Translated from *Uspekhi Khimii* **59** 1931–1959 (1990) U.D.C. 541.128.12

# Metal complex catalysis of oxidation reactions: principles and problems

**I I Moiseev, M N Vargaftik**
Kurnakov Institute of General and Inorganic Chemistry, USSR Academy of Sciences, Moscow

ABSTRACT. The mechanisms of the oxidation of organic substrates, mainly alkenes, in the presence of mononuclear and polynuclear transition metal complexes, including cluster complexes, are examined.

The bibliography includes 121 references.

## Contents

I. Introduction 1133
II. Mechanisms of the oxidation of alkenes 1133
III. Catalysis with participation of mononuclear complexes 1133
IV. Catalysis with participation of clusters 1136
V. Synthesis of catalytically active palladium clusters 1137
VI. Giant palladium clusters 1141
VII. Kinetics and mechanisms of oxidation reactions in solutions of giant palladium clusters 1145
VIII. Conclusion 1147

## I. Introduction

Metal complex-catalysed liquid-phase oxidation constitutes an extensive field of chemical reactions embracing reactions occurring both in living nature and under the conditions of industrial manufacture. Industrially important reactions of this type include liquid-phase oxidation of paraffins and alkylarenes, the oxidation of alkenes to carbonyl compounds and vinyl and allyl esters, numerous alkene epoxidation processes, etc.[1]

The study of oxidation reactions has played an important role in the establishment of metal complex catalysis and in the formulation of its principles. Thus the oxidation of alkenes in the presence of palladium salts has become the first example in metal complex catalysis where it has been possible to characterise reliably all the stages and to discover the role of the catalyst components in this important multi-stage reaction. Despite the fact that the individual details remain controversial,[2] this process is probably the most thoroughly investigated also nowadays.

The authors' aim is not a laborious and exhaustive survey of oxidation reactions occurring under the influence of coordination compounds. Attention is concentrated on the reactions of unsaturated substrates. In contrast to, for example, the reactions of alkanes, in these reactions both participants in the oxidation process—the unsaturated hydrocarbon and the oxidant—are capable of interacting jointly or separately with the catalyst. This not only introduces a great variety into the mechanisms of the processes but also makes the above reaction a convenient object for the study of the principal ideas and methods of metal complex catalysis.

## II. Mechanisms of the oxidation of alkenes

The functions of coordination compounds in the kinetics of oxidative homogeneous catalysis can be roughly reduced to the following schemes:

$$\begin{aligned} &M^n + Ox = A + M^m, \\ &A + Ol = P + Red; \end{aligned} \quad (1)$$

$$\begin{aligned} &M^n + Ox = M^m(A), \\ &M^m + Ol = P + M^n; \end{aligned} \quad (2)$$

$$\begin{aligned} &M^n + Ox = M^n(Ox), \\ &M^n(Ox) + Ol = P + M^n + Red; \end{aligned} \quad (3)$$

$$\begin{aligned} &M^n + Ol + Ox = Ol \cdot M^n \cdot Ox, \\ &Ol \cdot M^n \cdot Ox = P + M^n + Red; \end{aligned} \quad (4)$$

$$\begin{aligned} &M^m + Ol = M^n + P, \\ &M^n + Ox = M^m + Red, \end{aligned} \quad (5)$$

where M is the catalyst ($m > n$), Ox the oxidant, A the active form of the oxidant, Red its reduced form, Ol the substrate oxidised, and P the oxidation products.

In the first three schemes, the reaction product or its precursor arises as a consequence of the substrate being acted upon by the free (A) or bound in a complex [$M^n$(A)] active form of the oxidant or the complex of the catalyst and the oxidant [$M^n$(Ox)]. In scheme (4), the catalyst activates both the substrate and the oxidant, while in scheme (5) only the substrate is activated. Examples of olefin oxidation reactions via all the schemes indicated are known.[3,4]

## III. Catalysis with participation of mononuclear complexes

A typical example of the oxidation of alkenes with participation of mononuclear transition complexes may be provided by the reaction of substituted alkenes on treatment with Fenton's reagent ($Fe^{2+}/Fe^{3+} + H_2O_2$). According to scheme (1), an iron(+3) compound acts as a reactant in the stage involving the formation of active intermediate species (free radicals). Admittedly, the aquo-complexes of iron do not merely generate free radicals [the active form of the oxidant in terms of scheme (1)] in these systems, i.e.

$$\begin{aligned} &Fe^{2+} + H_2O_2 + H^+ = Fe^{3+} + HO^\cdot + H_2O, \\ &Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2^\cdot + H^+, \end{aligned}$$

but can also influence the nature of the product formed[6] by participating in the chain propagation and termination stages.[5]

Furthermore, in the interaction of iron compounds and hydrogen peroxide there is a possibility of the appearance of species which can be regarded as iron complexes containing the coordinated radical-anion $O^{\cdot}$ or as oxygen compounds of iron(+4). It has been suggested[3,7] that the oxygenyl complexes of iron(+5) or iron(+4) are responsible for the epoxidation of alkenes in the presence of haem-containing monoxidases, for example cytochrome P-450. Porphyrin complexes of iron, chromium, and manganese, modelling this enzyme, are known.[3,4,7,8] In all these systems, the catalyst interacts with the oxidant (which may be not only an inorganic or organic peroxide but also iodosobenzene,[9] the hypochlorite ion,[10] an amine *N*-oxide,[11] or 2-sulphonyloxyaziridine[12]) and abstracts from the latter an oxygen atom, which is coordinated to the catalyst and is then transferred to the substrate. Thus the main function of the catalyst in these processes is, according to scheme (2), the formation and stabilisation of the active form of the oxidant A (the oxygen atom) and also its transfer to the substrate undergoing oxidation. Direct interaction between the substrate and the catalyst is either very weak or does not occur at all. Thus analogues of cytochrome P-450 are capable of oxidising not only alkenes but also saturated hydrocarbons whose direct interaction with catalysts of this type is unlikely. Chromium complexes of Schiff bases,[13] copper nitrate,[14] and iron(+3) chloride and acetylacetonate[15] act similarly to metalloporphyrins.

In a number of instances, when $O_2$ interacts with the metal complex, its activation apparently reduces to its conversion into a coordinated superoxide ion.[8,16] Thus, in the epoxidation of ethylene in the gas phase, the interaction of $O_2$ with a silver atom or cluster can be completed by the transfer of an *s* electron from the silver atom to a molecule of dioxygen and the formation of a coordinated superoxide ion. The attack by the "free" valence of such a complex on the ethylene molecule and the subsequent intramolecular free-radical substitution should lead to an oxide form of the silver cluster [in the simplest case to silver(+2) oxide] and epoxyethane. After the reduction of silver oxide, the active form of the catalyst is regenerated and the catalytic cycle is closed. A palladium(+2) complex of the superoxide ion was obtained recently.[17] Modelling the reaction of the silver(+1) complex with the superoxide ion, it epoxidises alkenes smoothly.

The majority of the known catalysts of epoxidation by molecular oxygen actually effect the co-oxidation of the alkene when some kind of reductant, for example, ethylene and the products of its incomplete oxidation (in the gas-phase epoxidation of ethylene on a silver catalyst), of an alkene and an alkylarene (epoxidation of propene in the chalcone process), and of an alkene and $H_2$ or sodium tetrahydroborate (epoxidation catalysed by porphyrin complexes of manganese).

The first system in which both oxygen atoms are used to oxidise the alkene was discovered recently.[18] It was found that the interaction of dioxygen with tetramesitylporphyrinatoruthenium(II) involves the cleavage of the O=O bond and the formation of a ruthenium(+6) complex which contains two oxo-groups. This complex attacks the alkene and converts it into an epoxide. The ruthenium(+4) complex, arising under these conditions, disproportionates, regenerating the dioxide derivative of ruthenium(+6) and a ruthenium(+2) complex which on reaction with $O_2$ is also converted into the porphyrin complex of dioxoruthenium(+6).

A typical example of oxidation in accordance with scheme (3) is the epoxidation of alkenes by organic peroxides in the presence of molybdenum(+6) compounds.[19] A molybdenum(+6) atom with the non-bonding $d^0$ configuration is incapable of forming more or less stable π-complexes with alkenes.[20] Because of this, alkenes cannot compete with rigid oxo-ligands for a site in the coordination sphere of molybdenum(+6). The kinetic data[21–23] showing that, in the oxidation of propene by ethylphenyl hydroperoxide the alkene molecule not bound in a complex is attacked by the coordinated hydroperoxide molecule, are consistent with this finding. One of the mechanisms presupposes that the molybdenum(+6) complex of the hydroperoxide acts in the same way as an organic peracid in the Prilezhaev reaction.[19,23] However, the study of the stereochemistry of the oxidation of allyl alcohols led to the conclusion[4,24,25] that an oxygen atom bound directly to the metal is transferred to the alkene. In the transition state, this atom migrates to a neighbouring O atom of the coordinated alkyl peroxide ligand. To reach final conclusions, it is essential to investigate further this industrially important reaction. However, it is significant that in all these versions of the mechanism, the role of only the activator of the oxidant is attributed to the catalyst.

The reactions in which the catalyst activates simultaneously both the oxidant and the alkene [scheme (4)] are in the first place those catalysed by rhodium[26] and palladium[27–30] compounds.

In these reactions either the alkene is inserted between the catalyst metal atom and the oxidant molecule or the oxidant, interacting with the catalyst, influences the direction of the oxidation reaction. It is possible to obtain in this way, for example, glycol ethers instead of the aldehydes and ketones formed in the absence of an oxidant.[29] In addition, there also exists routes leading to the occurrence of scheme (4), in which both the oxidant and the alkene are coordinated to the catalyst, which effects the electron transfer between them.

Evidently, for the occurrence of such mediator[31] mechanism in the case of metals with the non-bonding $d^0$ configuration, special requirements must be met by the alkene structure. Since the double bond in the alkene cannot be used for its coordination to a metal atom with such electronic configuration, it is essential that the alkene should contain groups directly attached to the double bond, conjugated with the latter, and capable of coordination to the metal atom. All these conditions are satisfied, for example, by pentane-2,4-dione and its analogues in the enolic form.

In solutions of molybdates or tungstates, β-dicarbonyl compounds containing at least one hydrogen atom at the central carbon atom and hence capable of enolisation are smoothly oxidised by hydrogen peroxide.[32]

A $^1H$ NMR study of this reaction[33] showed that, even after the addition of only 0.5 mol of hydrogen peroxide per mole of acetylacetone (Hacac) under conditions where the reaction products (acetic acid and $CO_2$) are still absent, the signal due to the $CH_3$ groups of the coordinated $acac^-$ vanishes, the integral intensity of the signals of both forms of free Hacac diminishes, and a broadened singlet appears at 1.96 p.p.m., whose intensity increases as $H_2O_2$ is added, reaching a maximum for the ratio $[H_2O_2]:[Hacac] = 2$. Analysis of these data as well as comparison of the rates of oxidation of Hacac and a hypothetical intermediate which should have arisen in the oxidation of Hacac in accordance with the Baeyer–Villiger mechanism (formaldehyde and formic acid) showed that neither the free Hacac nor the coordinated $acac^-$ undergo oxidation in accordance with the Baeyer–Villiger mechanism under the experimental conditions. A complex containing the dianion of 2,2,4,4-tetrahydroxy-3-pentanone is the observed primary oxidation product. This complex was also synthesised independently from 3,3-dihydroxypentane-2,4-dione and sodium molybdate. The study of its IR and $^1H$ NMR spectra showed that the above ligand

forms in the coordination sphere a six-membered metallocycle incorporating the central metal atom.

The oxidation of Hacac by hydrogen peroxide takes place in the coordination sphere of molybdenum(+6) .[32] The key stage of this reaction includes the transfer of electrons from the coordinated $acac^-$ to the coordinated $O_2^{2-}$ in the inner coordination sphere of the complex. The absence of signals due to paramagnetic species in the EPR spectra at 77 and 300 K indicates the occurrence of the two-electron transfer.[33] Nevertheless, one cannot fully exclude the possibility of the occurrence of two successive one-electron processes, because the absence of the EPR signals may be associated with the exchange interaction between the paramagnetic ligands formed in the coordination sphere of the molybdenum atom. Regardless of these details of the mechanism, the resulting transfer of two electrons from the pseudo-aromatic (acac.Mo) system to the σ orbital of the $O_2^{2-}$ fragment destabilises the latter and leads to the appearance of the $O^{2-}$ ligand linked by multiple bonds to the central atom, which is promoted by the tendency of Mo atoms to form multiple bonds with π-donor ligands. In the coordinated $acac^+$, the positive charge is located predominantly at the C(3) atom to which the nucleophilic attack by the $H_2O$ molecule is directed. A short-lived molybdenum complex of 3-hydroxypentane-2,4-dione is apparently formed as a result of this attack. The repeated transfer of two electrons leads to the oxidation of this intermediate, which entails also the formation of the molybdenum complex of 3,3-dihydroxypentane-2,4-dione detected in the EPR spectrum. The subsequent oxidation of the organic ligand by hydrogen peroxide apparently proceeds via the mechanism of the Baeyer–Villiger reaction with or without the participation of $MoO_4^{2-}$.

One cannot rule out the possibility that inner-sphere electron transfer plays a much more important role in the catalysis by metal complexes having the non-bonding $d^0$ configuration than has been assumed until recently. In this connection, we may note kinetic data[34,35] showing that peroxides decompose in solutions of molybdenum(+6) compounds in water and of vanadium(+5) compounds in acetic acid via the intermediate formation of complexes containing at least two peroxide molecules at the metal atom.

