] The palladium superoxo complex of type I with the proposed structure $Pd_3(OAc)_5O_2$ (η^1) showed a rather high activity in the oxidation of alkenes and CO. As has already been mentioned, for the reaction with C_2H_4 the rates of formation of ethylene oxide and of decay of the palladium superoxo complex coincide, 1 ± 0.1 mol of ethylene oxide being formed per 1 ± 0.3 mol of the reacted superoxo complex. This corresponds to the formal scheme



(3)

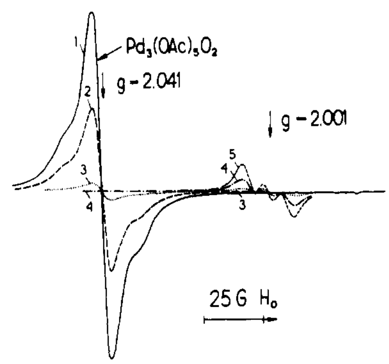


Figure 7. EPR spectra (T = 300 K) at different moments of time (min) after the beginning of the reaction of $Pd_3(OAc)_5O_2$ with ethylene in C_6H_6: 1, 1; 2, 5; 3, 15; 4, 23; 5, 36. $Pd_3(OAc)_5O_2$ = 0.005 M; C_2H_4 = 0.3 M. The samples contain the $Pd(OAc)(NO)_2$ impurity.

The attempts to observe the formation of $PdO^•$ radical directly by EPR methods were not successful. Nonetheless, we have obtained some indirect evidence that, along with ethylene oxide, some reactive PC is indeed formed during reaction 3. It is known that during synthesis, palladium acetate must be thoroughly washed by acetic acid in order to remove the impurity $Pd(OAc)NO_2$.[13] Working with the samples of $Pd(OAc)_2$ containing, a priori, $Pd(OAc)NO_2$, we observed that during the reaction of $Pd_3(OAc)_5O_2$ with both ethylene and CO in $CHCl_3$ or C_6H_6 the removal of the EPR signal of the superoxide is accompanied by the appearance of a triplet signal with $g_0 = 2.001$ and $A_0 = 8$ G. The growth of the triplet signal intensity lags relative to the removal of the EPR signal of the supposed $Pd_3(OAc)_5O_2$ and continues even after the disappearance of the EPR signal of the superoxo complex (see Figure 7). This observation implies that the interaction of $Pd_3(OAc)_5O_2$ with ethylene or with CO gives rise to both the oxidation products and a paramagnetic compound, whose decay produces the triplet signal observed. The result obtained can be explained by the reaction of $Pd(OAc)NO_2$ with $PdO^•$ to produce $Pd(OAc)NO_3^•$, $Pd(OAc)NO_2^•$, or $Pd(NO_3^{2-})$.

In this case $Pd(OAc)NO_2$ serves as a kind of spin trap for coordinated O^- species, producing $Pd(OAc)(NO_3^•)$, $Pd(NO_3^{2-})$ or $Pd(OAc)NO_2^•$ complex with the triplet EPR signal. The reason for the absence of an EPR spectrum from the original $PdO^•$ radical is not clear as yet. It may be caused by its EPR signal being too broad.

The EPR spectrum of the PC with $g_0 = 2.001$ at 77 K (see Figure 8) is also a triplet and has a 3-fold anisotropy of **g** and A tensors ($g_1 = 2.016$, $g_2 = 2.0056$, $g_3 = 1.982$, and $g_0' = \frac{1}{3}(g_1 + g_2 + g_3) \approx g_0 = 2.001$; $A_1 < 3$ G, $A_2 < 3$ G, and $A_3 = 18$ G). A triplet splitting seems to be due to the hyperfine coupling to a ^{14}N nucleus. However, the observed values of the **g** tensor (especially a relatively large value of g_1 in combination with $g_3 < 2.0023$) as well as A values are rather unusual for nitrogen-containing free radicals NO_3^{2-}, $NO_3^•$, and $NO_2^•$ (see literature

(39) Chkatsu, Y.; Tsuruta, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 188.
(40) Michalik, J.; Heming, M.; Kevan, L. *J. Phys. Chem.* **1986**, *90*, 2132.
(41) Michalik, J.; Nararana, M.; Kevan, L. *J. Phys. Chem.* **1985**, *89*, 4553.
(42) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387.
(43) Rosenthal, J.; Frimer, A. *Tetrahedron Lett.* **1975**, 3731.