If the peroxide disproportionates within the coordination sphere via the transfer of two electrons in one or two rapidly succeeding elementary steps, the primary product of such decomposition should be singlet oxygen or its complex with the metal atom. Indeed, the formation of $^1O_2$ has been detected in the oxidation of aromatic compounds by peroxides in the presence of molybdenum and vanadium compounds.[36,37] In the oxidation of anthracene by hydrogen peroxide in the presence of vanadium(+5) in acetic acid solutions, the product of the addition of $^1O_2$ to the substrate is also formed.[38] In addition, anthracene fully blocks the decomposition of $H_2O_2$ with formation of $O_2$. This fact as well as comparison of the rate constants for the physical quenching of $^1O_2$ and for the reaction of $^1O_2$ with anthracene demonstrate unambiguously that anthracene is oxidised not by the free singlet oxygen but by its precursor. Kinetic data and $^{51}V$ NMR spectra have led to the conclusion that the active intermediate—the agent transferring $^1O_2$ to the substrate molecule—is either the peroxo-complex V(+5) $(O_2^{2-})_3$ or a complex of the type V(+5)($^1O_2$).

Another active form of oxygen, also formed via a molecular pathway on decomposition of $H_2O_2$ in solutions of V(+5) in acetic and trifluoroacetic acids, is ozone, whose yield is 1 and 10% respectively.[39] The oxidative hydroxylation of cyclohexane[40,41] and methane[42] and the oxidative degradation of the multiple bonds of the electron-deficient perfluorobenzene[43] and perfluoroalkenes[44,45] with formation of perfluorocarboxylic acid fluorides also occur in the same systems under mild conditions. However, it has been found[46] that the rates of oxidation of all these substrates by ozone are much lower than the rates of oxidation of the same substrates by hydrogen peroxide. Thus, despite the fact that ozone is formed in the given system, it cannot be regarded as an active intermediate in the oxidation of the substrates indicated.

The involvement in the reaction of extremely unreactive electron-deficient perfluoroalkenes, which are incapable of reacting with free singlet oxygen, as well as the low yield of epoxides show that unsaturated perfluorohydrocarbons are oxidised with participation of oxygenyl complexes of vanadium as donors of $^1O_2$.

The mechanism of the formation of the active intermediates responsible for the evolution of $O_3$ and the oxidation of the substrates is apparently fairly complex. This is indicated by the following facts:

1. Cyclohexane, arenes, and perfluoroarenes completely block the evolution of ozone; α-perfluoroalkenes reduce by a factor of 3–5 the yield of $O_3$ while β-perfluoroalkenes do not affect the yield of ozone.

2. In the joint oxidation of substrates of different nature, each preceding member of the series—cyclohexane, arene, α-perfluoroarene, and β-perfluoroalkene—completely blocks the oxidation of any subsequent member, although in their separate oxidation the rates of consumption of all these substrates are comparable.[47]

All these facts can be reasonably explained within the framework of Scheme 1 according to which several (at least four) types of active intermediates are formed in the V(+5)–$H_2O_2$–RCOOH system, their concentrations being stationary and each of these species being responsible for the oxidation of a substrate of only one particular type.[48]

Exactly 30 years ago, the liquid-phase alkene oxidation reactions catalysed by palladium(+2) compounds were discovered:[49–51]

$$\begin{aligned} &C_2H_4 + {}^1/_2\,O_2 = CH_3CHO,\\ &C_2H_4 + {}^1/_2\,O_2 + AcOH = CH_2{=}CHOAc + H_2O,\\ &C_2H_4 + {}^1/_2\,O_2 + 2ROH = CH_3CH(OR)_2 + H_2O. \end{aligned} \qquad (6)$$

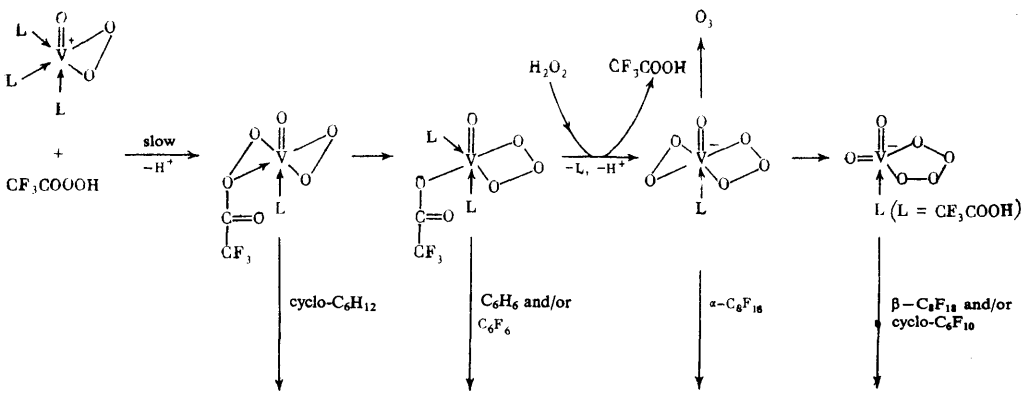
An important feature of these reactions, proceeding in accordance with scheme (5), is that the substrate activation (the key stage in which the alkene molecule is converted into a precursor of the final product) proceeds in the inner coordination sphere of the mononuclear palladium(+2) complex:[20]

$$\begin{aligned} &PdCl_4^{2-} + C_2H_4 = PdCl_3(\pi\text{-}C_2H_4)^- + Cl^-,\\ &PdCl_3(\pi\text{-}C_2H_4)^- + H_2O = PdCl_2(H_2O)(\pi\text{-}C_2H_4) + Cl^-,\\ &PdCl_2(H_2O)(\pi\text{-}C_2H_4) = PdCl_2(OH)(\pi\text{-}C_2H_4)^- + H^+,\\ &PdCl_2(OH)(\pi\text{-}C_2H_4)^- \rightarrow \sigma\text{-}Cl_2Pd{-}CH_2CH_2OH^-,\\ &\sigma\text{-}Cl_2Pd{-}CH_2CH_2OH^- \rightarrow Pd^0 + 2Cl^- + CH_3CHO,\\ &Pd^0 + Ox + 4Cl^- \rightarrow PdCl_4^{2-} + Red. \end{aligned} \qquad (7)$$

At high palladium(+2) concentrations, dinuclear palladium(+2) complexes of the type $Pd_2Cl_6^{2-}$ also participate in these reactions, but the mechanism of their action differs fundamentally from that presented in scheme (7) for mononuclear complexes.[52]

Since the discovery by Shilov and Shteinman[53,54] of deuterium exchange between methane and $D_2O$ in the presence of platinum salts, a vigorous search is being prosecuted throughout the world for transition metal complexes capable of catalysing reactions involving the oxidative functionalisation of alkanes. The recently published

Scheme 1




oxidation products

communications[55,56] about the oxidation of methane and certain other hydrocarbons by palladium(+2) salts may be included among the number of recent attempts to achieve the oxidation of an alkane in accordance with scheme (5). Palladium(+2) is usually introduced in the form of the trimeric acetate $Pd_3(OAc)_6$ into the trifluoroacetic acid solution where it is in all probability converted into the monomeric $Pd(OCOCF_3)_2$. Under fairly mild conditions, at 80 °C and 60–70 atm, methyl trifluoroacetate was obtained from methane in 60% yield:

$$CH_4 + Pd(OCOCF_3)_2 = CH_3OCOCF_3 + Pd^0 + CF_3COOH. \quad (8)$$

If this reaction is combined with the reoxidation of zerovalent palladium to palladium(+2), as had been done earlier in the oxidation of alkenes via reaction (6), it might be possible, in principle, to achieve the liquid-phase catalytic oxidation of methane by oxygen. Unfortunately, so far it has not been possible to reproduce in our laboratories the results obtained in the above studies.[55,56]

In the search for complexes of other transition metals capable of reacting with methane, it has recently been observed[57,58] that cobalt(+3) trifluoroacetate is reduced by methane under comparatively mild conditions ($CF_3COOH$ solution, 150–180 °C, 10–40 atm), converting it into methyl trifluoroacetate in a nearly quantitative yield [90 ± 10% with respect to Co(+3)]:

$$CH_4 + 2Co(OCOCF_3)_3 = CH_3OCOCF_3 + 2Co(OCOCF_3)_2 + CF_3COOH. \quad (9)$$

In the presence of oxygen, the cobalt(+2) formed is oxidised to cobalt(+3):

$$Co(OCOCF_3)_2 + {}^1/_2 O_2 + CF_3COOH = Co(OCOCF_3)_3 + H_2O,$$

which made it possible to achieve for the first time the highly selective catalytic conversion of methane into methyl trifluoroacetate:[58]

$$CH_4 + {}^1/_2 O_2 + CF_3COOH = CH_3OCOCF_3 + H_2O. \quad (10)$$

The state of cobalt(+3) and cobalt(+2) in these solutions has not so far been investigated. There is no complete certainty that the cobalt(+3) complex is in fact the electrophile which attacks the methane molecule. One cannot rule out the possibility that reaction (10) proceeds as a result of the participation of the oxygenyl complexes of cobalt(+4), which may have a polynuclear structure.

## IV. Catalysis with participation of clusters

A considerable amount of data indicating the existence of a specific field of catalysis in which the substrate is activated by polynuclear, mainly cluster, compounds of transition metals has accumulated recently. Among such palladium cluster-catalysed reactions, one may include, for example:

positional and geometrical isomerisation of alkenes;[59]
dimerisation and oligomerisation of alkenes;[60]
hydrogenation of acetylenes, dienes, nitro-compounds, quinones, and other unsaturated compounds;[61,62]
oxidative dehydrogenation of cyclohexene;[59]
oxidative acetoxylation of alkenes[63] and alkylarenes;[64]
alkoxycarbonylation of acetylene.[65]

The oxidative substitution of a hydrogen atom in alkenes (ethylene, propene) by the acetoxy-group, which has been achieved industrially, occupies a special place among these reactions:

$$C_nH_{2n} + {}^1/_2 O_2 + AcOH \xrightarrow[180\,^\circ C]{Pd/SiO_2} C_nH_{2n-1}OAc + H_2O. \quad (11)$$

This process is carried out in the vapour phase using metallic palladium with added alkali metal acetates on the surface of a porous carrier as the catalyst.[66]

It was initially postulated that the heterogeneous version of reaction (11) also proceeds via the mechanism characteristic of reactions (6) mentioned above, with participation of the mononuclear palladium(+2) complexes, via alternating stages in which palladium(+2) is reduced and zerovalent palladium is oxidised:

$$Pd(+2) + C_nH_{2n} + AcOH \rightarrow Pd(0) + C_nH_{2n-1}OAc + H_2O,$$
$$Pd(0) + {}^1/_2 O_2 \rightarrow Pd(+2) + H_2O.$$

However, the hypothesis of the involvement of palladium(+2) in reaction (11) agrees poorly with data concerning the selectivity of the oxidative acetoxylation of propene and ethylene.[67] Thus, in the

oxidation of propene by palladium(+2) acetate in solution in acetic acid, the yield of allyl acetate, which is high in the absence of water and at low temperatures (94% at 25 °C), falls sharply on raising the temperature and on increasing the water content (4% at 118 °C; the remainder consists of acetone and other side products).[68] On the other hand, in the presence of a heterogeneous palladium catalyst, the selectivity with respect to allyl acetate remains constantly high (~90%) even on raising the temperature to 180 °C and the water content to 10%.[69]

On interaction of $Pd(OAc)_2$ with the $C_3H_6-O_2$ mixture in solution in acetic acid containing NaOAc, propene is oxidised without the consumption of oxygen solely as a result of the reduction of palladium(+2). Under these conditions, a mixture of products is formed (isopropenyl acetate, n-propenyl acetate, allyl acetate, and acetone) with the same quantitative composition as in the absence of $O_2$.[70] However, after the complete reduction of palladium(+2), a slower catalytic reaction begins in which $O_2$ is consumed and the product of the allylic oxidation of propene (allyl acetate) is formed in a high yield.[67]

Significant differences between the selectivities of the action of palladium(+2) and heterogeneous palladium catalysts have been observed also in the oxidation of alkylarenes in the presence of carboxylic acids.[71,72] On treatment with palladium(+2) in solution in acetic or trifluoroacetic acid, toluene undergoes mainly oxidative coupling via the benzene rings with formation of a mixture of isomeric (*o*-, *m*-, and *p*-) bitolyls:

$$2C_6H_5CH_3 + Pd(+2) = CH_3C_6H_4-C_6H_4CH_3 + Pd(0) + 2H^+.$$

The reoxidation of the reduced form of palladium with oxygen makes it possible to carry out the process under catalytic conditions (with respect to palladium):

$$2C_6H_5CH_3 + {}^1/_2\,O_2 = CH_3C_6H_4-C_6H_4CH_3 + H_2O.$$

So long as an appreciable amount of reduced palladium does not accumulate in the system, the above toluene oxidation pathway remains unchanged. However, the accumulation of metallic palladium or the introduction of freshly prepared palladium black leads to a sharp alteration of the composition of the products. The main reaction pathway becomes the benzyl oxidation—the oxidative acetoxylation of toluene in the side chain: $C_6H_5CH_3 + \frac{1}{2}O_2 + AcOH = C_6H_5CH_2OAc = H_2O$.

Finally, the thermal instability of palladium(+2) carboxylates at temperatures above 100 °C, where the oxidative acetoxylation of alkenes and alkylarenes in the presence of a heterogeneous catalyst proceeds most readily at 150–200 °C, constitutes evidence against the participation of palladium(+2) in the heterogeneous-catalytic oxidation of alkenes.[63] All these data suggest that the active centres of the heterogeneous palladium catalysts, responsible for the oxidative acetoxylation of alkenes and alkylarenes, contain not palladium(+2) but palladium in a lower oxidation state.

As for other platinum metals, the lower oxidation state of palladium is represented, with few exceptions, by cluster compounds. However, stable coordinatively unsaturated clusters are as a rule catalytically inactive. Under the conditions of the catalytic reaction, it is also not possible to rule out the possibility of the decomposition of the cluster complex with formation of the catalytically active metal phase. Therefore, in order to elucidate the principal features of cluster catalysis, it is essential not only to synthesise a cluster suitable for the occurrence of the catalytic reaction but also it is necessary to make sure that the cluster and not its decomposition product is responsible for the catalysis of the given reaction.

## V. Synthesis of catalytically active palladium clusters

One of the most effective methods of synthesis of transition metal clusters is based on the monocarbonyls and polycarbonyls of these metals.[73] Unfortunately, palladium does not form binary carbonyls stable under the usual conditions.[74] Palladium complexes containing other ligands in addition to CO are therefore used as the initial compounds.

When solutions of palladium(+2) salts are treated with CO, palladium(+2) is usually reduced to the metal. Thus the reduction of $Pd(OAc)_2$ by carbon monoxide in glacial acetic acid containing alkali metal acetates leads to the formation of metallic palladium, acetic anhydride, and $CO_2$:[21]

$$Pd(OAc)_2 + CO \rightarrow Pd^0 + Ac_2O + CO_2.$$

In carboxylic acids or carboxylic acid + benzene mixtures in the absence of alkali metal acetates, fairly stable complexes [(RCOO).Pd(CO)].*n*RCOOH, where $n$ = 0.5 or 0, were obtained. Thus carbonylation of palladium(+2) acetate in glacial acetic acid at 50 °C leads to the compound $Pd_4(CO)_4(OAc)_4.2AcOH$. According to X-ray diffraction data,[76] the main structural unit of these crystals consists of the tetranuclear clusters $Pd_4(CO)_4(OAc)_4$ (PCA) with a rectangular metallic core (Fig. 1). The sides of the rectangle spanned by acetate bridges are longer (2.909 Å), while those linked by carbonyl bridges are shorter (2.603 Å) than the Pd–Pd distance in metallic palladium (2.751 Å).

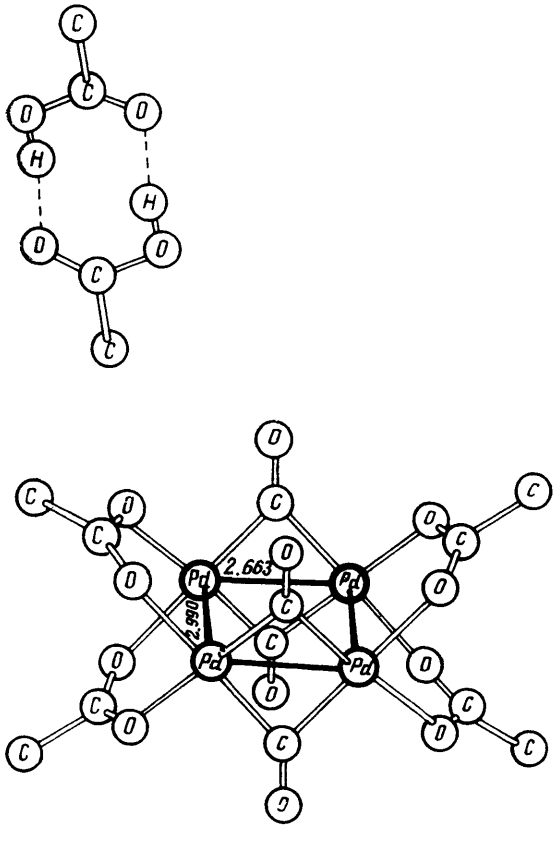



**Figure 1. The structure of the cluster $Pd_4(CO)_4(OAc)_4.2AcOH$.**

The reactions of $Pd(OCOEt)_2$ and $Pd(OCOPh)_2$ with CO afford the analogous clusters $Pd_4(CO)_4(OCOEt)_4$ and $Pd_4(CO)_4(OCOPh)_4$.[77] The similarity of the chemical properties and spectroscopic characteristics of these compounds suggested that they are all constructed similarly to PCA. Thus the synthesis of PCA, described by the equation

$$4Pd(OAc)_2+8CO=Pd_4(CO)_4(OAc)_4+2Ac_2O+4CO_2, \quad (12)$$

represents a general route to palladium(+1) carbonyl carboxylates.[77]

Studies on the kinetics and intermediates of reaction (12) led to the conclusion[78] that the formation of PCA from the trimeric palladium(+2) acetate is a reaction of the type of reductive condensation and involves the following stages:

(1) insertion of CO in the Pd–OAc bond;

(2) elimination of $CO_2$ with formation of the acyl fragment $Pd-C(O)-CH_3$;

(3) liberation of a molecule of acetic anhydride $Ac_2O$ and the formation of the Pd–Pd bond.

The coordinated acetate groups in PCA are readily substituted by other carboxylates on interaction of the corresponding acids with PCA:

$$Pd_4(CO)_4(OAc)_4 \xrightarrow[-AcOH]{RCOOH} [Pd(CO)(OCOR)]_4, \quad R = CD_3,\ Et,\ Ph,\ CF_3,\ CCl_3,\ CH_2Cl. \quad (13)$$

The similarity of the IR spectra, chemical behaviour, and stoichiometry of these compounds with the data for PCA suggests that all these complexes are analogues of PCA.[77]

Treatment of PCA with inorganic acids, for example, hydrochloric acid, also leads to the substitution of the acetate groups by $Cl^-$, but the carbonyl chloride complexes formed are unstable. It might have been supposed that the substitution of the acetate groups in PCA by an involved metal complex anion, for example, carbonyl metallate, does not lead to the decomposition of the metallic core and would make it possible to obtain a heteronuclear palladium-containing cluster.

Indeed, the interaction of PCA with $Na[CpMo(CO)_3]$ yielded the anionic octanuclear cluster $Na_2\{Pd[Mo(CO)_3Cp]\}_4.2THF$.[79] According to X-ray diffraction data, the principal structural units of crystals of this compound are the centrosymmetric anion $\{Pd[Mo(CO)_3Cp]\}_4^{2-}$, two $Na^+$ cations, and two THF molecules. The Pd atoms are arranged at the vertices of the square (Pd–Pd = 2.675–2.691 Å) (Fig. 2). Each Mo atom forms an almost regular triangle with two Pd atoms (Pd–Mo = 2.723–2.741 Å) and all the metal atoms lie in the same plane.

The formation of the octanuclear cluster involves not only the substitution of the acetate ligands by the anions $CpMo(CO)_3^-$ but also the displacement of the neutral CO molecules. The liberated vacancies in the coordination sphere of palladium are occupied by the CO molecules coordinated to Mo, which are converted into bridges linking atoms of different metals. Apparently the process is not restricted to the substitution of ligands: during the reaction, Pd(+1) atoms are reduced, probably as a result of the one-electron oxidation of the $CpMo(CO)_3^-$ anions. If it is assumed that the Mo atoms forming part of this complex have a zero oxidation state, which obtains in the initial compound, then the observed reaction can be regarded as the reduction of Pd(+1) to Pd(+5):

$$Pd_4(CO)_4(OAc)_4+6Na[CpMo(CO)_3]=Na_2[Pd_4Mo_4Cp_4(CO)_{12}]+4CO+[CpMo(CO)_3]_2+4NaOAc. \quad (14)$$

Reactions (13) and (14) are examples of the substitution of the acido-ligands in PCA by other acido-groups. The substitution of the neutral carbonyl ligand is observed on interaction of PCA with diphenyldiazomethane.[80] The interaction of PCA with $Ph_2CN_2$ in benzene leads to the displacement of the CO groups and the formation of a complex containing diphenylcarbene as the ligand:

$$Pd_4(CO)_4(OAc)_4+Ph_2CN_2\rightarrow Pd_4(CPh_2)_4(OAc)_4+CO+4N_2.$$

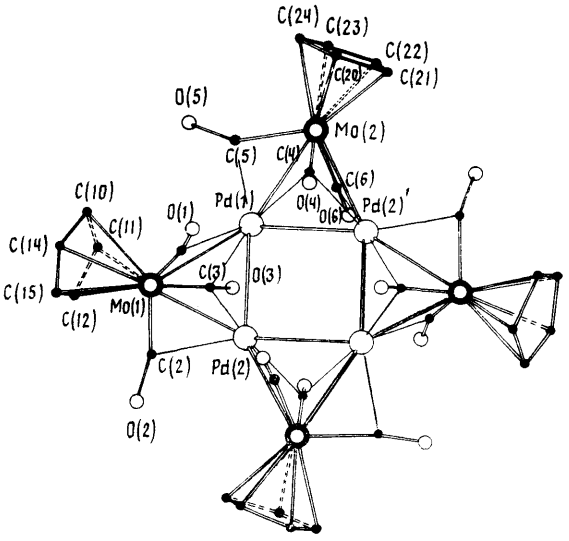



**Figure 2. The structure of the cluster dianion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$.**

The composition of the resulting complex as well as the results of physicochemical studies (elemental analysis, IR and $^1H$ NMR spectra, molecular weight measurements) can be equally attributed both to the formation of a complex with carbene ligands and a π-complex with tetraphenylethylene. However, the presence of carbene ligands in the complex is indicated by reactions leading to products characteristic of the free carbenes. Thus hydrogenation of the complex in benzene at 20 °C and 1 atm $H_2$ pressure leads to the dissociation of the Pd–C bonds and the formation of diphenylmethane:[81]

$$...Pd=CPh_2+H_2\rightarrow ...Pd+Ph_2CH_2.$$

Alkaline hydrolysis of the complex affords diphenylmethanol together with diphenylmethane and benzophenone:

$$...Pd=CPh_2+H_2O \xrightarrow{EtOH,\ KOH} ...Pd+Ph_2CHOH.$$

Interaction with alkenes results in the formation of the products of the cycloaddition of the carbene to the alkene, which is characteristic of both the free carbenes and of their complexes. For example, the reaction of the complex with hex-1-ene leads to 2-butyl-1,1-diphenyl-cyclopropane:

$$...Pd=CPh_2+CH_3(CH_2)_3CH=CH_2 \rightarrow ...Pd+CH_3(CH_2)_3CH(CPh_2)-CH_2.$$

The structure of the carbene complex was investigated by the EXAFS method.[82] The results confirmed the hypothesis that a rectangular metallic core is present (Fig. 3).

PCA reacts in a very complex manner with ligands such as $PPh_3$, pyridine (Py), phenanthroline (Phen), diphosphine (Diphos), and bipyridyl (Bipy). Depending on the initial Pd:ligand concentration ratio, complexes of different composition are formed.[83] The palladium compounds produced for the ratio $[Pd]_\Sigma:[L]_\Sigma \geqslant 2$ (L = ligand) are fairly unstable. As $[Pd]_\Sigma:[L]_\Sigma$ diminishes, more stable complexes are formed.

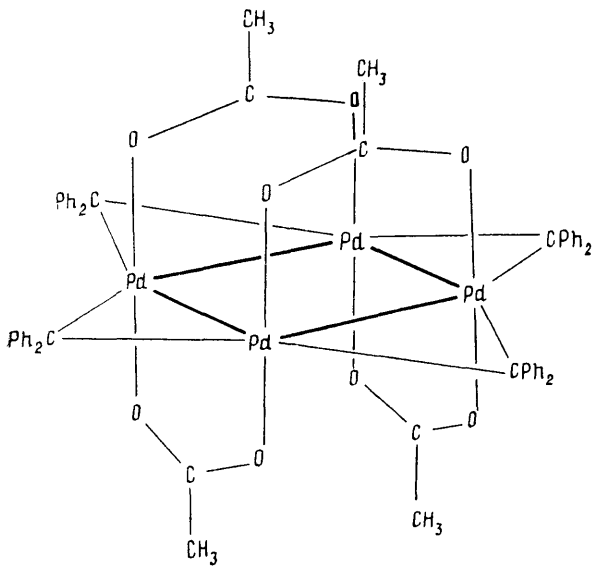


**Figure 3. The structure of the carbene cluster $Pd_4(CPh_2)_4(OAc)_4$ according to EXAFS data.**

The interaction of PCA with pyridine and its alkyl derivatives, using the ratio $[Pd]_\Sigma:[L]_\Sigma = 1:1$, involves the disproportionation of the Pd(+1) to Pd(+2) and Pd(0):

$$Pd_4(CO)_4(OAc)_4+4Py=2Pd^0+2PdPy_2(OAc)_2+4CO.$$

The reaction of PCA with diphosphine in benzene makes it possible to obtain the complex $Pd_2(Diphos)_2(CO)(OAc)_2.C_6H_6$:[84]

$$Pd_4(CO)_4(OAc)_4+4Diphos=2Pd_2(Diphos)_2(CO)(OAc)_2+2CO.$$

The interaction of PCA with a (5–10)-fold excess of diphosphine in tetrahydrofuran (THF) leads to the cationic complex $[Pd_2(\mu\text{-}CO)(Diphos)_4]^{2+}(OAc)_2$ with a different coordination of the diphosphine ligands:

$$Pd_4(CO)_4(OAc)_4+8Diphos=2Pd_2(CO)(Diphos)_4(OAc)_2+2CO.$$

When PCA is treated with $PPh_3$, the complex $Pd_2(CO).(PPh_3)_2(OAc)_2$ is formed:

$$Pd_4(CO)_4(OAc)_4+4PPh_3=2Pd_2(CO)(PPh_3)_2(OAc)_2+2CO.$$

This complex contains a CO bridging group [$\nu$(CO) = 1800 $cm^{-1}$]. Depending on the conditions of the synthesis, compounds differing in the mode of coordination of the acetate groups are produced. Thus, when the reaction was carried out in solution in THF, a complex with acetate bridges was obtained [$\nu_s$(COO) = 1530 $cm^{-1}$, $\nu_{as}$(COO) = 1400 $cm^{-1}$, and $\Delta\nu$ = 130 $cm^{-1}$], while the reaction of PCA with $PPh_3$ in benzene leads to a compound with terminal OAc groups [$\nu_s$(COO) = 1610 $cm^{-1}$, $\nu_{as}$(COO) = 1350 $cm^{-1}$, $\Delta\nu$ = 260 $cm^{-1}$]. The complex is unstable in solution and gradually disproportionates to Pd(+2) and Pd(0). The latter was isolated in the form of the mononuclear complex $Pd(PPh_3)_3$.[84]