Inorg. Chem. **1987**, *26*, 3878–3886

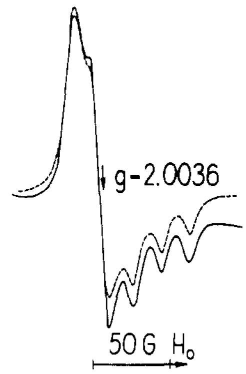


Figure 8. EPR spectrum of PC (g_0 = 2.001) observed after finishing of the reaction of $Pd_3(OAc)_5O_2$ with ethylene in C_6H_6 (the samples contain the $Pd(OAc)(NO_2)$ impurity) in the frozen-benzene solution (T = 77 K). The dotted line corresponds to a simulated spectrum.

values of g and A)[44] and suggest that we are dealing with a radical bound to a metal ion.

Interestingly, the formation of the triplet (g_0 = 2.001) was not observed if ethanol (concentration $\lesssim$ 0.3 M) had been added to the reaction mixture prior to the beginning of the reaction. Meanwhile, the addition of EtOH after the formation of the PCs with g_0 = 2.001 did not lead to their decay. It seems that Pd–O$^\bullet$ more rapidly reacts with ethanol than with $Pd(OAc)(NO_2)$ so that the nitrogen-containing free radical is not formed in the presence of ethanol. In contrast to PdO$^\bullet$, the PC with g_0 = 2.001 is quite stable. It does not react with ethanol, and its EPR signal remains unchanged, after the mixture is boiled in benzene for 5 min.

Thus, all the data discussed in this section are in agreement with the proposed mechanism of ethylene oxidation by palladium superoxo complexes via eq 3.

(44) Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Amsterdam, London, New York, 1967.

Conclusions

1. The interaction of palladium complexes such as $Pd(OAc)_2$, $Pd(OPr)_2$, $Pd(OOCCF_3)_2$, $Pd(acac)_2$, and $Pd(PPh_3)_4$ with H_2O_2 or KO_2 in various solvents produces superoxo complexes of two types—type I and type II. The difference in the g values and reactivity of complexes belonging to different types can be explained by assuming different types of O_2^- coordination to the metal (η^1 coordination for superoxo complexes of type I and η^2 coordination for those of type II). Coordination of η^1 appears to be characteristic of trimeric Pd complexes, while η^2 is characteristic of monomeric Pd complexes.

2. Superoxo complexes of type I oxidize alkenes and carbon monoxide. Those of type II are inert with regard to these compounds. Superoxo complexes of type I with the proposed structure $Pd_3(OAc)_5O_2^\bullet$ (η^1) rapidly oxidize ethylene to ethylene oxide, 1 ± 0.1 mol of ethylene oxide being formed per 1 ± 0.3 mol of the superoxo complex consumed, and propylene to propylene oxide and acetone in a 1:2 ratio.

Registry No. $Pd(acac)_2$, 14024-61-4; $Pd(PPh_3)_4$, 14221-01-3; $Pd_3(OAc)_6$, 53189-26-7; $Pd_3(OPr)_6$, 81352-62-7; 18-crown-6, 17455-13-9; ethylene, 74-85-1; propylene, 115-07-1; isobutylene, 115-11-7; tetramethylethylene, 563-79-1; carbon monoxide, 630-08-0; ethylene oxide, 75-21-8; propylene oxide, 75-56-9; acetone, 67-64-1.

Contribution from the Departments of Chemistry, Tulane University, New Orleans, Louisiana 70118, and Washington State University, Pullman, Washington 99164

Synthesis, Reactivity, Kinetics, and Photochemical Studies on Tetrakis(μ-pyrophosphito)diplatinate(II) and Dihalotetrakis(μ-pyrophosphito)diplatinate(III) Complexes. Comparison of the Substitution Mechanisms of the Diplatinum(III) Complexes with Those of Monomeric Platinum(II) and Platinum(IV) Compounds[1]

Samuel A. Bryan,[2a] Mark K. Dickson,[2b] and D. Max Roundhill*[2a]

Received April 16, 1987

The diplatinum(II) complex $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]\cdot 2H_2O$ with the bridging pyrophosphito-*P,P'* dianion has been synthesized by fusion of K_2PtCl_4 with phosphorous acid. Addition of halogens X_2 gives the diplatinum(III) complexes $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4X_2]$ (X = Cl, Br, I). The mixed-halide complexes $Pt_2(\mu\text{-}P_2O_5H_2)_4XY^{4-}$ can be prepared in solution by treating $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ with halogen X_2 in the presence of halide ion Y^- at low pH (X = I, Y = Cl, Br; X = Br, Y = Cl). Characterization methods include ^{31}P and ^{195}Pt NMR, UV–vis, and IR spectroscopy. The complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ is a dibasic acid, and the complexes $Pt_2(\mu\text{-}P_2O_5H_2)_4X_2^{4-}$ are tribasic acids. Rate data have been collected for the replacement of Cl^- in $Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2^{4-}$ by I^- and Br^- and for the replacement of Br^- in $Pt_2(\mu\text{-}P_2O_5H_2)_4Br_2^{4-}$ by I^-. In each case the reaction is catalyzed by added $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$. For the replacement of Cl^- in $Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2^{4-}$ by I^-, k_{obsd} is linearly dependent on $[Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}]$, but the plot against $[I^-]$, which is linear at low $[I^-]$, becomes independent of $[I^-]$ at high $[I^-]$. The reaction is inhibited by added Cl^-. Removal of the catalyst $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ with added iodine allows measurement of the second-order associative interchange or reductive-elimination–oxidative-addition (REOA) rate constant, 1.4 (2) × 10^{-3} M^{-1} s^{-1}, and the first-order dissociative rate constant, 8.9 (10) × 10^{-6} s^{-1}. The data for the catalyzed pathway can be fitted to a mechanism involving a preequilibrium between I^- and $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$, followed by reaction between $Pt_2(\mu\text{-}P_2O_5H_2)_4I^{5-}$ and $Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2^{4-}$. The association between $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ and I^- in aqueous solution has been independently observed by UV–vis and ^{195}Pt NMR spectroscopy and also by calorimetry. The kinetics of the replacement of Cl^- in $Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2^{4-}$ by Br^- can be explained by assuming a preequilibrium between $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ and $Pt_2(\mu\text{-}P_2O_5H_4)_4Cl_2^{4-}$, followed by reaction of $Pt_2(\mu\text{-}P_2O_5H_2)_4ClPt_2(\mu\text{-}P_2O_5H_2)_4Cl^{8-}$ with Br^-. Plots of k_{obsd} against $[Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}]$ show a linear dependence at low concentrations, but decreased dependence at larger values. For the replacement of Br^- in $Pt_2(\mu\text{-}P_2O_5H_2)_4Br_2^{4-}$ by I^-, we observe linear plots of k_{obsd} against both $[Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}]$ and $[I^-]$. These substitution reactions are all accelerated by light. For the photoconversion between $Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2^{4-}$ and $Pt_2(\mu\text{-}P_2O_5H_2)_4I_2^{4-}$ with added halide ions (I^- or Cl^-, respectively), the quantum yields are low ($\phi = 10^{-3}$–10^{-6}). The reaction pathway is proposed to involve the formation of a labile excited-state intermediate $d\sigma^1 d\sigma^{*1}$ that has a homolytically cleaved Pt(III)–Pt(III) bond. The respective quantum yields for the reductive elimination of X_2 from $Pt_2(\mu\text{-}P_2O_5H_2)_4X_2^{4-}$ are 7.3 (1) × 10^{-4}, 1.8 (1) × 10^{-4}, and 1.1 (1) × 10^{-5} for X = Cl, Br, and I.

Interest in the synthesis, structure, spectroscopy, and reaction chemistry of bimetallic transition-metal complexes continues to grow. The major focus of the majority of these studies is structural or spectroscopic, and there is little published work that quanti-