In the case of bipyridyl at an initial concentration of 0.5 M and a PCA concentration of $5 \times 10^{-3}$ M, all the coordinated CO molecules are displaced:[83]

$$Pd_4(CO)_4(OAc)_4+2Bipy=2Pd_2(Bipy)(OAc)_2+4CO.$$

At low bipyridyl concentrations ($\leqslant 5 \times 10^{-3}$ M), only half of the coordinated CO molecules are displaced from PCA:

$$Pd_4(CO)_4(OAc)_4+2Bipy=2Pd_2(Bipy)(CO)(OAc)_2+2CO.$$

In contrast to bipyridyl, *o*-phenanthroline at 20 °C displaces from PCA only half of the coordinated CO molecules at the highest ligand concentrations:

$$Pd_4(CO)_4(OAc)_4+4Phen=2Pd_2(CO)(Phen)_2(OAc)_2+2CO.$$

The last two complexes were also obtained directly by reducing with carbon monoxide a solution in acetic acid containing $Pd(OAc)_2$ and L.[84]

The interaction of PCA with *o*-phenanthroline in the proportions $[Pd]_\Sigma:[Phen]_\Sigma = 1:1$ in solution in acetic acid affords the complex $Pd_4(CO)_2(Phen)_4(OAc)_4$:[85]

$$Pd_4(CO)_4(OAc)_4+4Phen=Pd_4(CO)_2(Phen)_4(OAc)_4+2CO.$$

The same complex was obtained by reducing with carbon monoxide palladium(+2) acetate in solution in acetic acid containing *o*-phenanthroline. According to X-ray diffraction data, the crystals of the complex contain as the main structural unit the tetrahedral cluster cation $[Pd_4(CO)_2(Phen)_4]^{4+}$ (Fig. 4). The $OAc^-$ ligands are not linked directly to the palladium atoms but are located in the outer sphere. On formation of this complex from PCA, all the metal–metal distances change significantly: the lengths of the Pd–Pd bonds in the Pd(μ-CO)Pd fragments increase to 2.890 Å (in PCA this distance is 2.663 Å). None of the acetate groups in $[Pd_4(CO)_2(Phen)_4]^{4+}$ are coordinated to the palladium atoms, as in PCA, but are located in the outer sphere as the $OAc^-$ anions.

The complexes obtained behave as moderately strong electrolytes in aqueous solution. They undergo a reversible substitution of $OAc^-$ by $X^-$ anions:

$$Pd_2(CO)Phen_2(OAc)_2 \underset{OAc}{\overset{X^-}{\rightleftarrows}} Pd_2(CO)Phen_2X_2,$$

$$X^- = ClO_4^-,\ Cl^-,\ HSO_4^-,\ Cl_3CCOO^-,\ F_3CCOO^-,\ CNS^-.$$

Such complexes have been isolated and characterised by elemental analysis and IR spectroscopy.[83]

The study of PCA and its derivatives showed that none of these complexes react with ethylene, propene, and toluene in carboxylic acids and do not exhibit a catalytic activity in the oxidation of these

hydrocarbons by molecular $O_2$. A low catalytic activity in the oxidation of propene to allyl acetate and of toluene to benzyl acetate [~0.1 mol (mol Pd)$^{-1}$ h$^{-1}$ at 90 °C and 1 atm $O_2$] was observed only in the case of PCA after the latter had been kept in acetic acid solution containing 1 M sodium acetate for 0.5–1 h at 60–90 °C under a $O_2$ atmosphere. During this operation, PCA decomposes with formation of palladium black: $Pd_4(CO)_4(OAc)_4 = 4\,Pd + 2CO + 2CO_2 + 2Ac_2O$, while the CO, evolved as a result of this reaction and sorbed on the surface of metallic palladium, is oxidised by oxygen to $CO_2$, which makes the surface of the metal accessible to hydrocarbons.

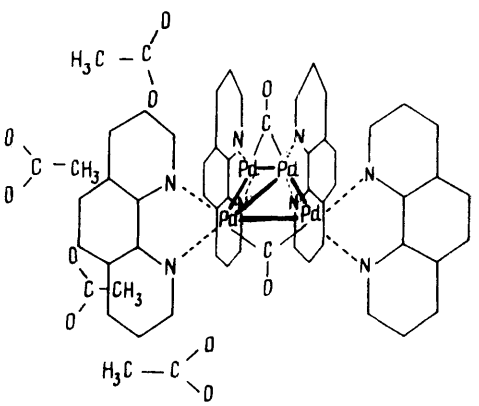
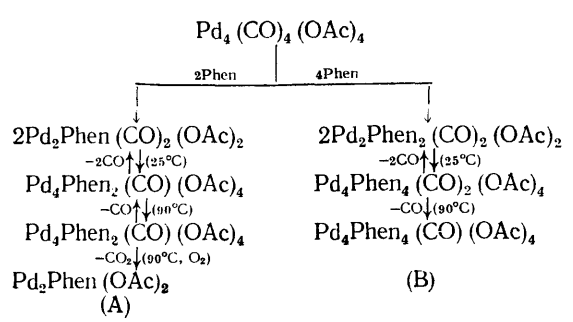


**Figure 4. The structure of the cluster $[Pd_4(CO)_2Phen_4](OAc)_4$.**

None of the remaining carbonyl carboxylate clusters described in this section exhibits a catalytic activity either because of their coordinative unsaturation and a low tendency towards the formation of intermediate complexes with an alkene or alkylarene molecule or as a consequence of their decomposition to other relatively inactive and also coordinatively unsaturated palladium complexes.

In contrast to this, the more labile palladium complexes formed in the reaction of PCA with *o*-phenanthroline or bipyridyl in solution in acetic acid using a concentration ratio $[Pd]_\Sigma:[L]_\Sigma \geqslant 1:1$ proved to be catalytically active.[64]

Studies on the reactions occurring between PCA and *o*-phenanthroline at different concentrations in solution in acetic acid led to the conclusion that the reactions in this system can be represented by the following scheme.[64]




The complexes of the (B) series, formed at comparatively high *o*-phenanthroline concentrations, lead at 25 °C to the stable cationic cluster $Pd_4Phen_4(CO)_2(OAc)_4$ with a tetrahedral metallic core (see above). The more labile series (A) complexes, formed at a concentration [Phen] $\leqslant 10^{-2}$ M are catalytically inactive so long as their composition includes even one coordinated CO molecule. The removal of the latter is achieved only in an $O_2$ atmosphere at $T \geqslant 90$ °C, which leads to the formation of a catalytically active substance whose elemental composition corresponds approximately to the formula $Pd_2(Phen)(OAc)_2$.[64]

A more exact chemical composition of the palladium-containing complex responsible for the catalytic activity in this system was not determined. Nevertheless the study of its catalytic properties permitted the conclusion that the catalytic reactions proceed in this instance without the involvement of divalent palladium. This is indicated by the following data:[67]

1. The reduction of palladium(+2) in acetic acid containing alkenes and toluene is sharply inhibited after the introduction of 0.1–0.5 M mol of *o*-phenanthroline, bipyridyl, or $PPh_3$ per mole of palladium. The addition of these ligands to a system based on PCA + Phen which has passed the catalyst formation stage [in accordance with scheme (A)] hardly affects the rate of the oxidative acetoxylation of propene and toluene even at an added ligand concentration exceeding by a factor of 2–5 the overall palladium concentration.

2. In the oxidation of propene in the catalytic system indicated, allyl acetate is formed in 100 ± 5% yield relative to the propene which has reacted and even traces of acetone, propenyl acetate, or isopropenyl acetate are absent; in the oxidation of toluene, there are no oxidative coupling and ring-acetoxylation products, only the products of the oxidative acetoxylation of the side chain being formed—benzyl acetate (⩾90%) and benzylidene diacetate (⩽10%).

3. The addition of 10–15% of water to a solution of the catalyst based on PCA + Phen does not lead to the appearance of acetaldehyde on oxidation of ethylene and acetone accompanying the oxidation of propene, which is not characteristic of catalytic systems based on palladium(+2).

4. When $Pd(OAc)_2$ is added to the catalytic system indicated, the selectivity of the oxidation of ethylene and toluene falls as a consequence of the formation of vinyl ethers and bitolyl respectively; acetone appears in the propene oxidation products.

Catalytic systems based on PCA + Phen (or Bipy, $PPh_3$) exhibit a comparatively high activity in the oxidative acetoxylation of ethylene, propene, and toluene under mild conditions (60–100 °C, 1 atm, 5–10 mol of the ester per mole of palladium per hour), which exceeds the activity of palladium black by a factor of 2–10. A deficiency of these catalytic systems is their low stability as a function of time: after continuous operation for 3–10 h at 60–90 °C, a deposit of palladium black is produced and the activity falls by a factor of 3–5.[64]

Apart from the oxidative acetoxylation reactions, the system based on PCA + Phen makes it possible to achieve the catalytic oxidative acetoxylation reaction. Thus, in solution in methanol propene is oxidised to allyl methyl ether:[86]

$$CH_2{=}CHMe + MeOH + {}^1/_2O_2 = CH_2{=}CHCH_2OMe + H_2O,$$

whereas isobutene is oxidised to methallyl methyl ether:

$$CH_2{=}CMe_2 + MeOH + {}^1/_2O_2 = CH_2{=}CMeCH_2OMe + H_2O.$$

Since catalytic activity is shown by products of the reaction of palladium(+1) carbonyl acetate not containing coordinated CO, it is useful to obtain a catalytically active palladium cluster by another procedure, bypassing the carbonyl complex formation stage.

It was observed[88] that solutions catalytically active in oxidative alkene acetoxylation reactions are formed when $Pd(OAc)_2$ is reduced in acetic acid containing *o*-phenanthroline, bipyridyl, and their analogues by various reductants, among which $H_2$ is the most convenient. The dependence of the catalytic activity on the overall content of the ligand L passes through a maximum in the region of ratios $[Pd]_\Sigma:[L]_\Sigma$ from 2:1 to 4:1.[63,88]

If it is postulated that the ratio $\{[Pd]_\Sigma:[L]_\Sigma\}_{max}$ indicates the composition of the compound responsible for the catalysis, one may conclude that the oxidation of alkenes is catalysed by ligand-deficient cluster compounds. In order to elucidate the nature of these compounds, their compositions and structures as well as the stoichiometry of the stages leading to the formation of catalytically active compounds were investigated.

The product of the reduction of palladium(+2) acetate by hydrogen in solution in acetic acid containing 0.5 mol of *o*-phenanthroline per palladium atom was isolated. It is an X-ray-amorphous substance whose composition corresponds to the very simple formula $Pd_4(Phen)(OAc)_2$.[89] It has been shown by volumetric measurements that 1.3 ± 0.05 mol of $H_2$ is consumed per mole of palladium(+2) in the formation of this substance, which could correspond to the following reaction stoichiometry:

$$4Pd_3(OAc)_6+3Phen+15H_2=3Pd_4Phen(OAc)_2H_4+6AcOH.$$

In order to confirm the conclusion that the complex is of the hydride type, its $^1H$ NMR spectra were investigated. In the range of chemical shifts δ = 0 to −80 p.p.m., no signals due to hydride atoms were detected in the high-resolution spectra (25 kHz frequency range) of solutions of the complex in $CD_3OD$, although a broad band with a maximum in the range δ = −30 to −50 p.p.m. (width 5 kHz) was found in the broad-band spectrum (250 kHz frequency range). Similar data have been obtained for the analogue of this complex containing bipyridyl instead of *o*-phenanthroline. The spectrum of the solid specimen, recorded with rotation at the "magic angle", contains three somewhat narrower (~2 kHz) bands in the range of δ from −35 to −50 p.p.m. These data confirm the hypothesis that the complexes obtained are of the hydride type.

The appreciable broadening of the hydride signal can be explained by the fact that the Pd atoms in these complexes form a polynuclear structure with a system of metal–metal bonds similar to that in the lattice of metallic palladium or its hydride phases. The protons of the $OCOCH_3$ groups are observed in the $^1H$ NMR spectrum as a narrow signal at δ = 2.0 p.p.m., while the signal of the *o*-phenanthroline protons consists of a complex unresolved multiplet in the range of δ from 6 to 9 p.p.m. The broadening of the usually resolved multiplet of the *o*-phenanthroline protons can be explained by the coordination of this ligand to the palladium atoms of the paramagnetic metallopolymer. This was confirmed by the weak temperature-independent paramagnetism found for the complex ($\chi_g^{300} = 0.5 \times 10^{-6}$ CGSU).[90]

The study of this complex by high-resolution transmission electron microscopy showed that its particles contain an approximately spherical metallic core 20 ± 5 Å in diameter.[89] The observed value agrees well with the average diameter of the particles obtained by the small angle X-ray scattering method (18 ± 5 Å).

The study of solid specimens of the hydrido-complex by the EXAFS method yielded the radial distribution curve for the atoms (RDA) on which there is one maximum corresponding to the Pd–N = 2.1 ± 0.1 Å interatomic distance and a signle peak corresponding to the Pd–Pd = 2.62 ± 0.05 Å distance. Maxima corresponding to more remote palladium atoms were not detected, which may be explained by the absence of long-range order in their arrangements as a consequence of the not completely regular incorporation of the H atoms in the core of the complex.[89]

The observed dimensions of the metallic core of the hydrido-complex molecule make it possible to estimate the value of *n* in the idealised formula $[Pd_4Phen(OAc)_2H_4]_n$ as approximately 100 on the assumption that the packing density of the palladium atoms in the core of this cluster is the same as in the metallic palladium lattice.

The chemical properties of the hydrido-complex indicate its high reactivity. Table 1 shows that treatment of the polynuclear hydrido-complex with various reagents leads as a rule to unstable products which decompose into mononuclear or oligonuclear palladium complexes. In contrast to this, the reaction with $O_2$ leads to the formation of clusters in which a massive metallic core is retained. These clusters proved to be effective catalysts of many oxidation reactions.

**Table 1. The principal palladium-containing products of the reaction of a polynuclear hydrido-complex with various reagents at 293 K.**

| Reagent | Solvent, reaction time | Reaction products |
|---|---|---|
| Hg | AcOH, 2 h | $H_2$, Pd amalgam |
| $PPh_3$ | DMF, 3 h | $H_2$, $Pd(PPh_3)_3$ |
| CO | RCOOH (R = Me, Et, t-Bu), 1–3 h | $[Pd_4Phen_3(CO)_3H_2(OCOR)_3]_n$* |
| NO | AcOH, 1 h | $Pd_4(NO)_2(OAc)_6$ |
| $H_2NCON(Me)NO$ | DMF, 24 h | $PdPhen(NCO)_2$ (Ref.92) |
| Tetrachloro-*o*-benzoquinone | DMF, 3 h | $(C_6O_2Cl_4)Pd(DmPhen)$** |
| $PhenH^+X$, where X = $BPh_4$, $PF_6$, $AsF_6$ | AcOH, 1–3 h | $PdPhen_2X$ |
| $O_2$ | AcOH, 10–30 min | $[Pd_9Phen(OAc)_3]_{60}$ |

*Polynuclear hydride complex with $n \simeq 2.3$.[93]

**DmPhen = 2,9-dimethyl-1,10-phenthroline was used instead of Phen in the synthesis of the hydrido-complex.

## VI. Giant palladium clusters

In the reaction with $O_2$ the polynuclear hydrido-complex loses the hydride atoms forming part of its composition, which are bound in $H_2O$. A small proportion of the palladium atoms are then oxidised to palladium(+2) complexes, while the main bulk of them are converted into a cluster type substance whose simplest formula is $Pd_9(Phen)(OAc)_3$ (I) and which is stable in air and is soluble, like the hydrido-complex, in water and polar organic solvents.[94]

### 1. The structure of giant palladium clusters

The rate of sedimentation of compound (I) in aqueous solution obtained with the aid of an ultracentrifuge made it possible to estimate the molecular weight as (1.0 ± 0.05) × $10^5$. More definite

information about the size of the molecules of compound (I) was obtained with the aid of the small angle X-ray diffraction method, high-resolution transmission electron microscopy, and electron diffraction.[90,91,94,95]

On the electron photomicrographs, the metallic cores of the molecules of compound (I) appear as almost regular spherical particles 26 ± 3.5 Å in diameter. The electron diffraction patterns, recorded for the same specimens of compound (I), contain 5–6 diffuse rings whose positions are close to those for metallic palladium.

The similarity between the sets of interplanar spacings for compound (I) and metallic palladium might indicate the identity of the principal parameters of the structures of the metallic core of compound (I) and the space-centred cubic lattice of metallic palladium. However, this hypothesis conflicts with EXAFS data, which definitely indicate eicosahedral packing of the palladium atoms in the molecules of compound (I) (see below). It is reasonable to postulate that the cause of the similarity between the electron diffraction patterns of compound (I) and metallic palladium is the degradation of the molecules of compound (I) leading to the formation of metallic particles on exposure to the electron beam.

The destructive effect of the electron beam on the cluster molecules was observed in electron microscope studies on the $Au_{55}(PPh_3)_{12}Cl_6$ [96,97] and $[Ni_{38}Pt_6(CO)_{48}H](Me_3NCH_2Ph)_5$ [98] clusters. As a result of the loss of ligands, the initial eicosahedral skeleton of the cluster can relax to a crystallite with a cubic face-centred lattice (for example in the form of a cubo-octahedron). It may be that similar processes occurred also in the electron microscope study of the recently synthesised platinum cluster $Pt_{309}L_{36}O_{30\pm10}$ (L = bis-sulphophenyl-1,10-phenanthroline) for which a cubo-octahedral structure of the cluster core was found by transmission electron microscopy.[99]

Apparently the conclusions about the structure of the clusters reached on the basis of electron microscope studies should be treated with much caution. However, if the agglomeration or breakdown of metallic particles are not observed in the course of the electron microscope study, as happened in the case of the palladium cluster, then electron diffraction patterns can be used for the independent estimation of the particle sizes.

The size of the particles responsible for diffraction, estimated from the half-widths of the diffraction rings, is approximately 25 Å for the cluster (I), which agrees with electron microscope and small angle X-ray diffraction data (Fig. 5):

| Method | $d$, Å |
|---|---|
| Electron microscopy | 26±3.5 |
| Electron diffraction | 25 |
| Small angle X-ray diffraction | 20 |

The small angle X-ray diffraction data also indicate the virtually unimodal nature of the size distribution of the particles.

The packing of the palladium atoms in the metallic core of compound (I) was determined with the aid of EXAFS spectra.[94] The RDA curve obtained on the basis of these spectra has a peak which corresponds to a Pd–O (or Pd–N) distance of 2.1 ± 0.1 Å. Four intense peaks correspond to the shortest Pd–Pd distances (Table 2). The observed set of interatomic Pd–Pd distances agrees best with the eicosahedral packing of the palladium atoms in the metallic core of the cluster (I) (the expected interatomic distances between the nearest neighbouring atoms in the eicosahedron are in the proportions 1:1.2:1.4:1.6) and differs appreciably from the expected set of distances for the face-centred cubic and hexagonal close packing.

The average atomic volume of palladium in the eicosahedral metallic core of compound (I), calculated using the interatomic distances from Table 2, is approximately 16 Å$^3$, which exceeds only slightly the atomic volume for metallic palladium (14.7 Å$^3$). This result rules out the possibility of the coordination of the Phen and OAc ligands to the inner palladium atoms in the cluster. Consequently the Phen and OAc groups are arranged on the periphery of the metallic core of the cluster (I).

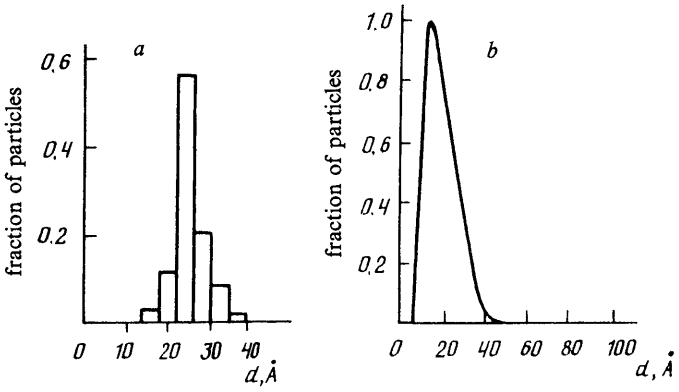



**Figure 5.** The size distribution of the metallic cores of the giant clusters (I) according to electron microscope (*a*) and small angle X-ray diffraction (*b*) data.

**Table 2.** Experimental (based on EXAFS data) shortest interatomic Pd–Pd distances in the metallic core of the cluster (I) and the values expected for different types of packing.

| Type of data | Pd–Pd distance, Å | | | | |
|---|---|---|---|---|---|
| Experimental | 2.60±0.004 | 3.10±0.1 | 3.66±0.1 | 4.08±0.1 | |
| Calculated for different types of packing: | | | | | |
| face-centred cubic | 2.60 | | 3.66 | | |
| hexagonal | 2.60 | | 3.66 | | 4.50 |
| eicosahedral | 2.60 | 3.10 | 3.66 | 4.10 | |

Note. The smallest of the shortest distances was assumed to be 2.60 Å in the calculations for all types of packing.

Knowing the nature of the packing of the palladium atoms and the distances between the nearest neighbouring palladium atoms, it is possible to estimate the number of palladium atoms in the cluster molecule. For a sphere approximately 25 Å in diameter, this number $N_\Sigma$ approximately equals 570. On the basis of this value and the chemical composition obtained from the results of elemental analysis, the molecule of compound (I) can be represented approximately by the formula $Pd_{570\pm30}Phen_{63\pm3}(OAc)_{190\pm10}$. The molecular weight corresponding to this formula ($N$ = 83 200) agrees with the result of the direct determination from the rate of sedimentation from aqueous solution.

The observed value $n = 570$ agrees well with the value of $N_\Sigma$ for the idealised model comprising a 5-layer eicosahedron containing 561 metal atoms in conformity with the formula

$$N_\Sigma = {}^1/_3(10m^3+15m^2+11m+3) = 561 \quad [100],$$

where $m$ is the number of eicosahedral layers ($m = 5$). Taking into account the chemical composition, the idealised formula $Pd_{561}Phen_{60}(OAc)_{180}$ was proposed for the eicosahedral cluster (I). This idealised formula apparently corresponds to the average size and composition of the cluster and not to definite fixed dimensions and chemical composition. In other words, the distribution of the particles of compound (I) about an average size $d \simeq 25$ Å and the idealised composition $Pd_{561}Phen_{60}(OAc)_{180}$.

This situation resembles to some extent organic polymers in which different molecules contain different numbers of monomeric units. Bearing in mind that the average Pd–Pd bond energy is fairly small (40–60 kJ mol$^{-1}$), one may expect that such giant clusters have certain defects ("apices", "niches", etc.) which are difficult to detect by electron microscopy.

Analysis of molecular models showed that the Phen ligands coordinated as bidentate species can be coordinated only at the apices and edges of the eicosahedron because of the steric hindrance generated by the H atoms in the 2- and 2'-positions in the *o*-phenanthroline molecule. As a result of this, out of the 252 metal atoms in the outer layer of the idealised eicosahedron only about 60 can be linked to the *o*-phenanthroline ligands involved in the bidentate coordination. The complete formal charge on the metallic core together with the electrically neutral Phen ligands is 180+ and is balanced by 180 anionic $OAc^-$ ligands.

In this arrangement, almost the entire surface of the metallic core is sterically shielded by the bulky *o*-phenanthroline groups. The acetate anions can therefore be arranged only in the outer sphere of the cluster cation (I) (Fig. 6). We may note that a similar outer-sphere disposition of acetate anions was observed by X-ray diffraction in the tetranuclear cluster $[Pd_4Phen_4(CO)_2](OAc)_4$ [34] (Fig. 4).

The conclusion that the ligands $OAc^-$ are involved in outer-sphere coordination was also confirmed by IR spectroscopic data [the frequency difference is $\nu_{as}(OCO)-\nu_s(OCO) = 165$ cm$^{-1}$, as in solid $CH_3COONa$] and $^1H$ NMR data (the line due to the protons of the $OAc^-$ groups is observed as a narrow singlet at $\delta = 2.0$ p.p.m., in contrast to the appreciably broadened Phen multiplet).

The cluster (I) can be precipitated from aqueous solution by adding salts such as NaX or KX ($X^- = Cl^-$, $Br^-$, $ClO_4^-$, $HSO_4^-$, $PF_6^-$, $AsF_6^-$) with substitution of the $OAc^-$ anions by $X^-$. Treatment of compound (I) with the salt $KPF_6$ yielded a cluster with the idealised formula $Pd_{561}Phen_{60}O_{60}(PF_6)_{60}$ (II), which is soluble in acetonitrile.[90,91]

Electron microscope data showed[91] that the metallic core of this cluster is almost spherical and has a diameter of 28 ± 5 Å, which agrees with small angle scattering data.

The results of chemical analysis and the stoichiometry of the conversion of the cluster (I) into (II) showed that the substitution of the outer-sphere $OAc^-$ ligands in aqueous solution is accompanied by the partial hydrolysis of the cluster, as a result of which only 60 out of the 180 $OAc^-$ anions are substituted by the $PF_6^-$ anions, while the remaining 120 $OAc^-$ anions are substituted by $O^{2-}$:[90]

$$Pd_{561}Phen_{60}(OAc)_{180}+60\,PF_6^-+60\,H_2O = Pd_{561}Phen_{60}(PF_6)_{60}O_{60}+ +120\,AcOH+60\,AcO^-.$$

Molecular clusters containing between 4 and 38 palladium atoms are known to be diamagnetic.[85,101] In contrast to this, the clusters (I) and (II), containing several hundreds of palladium atoms in the metallic core, possess metal-like properties, such as temperature-independent paramagnetism. The specific magnetic susceptibility at 300 K [$\chi_g^{300} = 1.0 \times 10^{-6}$ CGSU for (I) and $0.8 \times 10^{-6}$ CGSU for (II)[90]] is close to that for metallic palladium particles deposited on $SiO_2$ [degree of dispersion 0.2–0.5; $\chi_g^{300} = (0.8 \pm 0.2) \times 10^{-6}$ CGSU[102]].

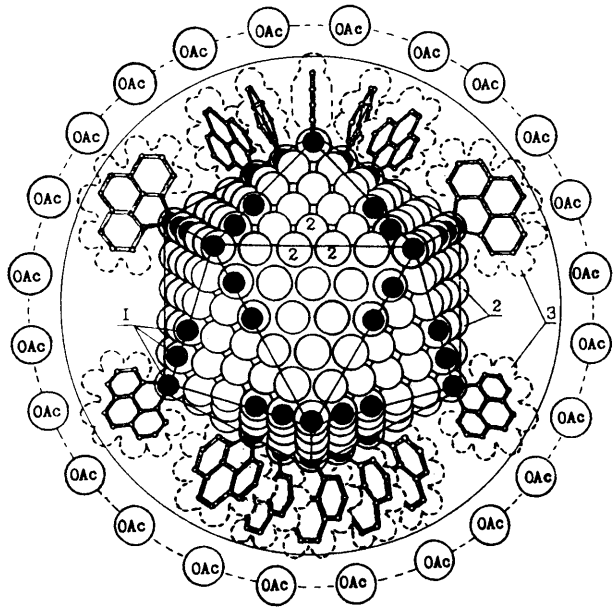



**Figure 6. Idealised model of the giant cluster (I): *1*, palladium atoms coordinated to the phenanthroline ligand; *2*, palladium atoms available for coordination to the $OAc^-$ anions or substrate molecules; *3*, van der Waals limits of the coordinated phenanthroline molecules.**

The metallic core of the cluster (II) was also investigated by the EXAFS method.[90] The RDA curve for freshly prepared specimens of the cluster indicates the presence of Pd–Pd distances characteristic of both eicosahedral and cubo-octahedral cores. However, 30–100 days after the preparation of the specimen, only the peaks corresponding to a face-centred cubic lattice (cubo-octahedron) remain on the RDA curve. Similar changes in the structure of the metallic core were observed also after the replacement of the outer-sphere $OAc^-$ anions by the $BF_4^-$, $HSO_4^-$, $ClO_4^-$, etc. anions. These data indicate the ease with which the eicosahedral packing of the metal atoms in the skeleton of the giant cluster relaxes to the cubo-octahedral packing as a result of the substitution of the ligands and standing for a long time even at room temperature.

Analysis of our molecular models showed that 60 oxygen atoms can be accommodated as bridging groups between the surface palladium atoms of the metallic core on the faces of a cubo-octahedron with a diameter of 28 Å without steric hindrance due to the 60 coordinated *o*-phenanthroline molecules.

The possibility of the coordination of oxygen atoms to the surface atoms of the metallic core in giant clusters was recently confirmed by the synthesis of a platinum cluster with the idealised formula $Pt_{309}L_{36}O_{30\pm10}$ (L = bis-sulphophenylphenanthroline),[99] which was obtained by the same method as the cluster (II) using platinum(+2) acetate instead of palladium(+2) acetate and a phenanthroline derivative in the form of the sodium salt of the corresponding sulphonic acid (see above). In the case of palladium, these investigators obtained a giant cluster with 561 palladium atoms in the idealised formula and a somewhat different composition of the coordination shell.[103]

The giant clusters obtained apparently serve as a bridge between the usual molecular clusters and colloidal metals. The size of the metallic core in giant clusters exceeds appreciably the size of the usual molecular clusters such as $Pd_{38}(CO)_{28}(PEt_3)_{12}$ [101] and $Au_{55}(PPh_3)_{12}Cl_6$,[104] approaching the lower limit of the sizes of colloidal metal particles. In contrast to the latter, giant clusters have a distinct ligand environment with a definite stoichiometry of the type characteristic of molecular clusters. However, in both cases when the number of metal atoms approaches several hundreds, a set of more or less imperfect metallopolyhedra is formed with a certain distribution with respect to size and chemical composition.

In principle, the metallic cores of such clusters need not necessarily contain the "magic number" of metal atoms.[100,105] Nevertheless large and giant clusters with metallic cores in the form of two-layer ($M_{55}$),[96] four-layer ($M_{309}$),[99] and five-layer ($M_{561}$)[91] 12-vertex particles are now known.

Since the relaxation energy of the close packing is extremely small, such metallopolyhedra can readily undergo interconversions and, depending on the ligand environment, temperature, and other factors, can be stabilised as isomeric cubo-octahedra, eicosahedra, and anticubo-octahedra.[105] The solution of the problem of their true geometry requires the application of experimental methods, for example EXAFS, which do not have a destructive or some other strong effect on the substance.

The use of idealised formulae based on data obtained by the above methods is useful for the construction of models characterising the average size and composition of the giant clusters and suitable for the examination of their catalytic properties.

## 2. Catalytic properties of the giant clusters (I) and (II)

**(a) Oxidative acetoxylation.** In the presence of acetic acid in solutions of the clusters (I) and (II), oxidative acetoxylation reactions take place, involving the conversion of ethylene into vinyl acetate:

$$C_2H_4+{}^1/_2O_2+AcOH = CH_2{=}CHOAc+H_2O,$$

of propene into allyl acetate:

$$C_3H_6+{}^1/_2O_2+AcOH = CH_2{=}CHCH_2OAc+H_2O,$$

and of toluene into benzyl acetate:

$$PhCH_3+{}^1/_2O_2+AcOH = PhCH_2OAc+H_2O.$$

Their selectivity is 95–98%.[91] The only side reaction observed in the presence of these catalysts is further oxidation of the alkenyl and benzyl esters, as they accumulate, to ethylidene, allylidene, and benzylidene acetates respectively. Compared with metallic palladium catalysts, whose activity is manifested at higher temperatures,[106,107] the clusters (I) and (II) facilitate side reactions to a lesser extent.

**(b) Oxidation of alcohols.** The clusters (I) and (II) effectively catalyse the oxidation by molecular $O_2$ of primary aliphatic alcohols to esters in which the alcoholic and acid components have the same carbon skeleton as the initial alcohol:[108]

$$2RCH_2OH+O_2 = RCOOCH_2R+2H_2O.$$

Together with esters, the oxidation of primary alcohols leads to the formation of the aldehydes and the corresponding acetals (Table 3).

Secondary alcohols are smoothly oxidised to ketones:

$$(CH_3)_2CHOH+{}^1/_2O_2 = (CH_3)_2CO+H_2O.$$

**Table 3. Oxidation of alcohols by oxygen (1 atm) in the presence of the cluster (II) (suspension of 0.1 g of the cluster in 2.5 ml of the alcohol).**

| Alcohol | Temperature, °C | $10^3 W_0$, mol litre$^{-1}$ h$^{-1}$ | Composition of products | Yield, % |
|---|---|---|---|---|
| $C_2H_5OH$ | 60 | 2.3 | $CH_3COOC_2H_5$ | 27 |
| | | | $CH_3CH(OC_2H_5)_2$ | 55 |
| | | | $CH_3CHO$ | 18 |
| n-$C_3H_7OH$ | 60 | 2.0 | $C_2H_5COOC_3H_7$ | 7 |
| | | | $C_2H_5CH(OC_3H_7)_2$ | 16 |
| | | | $C_2H_5CHO$ | 77 |
| iso-$C_3H_7OH$ | 20 | 2.1 | $(CH_3)_2CO$ | 100 |
| n-$C_4H_9OH$ | 60 | 1.3 | $C_3H_7COOC_4H_9$ | 59 |
| | | | $C_3H_7CH(OC_4H_9)_2$ | 38 |
| | | | $C_3H_7CHO$ | 3 |

**(c) The formation of acetals from carbonyl compounds and alcohols.** Presumably the oxidation of primary alcohols proceeds via the intermediate formation of aldehydes. This hypothesis is supported by the finding that, in the absence of $O_2$, acetaldehyde introduced into an alcoholic suspension of a cluster (II) is converted into the acetal:[109]

$$CH_3CHO+2EtOH = CH_3CH(OEt)_2+H_2O.$$

This reaction is of a general character and is catalysed not only by the clusters (I) and (II) but also by different types of palladium black.

**(d) Oxidation of formic acid.** The gas-phase decomposition of HCOOH into $CO_2$ and $H_2$ takes place at an appreciable rate on deposited palladium catalysts even at 50 °C.[110] The clusters (I) and (II) as well as palladium black catalyse the decomposition of HCOOH in the gas phase in the absence of $O_2$ at 50 °C. However, in the liquid phase at the same temperature the decomposition of HCOOH is not observed. In the presence of $O_2$ in solutions containing the clusters (I) and (II), formic acid is oxidised at 20–70 °C:[111]

$$HCOOH+{}^1/_2O_2 = CO_2+H_2O.$$

In solutions of the clusters (I) and (II) in acetonitrile, the reaction kinetics are described by an equation of the Michaelis–Menten type:

$$W = k[\text{Clust}][\text{HCOOH}]\frac{[O_2]}{K + [O_2]}.$$

The observed isotope kinetic effects $k_{HCOOH}/k_{HCOOD} = 1.1 \pm 0.1$ and $k_{HCOOH}/k_{DCOOD} = 1.0 \pm 0.1$ show that the C–H and O–H bonds are not ruptured in either the rate-limiting or the preceding stages. A reaction mechanism was proposed on the basis of these data[111] in which the rate-limiting stage is the coordination of the undissociated HCOOH molecule to the palladium atoms on the surface of the metallic core. The subsequent stages—the dissociation of the coordinated HCOOH, the transfer of an H atom to the coordinated $O_2$, and the removal of the products from the surface of the metallic core of the cluster—are rapid and are not reflected in the reaction kinetics.

Thus giant palladium clusters exhibit a varied catalytic activity in both oxidation reactions and in the reactions which traditionally belong to the field of acid–basis catalysis. The mechanism of these reactions has been studied in greatest detail in relation to the oxidative acetoxylation of ethylene and propene.

## VII. Kinetics and mechanisms of oxidation reactions in solutions of giant palladium clusters

The kinetics of the oxidation of ethylene in solutions of the cluster (II) in acetic acid–acetonitrile mixtures obey the following kinetic equation:[112]

$$r_0 = k[\text{Clust}]\frac{[C_2H_4]\cdot[O_2]\cdot[\text{AcOH}]}{(K_I + [C_2H_4])(K_{II} + [O_2])(K_{III} + [\text{AcOH}])},$$

where $r_0$ is the rate of formation of vinyl acetate from ethylene and $K_I$, $K_{II}$, and $K_{III}$ are Michaelis constants.

The rate of accumulation of allyl acetate in the oxidation of propene in solutions of the clusters (I) and (II) is also directly proportional to the cluster concentration. In contrast to ethylene, deviations from linearity are not observed in the relation between $r_0$ and the propene concentration. However, when the $O_2$ concentration is varied, the rate of reaction changes in a more complex manner than was observed in the oxidation of ethylene. At a propene partial pressure greater than 0.9 atm, this variation is represented by a curve with a plateau, but, as the propene partial pressure is reduced to 0.5 atm, a maximum characteristic of the inhibition of the reaction by the initial reactant (in the given case oxygen) appears on the $r_0 = f(P_{O_2})$ curve. For $P_{C_3H_6} > 0.7$ atm, i.e. under conditions where the reaction is not inhibited by oxygen, the rate is described by an equation analogous to the kinetic equation for ethylene with the sole difference that the Michaelis constant for propene is much greater than that for ethylene (Table 4).[113] Comparison shows that the rate constants for the oxidation of ethylene and propene in the presence of both clusters differ by less than a factor of three. The range of variation of the Michaelis constants $K_{II}$ and $K_{III}$ on passing from one alkene to another and on replacing the cluster (I) by (II) is also not very great.

The greatest difference between the kinetic characteristics of the ethylene and propene oxidation reactions involves the appreciable alteration of the constant $K_I$.

The Michaelis nature of the kinetics of these reactions suggests that the oxidation-reduction reactions are preceded by stages involving the reversible coordination of the alkene, $O_2$, and AcOH to the cluster and that propene is coordinated much more weakly than ethylene, $O_2$, and AcOH.

In homogeneous alkene oxidation reactions with participation of mononuclear and dinuclear palladium(+2) complexes, the oxidation product is formed in the absence of $O_2$ in stoichiometric amounts relative to the palladium(+2) which has reacted. In contrast to this, in solutions of the clusters (I) and (II) the oxidation of alkenes in the absence of $O_2$ is not observed. This fact also indicates that the reactions of ethylene and propene in solutions of giant clusters cannot be explained by the alternation of oxidation-reduction reactions of the cluster with the substrate and the oxidant. The lower formation constants of the π-complexes of propene compared with ethylene can be accounted for by the greater size of the molecule of this substrate.

**Table 4.** Constants of the kinetic equation for the oxidation of ethylene and propene in solutions of the clusters (I) and (II) at 60 °C.

| Substrate | Cluster | $k$, $min^{-1}$ | $K$, mol $litre^{-1}$ | | |
|---|---|---|---|---|---|
| | | | $10^3 K_I$ | $10^4 K_{II}$ | $K_{III}$ |
| Ethylene | (II) | 8.2±0.7 | 5.8±0.3 | 3.0±0.2 | 1.3±0.1 |
| Propene | (I) | 3.3±0.3 | 30 | 5.2±0.3 | 0.67±0.05 |
| Propene | (II) | 5.6±0.5 | 30 | 1.2±0.1 | 4.8±0.5 |

Indeed, the surface of the metallic core of the cluster is sterically blocked by the bulky phenanthroline ligands. Analysis of the idealised molecular model showed that, on the surface of the metallic core of the cluster (I), there are approximately 20 palladium atoms sterically available for the coordination of the solvent or reactant molecules. However, the smaller $C_2H_4$ molecules are presumably coordinated more strongly at these sites than the $C_3H_6$ molecules whose steric requirements are more stringent. For the real molecules of a giant cluster, which probably differ to a greater or lesser extent from an ideal polyhedron, the number of accessible sites differs from that for the idealised model. This number can be determined experimentally by introducing into the solution of the cluster some kind of ligand (catalytic poison) which is strongly bound to the accessible palladium atoms on the surface of the metallic core. The results obtained for the influence of different poisons (Fig. 7) showed that ligands which are bulky ($PPh_3$, phenanthroline) but are effectively coordinated to palladium hardly affect the rate of oxidation of alkenes, since they do not apparently find on the surface of the cluster sites available for their coordination. Smaller ligands (mercaptans, thiocyanate, etc.) effectively block the cluster.

A similar picture has been observed also for the HCOOH oxidation reaction.[111] The complete inhibition of the ethylene oxidation reaction requires the blocking of approximately 50 palladium atoms, whereas for propene it is sufficient to bind only 15 metal atoms in the cluster to the poison ligand for the cluster to lose its catalytic activity.[112,113] These data confirm the above hypothesis that the steric factor plays a decisive role in the formation of complexes between the substrate and the cluster.

Oxidative alkene acetoxylation reactions reduce to the dissociation of the C–H bonds in the initial alkene and the substitution of the H atom by the OAc group. The kinetic data obtained have shown, however, that in solutions of the giant clusters both reactions take place at similar rates despite the considerable differences between the strengths of the C–H bonds in ethylene (the strength of the vinyl–H bond is 106 ± 2 kcal) and in propene (the strength of the allyl–H bond is 86.2 ± 2 kcal) (see Ref. 114, p. 39). This finding shows that, despite the common form of the kinetic equation, the rate-limiting states in the ethylene and propene reactions are significantly different. This hypothesis is supported by the kinetic isotope effects obtained (Table 5).[91]

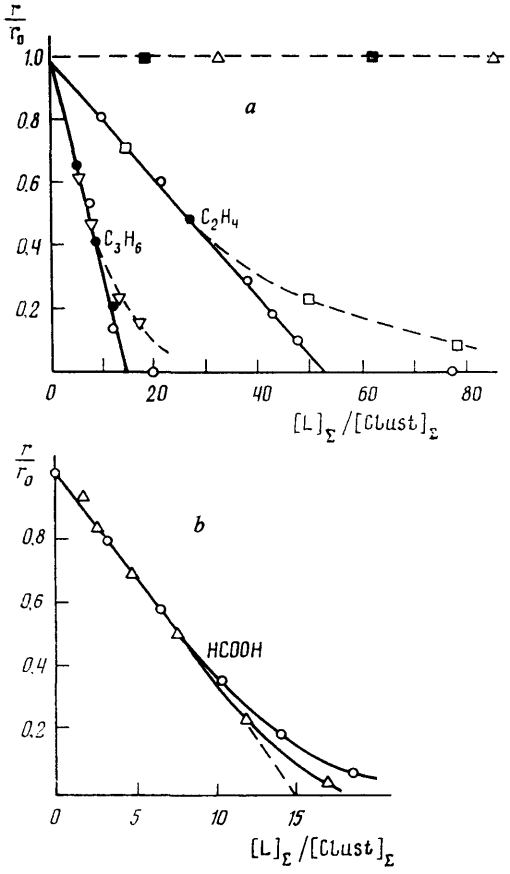
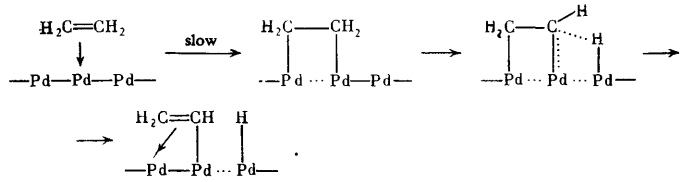



**Figure 7.** Dependence of the relative rates of oxidation of alkenes (*a*) and formic acid (*b*) by oxygen in solutions of the giant cluster (II) on the concentration of ligand-inhibitors: *a*, ○—$(C_2H_5)_2NCS_2Na$; ●—$C_2H_5SH$; ▽—$I_2$; □—KSCN; Δ—Phen; ■—$PPh_3$. *b*, ○—NaSCN; Δ—$(C_2H_5)_2NCS_2Na$.

In the ethylene molecule, the C=C π-bond is weakest (~60 kcal). The data in Table 5 are consistent with the fact that hydrogen atoms are transferred from the coordinated $C_2H_4$ and $CH_3COOH$ molecules in rapid stages following the rate-limiting stage. The closeness of the isotope effect H/D for ethylene to unity can be explained by the fact that in the slow stage the π-coordinated $C_2H_4$ molecule undergoes oxidative addition (with opening of the C=C π-bond) to the Pd–Pd group of the cluster with formation of the σ,σ-coordinated group...Pd–$CH_2CH_2$–Pd...:

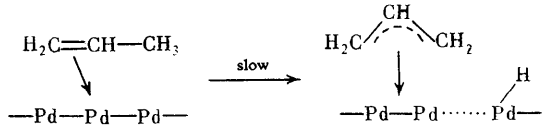



One cannot rule out the possibility that the subsequent dissociation of the C–H bond in this group is facilitated because of the possibility of the formation of a Pd–C multiple bond in the transition state.[115]

Analogous forms of adsorption had been postulated earlier for the hydrogenation and dehydrogenation of ethylene and the H/D exchange involving it on the surfaces of metallic catalysts.[116] Reliable evidence for the formation of σ,σ-coordinated ethylene and a π,σ-coordinated vinyl group on the surface of Pd(100) was obtained recently by means of a combination of thermoprogrammed reaction spectroscopy (TPRS) and high-resolution electron energy loss spectroscopy (HREELS).[117]

The intermediate formation of σ-bound organopalladium compounds $XPdCH_2CH_2OR$ had been established earlier in reactions involving the oxidation of ethylene by palladium(+2) salts.[118] In the case of the giant clusters (I) and (II), the palladium atoms at the metallic core of the cluster in an oxidation state close to zero participate in the reaction; as a result of the formation of the σ,σ-complex, the formal oxidation state of each of these atoms increases by unity, returning to the initial oxidation state after the completion of the catalytic cycle.

In the case of propene, the difference between the strengths of the π-C=C and allyl–H bonds is much smaller than the difference between the energies of the π-C=C and vinyl–H bonds in ethylene. The insertion of propene in the Pd–Pd bond of the cluster with dissociation of the allyl–H bond probably leads to a π-allyl complex and a coordinated hydride:



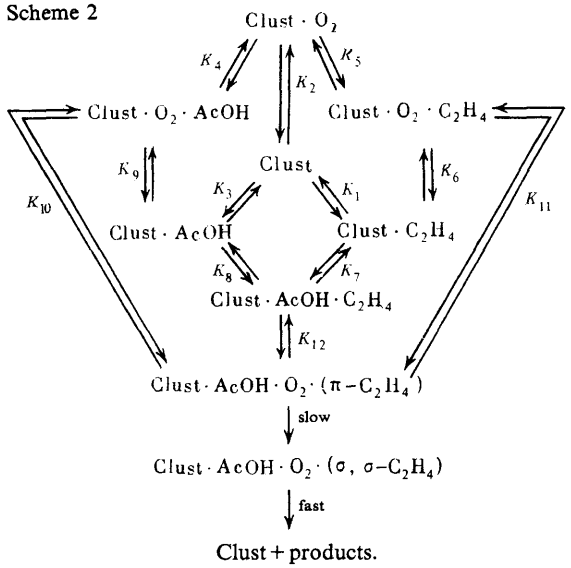

The stabilisation of the π-allyl complex as a result of the formation of a surface π-allyl group probably favours the situation where the competition between the vinyl and allyl reaction pathways is won by the latter and the oxidative acetoxylation of propene on clusters (I) and (II) proceeds only via the allyl pathway. The experimental kinetic isotope effects are consistent with the scheme (Table 5).

**Table 5.** Kinetic isotope effects in the oxidation of ethylene and propene by oxygen in solutions of the clusters (I) and (II) at 60 °C.

| Substrate | Cluster | $k_{C_nH_{2n}}/k_{C_nD_{2n}}$ | $k_{CH_3COOH}/k_{CD_3COOD}$ |
|---|---|---|---|
| Ethylene | (II) | 1.1±0.1 | 1.1±0.1 |
| Propene | (I) | 2.2±0.2 | 1.0±0.05 |
| Propene | (II) | 3.6±0.2 | 1.0±0.05 |

The subsequent reactions of the coordinated vinyl and allyl groups and H atoms on the surface of the metallic core of the cluster are apparently rapid and are not reflected in the rates of the overall reactions (see Scheme 2).

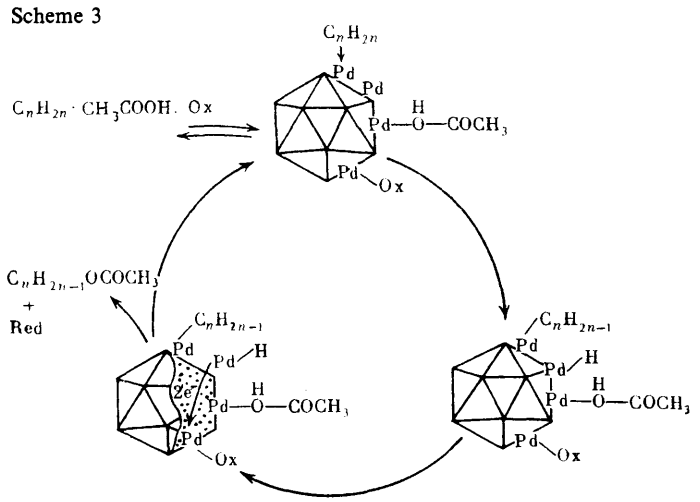
Scheme 2




The data for the inhibition of the alkene and HCOOH oxidation reactions by ligands[91,111] showed that only about 20% of the surface palladium atoms are accessible to the reactant molecules in the oxidation of ethylene and only about 5–6% of the total number of these atoms are accessible in the oxidation of propene and formic acid. It is unlikely that on the surface of the metallic core of the cluster shielded to such an extent all three molecules—$O_2$, the substrate undergoing oxidation, and AcOH—would be coordinated to neighbouring palladium atoms of the same section of the cluster. Apparently there are better grounds for the expectation that the alkene or HCOOH molecule is bound to one section of the cluster, the $O_2$ molecule is coordinated to another, not necessarily neighbouring, section, and electron transfer from the Pd–alkenyl, Pd–formyl, or Pd–H fragment to the coordinated $O_2$ molecule proceeds via the metallic core of the cluster, which plays the role of an "electronic mediator".[31]

The overall reaction scheme can be represented as follows:

Scheme 3




Not only $O_2$ but also palladium(+2) salts can function as electron acceptors in cluster catalytic systems. Thus propene is oxidised to allyl acetate in the stoichiometric reaction of $C_3H_6$ with $Pd(OCOCH_3)_2$ in $CH_3COOH$. The particles of dispersed metallic palladium, formed in the initial period of this reaction, can then play the role of the cluster catalysing the allyl oxidation of propene.[119] This approach makes it possible to explain the previously observed[68,120] change in the selectivity of the reaction of palladium(+2) with propene in acetic acid. For a comparatively small change in conditions (temperature, AcONa concentration, $H_2O$, added oxidants), the yield of allyl acetate varies from 4 to approximately 90%.

In the presence of the clusters (I) and (II), benzoyl peroxide can also serve as the electron acceptor. Thus in solution in acetic acid containing the clusters (I) and (II), the reaction

$$C_3H_6 + (C_6H_5COO)_2 + CH_3COOH = CH_2{=}CHCH_2OCOCH_3 + 2C_6H_5COOH,$$

takes place at 20 °C with a selectivity of 98–100% with respect to allyl acetate.[121]

Although outwardly this reaction looks like peroxide oxidation, it proceeds fundamentally via the same mechanism as the oxidation by oxygen or palladium(+2) on clusters, in the absence of which the reaction does not occur under the conditions indicated.

## VIII. Conclusion

Thirty years ago, the oxidative metal complex catalysis was represented by mainly free-radical processes. Against the background of this extensive class of reactions, the molecular oxidation of alkenes in solutions of palladium salts, where the unsaturated substrate encounters neither oxygen nor its partial reduction products, appeared to be a glaring exception. Nowadays oxidation reactions without the participation of free radicals occupy a due place both in the arsenal of industrial chemistry and in laboratory practice.

The field of molecular oxidative catalysis has been continuously developing. Together with complexes containing metal atoms in stable oxidation states, cluster compounds containing metal atoms in unusual oxidation states begin to be used in catalytic practice. The application of metal complexes made it possible to generate singlet oxygen and ozone from hydrogen peroxide. The coordination compounds responsible for these reactions contain ligands in which the oxygen atoms have unusually low fractional oxidation states. Apparently, as metal complex catalysis develops, chemists will encounter increasingly new examples of unusual oxidation states of both the central atoms and the ligand atoms. We suggest that the advances in metal complex catalysis and in coordination chemistry are in many respects inter-related and depend on the interaction of these two branches of chemical science.

## References


1. I I Moiseev *Khim. Prom.*, 1985, (4) 226
2. J T Bakvall *Acc. Chem. Res.*, 1983, **16** 325
3. R A Sheldon, J K Kochi *Metal-Catalyzed Oxidations of Organic Compounds*, Acad. Press, New York, 1981, 423 pp.
4. V G Dryuk *Usp. Khim.*, 1985, **54**(10) 1674 [English translation in *Russ. Chem. Rev.*, 1985(10)]
5. N M Emanuel', E T Denisov, Z K Maizus *Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze* (Chain Oxidation Reactions of Hydrocarbons in the Liquid Phase), Izd. Nauka, Moscow, 1965, 375 pp.
6. C Walling *Acc. Chem. Res.*, 1975, **8** 125
7. D Mansuy *Biochemie*, 1978, **60** 969
8. A B Solov'eva, E I Karakozova, K A Bogdanova, et al. *Dokl. Akad. Nauk SSSR*, 1983, **269** 160; *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2327
9. J T Groves, T E Nemo, R S Meyers *J. Am. Chem. Soc.*, 1979, **101** 1032
10. J P Collman, J I Brauman, B Meunier, et al. *Proc. Natl. Acad. Sci. USA*, **81** 3245
11. J P Renaud, P Battioni, J F Bortoli, D Mansuy *J. Chem. Soc., Chem. Commun.*, 1985, 888
12. L S Yuan, T S Bruice *J. Chem. Soc., Chem. Commun.*, 1985, 868
13. T L Sidall, N Miyara, J C Hoffman, J K Kochi *J. Chem. Soc., Chem. Commun.*, 1983, 1185
14. C C Franklin, R B van Atta, A Fan Tai, J S Valentine *J. Am. Chem. Soc.*, 1984, **106** 814
15. M Fontecave, D Mansuy *J. Chem. Soc., Chem. Commun.*, 1984, 879
16. I P Skibida *Usp. Khim.*, 1985, **54**(10) 1487 [English translation in *Russ. Chem. Rev.*, 1985(10)]
17. E P Talsi, V P Babenko, V A Likholobov, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 1768
18. J T Groves, R Quinn *J. Am. Chem. Soc.*, 1985, **107** 5790
19. G A Tolstikov *Reaktsii Gidroperekisnogo Okisleniya* (Hydroperoxide Oxidation Reactions), Izd. Nauka, Moscow, 1976, 250 pp.
20. I I Moiseev *π-Kompleksy v Zhidkofazmom Okislenii Olefinov* (π-Complexes in the Liquid-Phase Oxidation of Olefins), Izd. Nauka, Moscow, 1970, 326 pp.
21. V A Gavrilenko, E I Evzerikhin, V A Kolosov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1954
22. V A Gavrilenko, E I Evzerikhin, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975; 1977, 2934
23. V A Gavrilenko, E I Evzerikhin, I I Moiseev, I Sh Fish *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1746
24. A O Chong, K B Sharpless *J. Org. Chem.*, 1977, **42** 1587
25. R S Michaelson, R E Palermo, K B Sherpless *J. Am. Chem. Soc.*, 1977, **99** 1990
26. C Dudley, G Read *Tetrahedron Lett.*, 1972, 5273
27. A B Pshenichnikova, Candidate's Thesis in Chemical Sciences, Lomonosov Moscow Institute of Fine Chemical Engineering, Moscow, 1985
28. A B Svetlova, S M Brailovskii, O N Temkin *Kinet. Katal.*, 1978, **19** 1588
29. V A Likholobov, Yu I Ermakov *Kinet. Katal.*, 1976, **17** 123, 133
30. N I Kuznetsova, V A Likholobov, Yu I Ermakov *Kinet. Katal.*, 1981, **22** 157
31. K B Yatsimirskii *Ukr. Khim. Zh.*, 1963, **29** 889
32. I I Moiseev, V A Bochkareva, A E Gekhman, et al. *Dokl. Akad. Nauk SSSR*, 1977, **233** 375
33. A E Gekhman, V M Nekipelov, S G Sakharov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1242
34. J H Baxendale *Catalysis—Investigation of Homogeneous Processes* (Translated into Russian), Inostr. Lit., Moscow, 1957, 155 pp.
35. A P Makarov, A E Gekhman, O Ya Polotnyuk, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 765; 1985, 1899
36. G Read, P J C Walker *J. Chem. Soc., Dalton Trans.*, 1977, 883
37. Y Hayashi, S Shioi, T Sakan *Chem. Lett.*, 1973, 651
38. A E Gekhman, A P Makarov, V N Nekipelov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1686
39. A E Gekhman, N I Moiseeva, E A Blyumberg, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2653
40. A E Gekhman, A P Makarov, V M Nekipelov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1914
41. I I Moiseev, A E Gekhman, D I Shishkin *New. J. Chem.*, 1989, **13** 683
42. D I Shishkin, A E Gekhman, I I Moiseev *Kinet. Katal.*, 1989, **30** 1513
43. N I Moiseeva, A E Gekhman, E A Blyumberg, I I Moiseev *Kinet. Katal.*, 1988, **29** 534
44. N I Moiseeva, A E Gekhman, S G Sakharov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2396
45. N I Moiseeva, A E Gekhman, S G Sakharov, et al. *Dokl. Akad. Nauk SSSR*, 1989, **304** 118
46. N I Moiseeva, A E Gekhman, E S Rumyan'tsev, et al. *Dokl. Akad. Nauk SSSR*, 1989, **309** 1136
47. A E Gekhman, N I Moiseeva, D I Shishkin, et al. *XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii: Referaty Dokladov i Soobshchenii. Tashkent* (The XIth Mendeleev Congress on General and Applied Chemistry: Abstracts of Reports and Communications. Tashkent), Tashkent, 1989, Vol. 1, p. 62
48. I I Moiseev, A E Gekhman, N I Moiseeva, D I Shishkin *Trudy I Sovetsko-Kitaiskogo Seminara po Katalizu. Novosibirsk* (Proceedings of the Ist Soviet-Chinese Seminar on Catalysis. Novosibirsk), Novosibirsk, 1990
49. J Smidt, W Hafner, R Jira, et al. *Angew. Chem.*, 1959, **71**(5) 176
50. I I Moiseev, M N Vargaftik, Ya K Syrkin *Dokl. Akad. Nauk SSSR*, 1960, **130** 820; 1963, **133** 377
51. I I Moiseev, M N Vargaftik, Ya K Syrkin *Dokl. Akad. Nauk SSSR*, 1963, **153** 140
52. I I Moiseev, S V Pestrikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1717; *Dokl. Akad. Nauk SSSR*, 1966, **171** 151
53. A E Shilov *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, D Reidel, Dordrecht, 1984
54. C L Hill (Editor) *Activation and Functionalisation of Alkanes*, Wiley, New York, 1989
55. E Gretz, T F Oliver, A Sen *J. Am. Chem. Soc.*, 1987, **109** 8109
56. A Sen, E Gretz, T F Oliver, Z Jiang *New. J. Chem.*, 1989, **13** 755
57. M N Vargaftik, I P Stolyarov, I I Moiseev *Kinet. Katal.*, 1989, **30** 1517
58. M N Vargaftik, I P Stolarov, I I Moiseev *J. Chem. Soc., Chem. Commun.*, 1990, 1049

59. I I Moiseev *Kinetika i Kataliz. Itogi Nauki i Tekhniki* (Kinetics and Catalysis. Advances in Science and Engineering), Izd. VINITI, Moscow, 1984, Vol. 13, 147 pp.
60. G Lefebre, Y Chauvin *Aspects of Homogeneous Catalysis* (Edited by R Ugo), Carlo Manfredi, Milan, 1970, p. 108
61. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2157
62. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *J. Organomet. Chem.*, 1982, **234** 219
63. I P Stolyarov, M N Vargaftik, O M Nefedov, I I Moiseev *Kinet. Katal.*, 1982, **23** 376
64. M K Starchevskii, M N Vargaftik, I I Moiseev *Kinet. Katal.*, 1979, **20** 1163; 1980, **21** 1451
65. L G Bruk, O N Temkin, Z V Goncharova, et al. *React. Kinet. Catal. Lett.*, 1978, **9** 303
66. K Fujimoto, T Kunugi *J. Jpn. Petrol. Inst.*, 1974, **17**(9) 739
67. M N Vargaftik *Khimicheskaya Svyaz' i Stroenie Molekul* (The Chemical Bond in Molecular Structure), Izd. Nauka, Moscow, 1984, p. 263
68. S Winstein, J McCaskie, H-B Lee, P M Henry *J. Am. Chem. Soc.*, 1976, **98**(22) 6913
69. V K Boyadzhyan, G G Stepanyan, V K Eritsyan, et al. *Plastmassy*, 1978, (7) 52
70. I I Moiseev, A P Belov, Ya K Syrkin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 1527
71. I V Kozhevnikov, K I Matveev *Usp. Khim.*, 1978, **47**(7) 1231 [English translation in *Russ. Chem. Rev.*, 1978(7)]
72. M K Starchevskii, M N Vargaftik, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 242
73. N K Eremenko, E T Mednikov, S S Kurasov *Usp. Khim.*, 1985, **54**(4) 671 [English translation in *Russ. Chem. Rev.*, 1985(4)]
74. M N Vargaftik, T A Stromnova, I I Moiseev *Zh. Neorg. Khim.*, 1980, **25**(1) 236 [English translation in *Russ. J. Inorg. Chem.*, 1980(1)]
75. I I Moiseev, M N Vargaftik, I V Kalechits, et al. *Dokl. Akad. Nauk SSSR*, 1977, **237** 645
76. I I Moiseev, T A Stromnova, M N Vargaftik, et al. *J. Chem. Soc., Chem. Commun.*, 1978, 27
77. T A Stromnova, L G Kuz'mina, M N Vargaftik, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 720
78. T A Stromnova, M N Vargaftik, I I Moiseev *J. Organomet. Chem.*, 1983, **252** 113
79. T A Stromnova, I N Busygina, S B Katser, et al. *J. Chem. Soc., Chem. Commun.*, 1988, 114
80. I N Busygina, T A Stromnova, S G Sakharov, et al. *Trudy IV Vsesoyuznoi Konferentsii po Khimii Karbenov. Moskva* (Proceedings of the IVth All-Union Conference on the Chemistry of Carbenes. Moscow), Izd. Nauka, Moscow, 1987, p. 97
81. I N Busygina, T A Stromnova, S B Katser, et al. *Metalloorg. Khim.*, 1990, **3**(1) 312 [English translation in *Organomet. Chem. USSR*, 1990(1)]
82. T A Stromnova, I N Busygina, D I Kochubei, I I Moiseev *Metalloorg. Khim.* (in the press)
83. T A Stromnova, M N Vargaftik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1411
84. T A Stromnova, V S Sergienko, A V Kisin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 894
85. M N Vargaftik, T A Stromnova, T S Khodasheva, et al. *Koord. Khim.*, 1981, 132
86. T A Stromnova, M N Vargaftik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 478
87. M N Vargaftik, V P Zagorodnikov, I I Moiseev *Kinet. Katal.*, 1981, **22** 951
88. M N Vargaftik, V P Zagorodnikov, I I Moiseev *Kinet. Katal.*, 1981, **22** 951
89. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2381
90. V P Zagorodnikov, M N Vargaftik, D I Kochubei, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 849
91. M N Vargaftik, V P Zagorodnikov, I P Stolarov, et al. *J. Mol. Catal.*, 1989, **53**(3) 315
92. V P Zagorodnikov, T S Khodashova, M N Vargaftik, et al. *Koord. Khim.*, 1985, **11** 95
93. I P Stolyarov, T A Stromnova, V P Zagorodnikov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 942
94. M N Vargaftik, V P Zagorodnikov, I P Stolarov, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 937
95. M N Vargaftik, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, **284** 890
96. G Schmid *Structure and Bonding*, Springer Verlag, Berlin–Heidelberg, 1985, Vol. 62, p. 51
97. L R Wallenberg, J-O Bovin, G Schmid *Surf. Sci.*, 1985, **156** 256
98. B T Heaton, P Ingallina, R Devenish, et al. *J. Chem. Soc., Chem. Commun.*, 1987, 765
99. G Schmid, B Morun, J-O Malm *Angew. Chem.*, 1989, **101** 772
100. B K Teo, N J A Sloane *Inorg. Chem.*, 1985, **24** 4545
101. E G Mednikov, et al. *J. Chem. Soc., Chem. Commun.*, 1987, 218
102. S Ladas, R A Dalla Betta, M Boudart *J. Catal.*, 1978, **53** 356
103. G Schmid *Nachr. Chem. Tech. Lab.*, 1987, **34** 249
104. G Schmid, R Pfeil, R Boese, et al. *Chem. Ber.*, 1981, **114** 3534
105. P Chini *Gazz. Chim. Ital.*, 1979, **109** 225
106. T Shimidzu, M Tamura *Shokubai*, 1974, **16** 84
107. S Nakamura, T Yasui *J. Catal.*, 1971, **23** 315
108. V P Zagorodnikov, M N Vargaftik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2652
109. V P Zagorodnikov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1495
110. P Brill, A M Watson *Z. Phys. Chem. (Munich)*, 1969, **64** 245
111. N M Zhavoronkov, Yu A Pazdersky, M K Starchevsky, et al. *Z. Anorg. Allg. Chem.*, 1989, **576** 284
112. V P Zagorodnikov, M N Vargaftik *Kinet. Katal.*, 1986, **27** 851
113. I P Stolyarov, M N Vargaftik, I I Moiseev *Kinet. Katal.*, 1987, **28** 1359
114. V N Kondrat'ev (Editor) *Energii Khimicheskikh Svyazei, Ionizatsionnye Potentsialy i Elektronnoe Srodstvo* (Chemical Bond Energies, Ionisation Potentials, and Electron Affinities), Izd. Nauka, Moscow, 1974
115. I I Moiseev *Fundamental Research in Homogeneous Catalysis* (Edited by A T Shilov), Gorden and Breach, New York–London, 1986, Vol. 4, p. 39
116. A Farkas, L Farkas *J. Am. Chem. Soc.*, 1938, **60** 105
117. E M Stuve, R J Madix *J. Phys. Chem.*, 1985, **89** 105
118. I I Moiseev, M N Vargaftik *Dokl. Akad. Nauk SSSR*, 1966, **166** 370
119. I P Stolyarov, et al. *Kinet. Katal.*, 1982, **23** 376
120. I I Moiseev, et al. *Dokl. Akad. Nauk SSSR*, 1967, **173** 863
121. I P Stolyarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1455