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Some of the most significant results in the field of catalysis by metal complexes (an expert assessment)

G V Lisichkin, A Ya Yuffa

We have set out below the most important achievements in complex metal catalysis over recent years. In order to reduce the subjective element (which understandably cannot be avoided completely), we have also drawn on the expert opinions of I S Akhrem, M N Vargaftik and G B Shul'pin. However, our experts have not examined achievements in heterogeneous complex metal catalysis nor in polymerisation catalysis.

1. Activation and functionalisation of alkanes

a) Oxidative functionalisation of alkanes in the presence of palladium salts—(stoichiometric reaction):

$$RH + Pd(OCOCF_3)_2 = ROCOCF_3 + Pd + CF_3COOH,$$

where R = Me, adamantyl, Ph reaction proceeds at 80 °C and 60 atm over 3–4 h; the yield of $ROCOCF_3$ is 60% for R = Me. By using a reoxidant for the conversion of Pd(0) to Pd(II), the reaction can be performed with a catalytic amount of palladium, as in the Wacker process for oxidation of olefins.[1,2] The authors have shown that the reaction is sensitive to the purity of palladium(II) acetate.

b) Highly selective partial oxidation of methane to methyl trifluoroacetate:
stoichiometric

$$CH_4 + 2M(OCOCF_3)_3 = CH_3OCOF_3 + 2M(OCOCF_3)_2 + CF_3COOH, \qquad M = Co, Mn;$$

catalytic

$$CH_4 + {}^1/_2O_2 + CF_3COOH = CH_3OCOCF_3 + H_2O.$$

Reaction is carried out in trifluoroacetic acid with Co(II), Co(III), Mn(II), or Mn(III) trifluoroacetate as catalyst; at 160–180 °C and 10–30 atm the yield of methyl trifluoroacetate was 90% (relative to Co(III) in the stoichiometric reaction, and in the catalytic reaction the turnover of M(II) was 1–2 after 1 h.[3]

c) Selective hydroxylation of methyl groups in the presence of platinum salts in aqueous media. The direct conversion of ethanol into ethylene glycol:

$$C_2H_5OH + Pt(IV) \xrightarrow[120\ ^\circ C,\ 3h]{Pt(II)} \underset{5\%}{HOCH_2CH_2OH} + \underset{2\%}{HOCH_2CH_2Cl} + \underset{5\%}{CH_3CH(OH)_2} + \underset{7\%}{CH_3COOH} + \underset{5\%}{HOCH_2COOH} + \underset{8\%}{CO_2}.$$

In this reaction, it is thought that Pt(II) serves as catalyst, and Pt(IV) as oxidant. It has been shown that reaction is highly selective for the methyl group in preference to CH_2 and CH groups.[4]

d) Oxidation of saturated and arylalkyl hydrocarbons by air in solution at room temperature and on irradiation in the presence of catalytic amounts of the transition metal oxo-complexes, $H_3PW_{12}O_{40}$,[5,6] and $W_{10}O_{32}^{4-}$,[7,8] or chloride complexes, such as $FeCl_3^9$ and $NaAuCl_4$[10]. Irradiation of a solution of alkane and catalyst $H_3PW_{12}O_{40}$ in acetonitrile in the absence of oxygen affords the corresponding alkene and H_2.[11] Such reactions facilitate the chemical processing of inert hydrocarbons, and constitute a method of storing solar energy in the form of chemical compounds.

It has been shown[12,13] that dehydrogenation of alkanes can be achieved under mild conditions (40–80 °C) without irradiation. Thus, the complex $(PPh_4)_2[PtCl_2(SnCl_3)_2]$ activates the dehydrogenation of ethylbenzene to styrene.[13]

2. Hydromethylation

In connection with alkane activation, there is much interest in the hydromethylation of ethylene, acetylene and carbon monoxide:

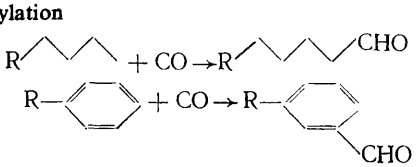
$$CH_4 + C_2H_4 \rightarrow C_3H_8,\ CH_4 + C_2H_2 \rightarrow C_3H_6,\ CH_4 + CO \rightarrow CH_3CHO.$$

Reactions are conducted at 20–50 °C with complexes of titanium, iron or nickel and organoaluminium compounds as catalyst.[14]

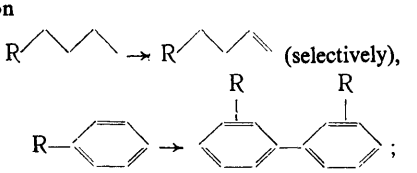
3. Catalytic functionalisation of alkanes and arenes under irradiation

The rhodium complex, $RhCl(CO)(PMe_3)_2$, has been shown to possess a wide spectrum of catalytic activity in functionalisation under irradiation:[15–22]

a) carbonylation



b) dehydrogenation



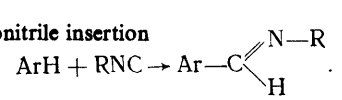
c) olefin insertion

$$ArH + CH_2 = CHCO_2Me \rightarrow ArCH = CHCO_2Me \text{ (selectively);}$$

d) hydrosilylation

$$XC_6H_5 + R_3SiH \rightarrow m\text{-}XC_6H_4SiR_3 \text{ (selectively);}$$

e) isonitrile insertion



4. Activation of the C—C bond in saturated hydrocarbons

With the discovery of new aprotic organic superacids of structure $RCO^+Al_2X_7^-$, there is the potential of effecting a broad range of alkane and cycloalkane conversions in their presence. This is a new stage in the development of the low-temperature chemistry of paraffins.[23]

The first examples of liquid-phase catalytic cleavage of the C—C bond in alkanes and cycloalkanes have been demonstrated by using Ziegler-type systems.[24]

5. Expoxidation of olefins

a) Recently,[25] a complex metal catalyst, namely tetramesitylporphyrinatoruthenium(VI), has been used for the first time in an olefin epoxidation where both atoms of the oxygen molecule participate in epoxide formation (2 moles of epoxide for each mole of O_2). (Usually, only one atom of O_2 participates, the second atom being involved with oxidation of another component of the oxidising system.)

b) One of the most significant achievements in the area of complex metal catalysis over the last decade has been the development of enantioselective epoxidation techniques (such as the Katsuki-Sharpless method).[26–28] For example, racemic isopropyl(vinyl)carbinol affords almost exclusively a single epoxide enantiomer on treatment with $Ti(OPr\text{-}i)_4$, tert-BuOOH and (*R*, *R*)-(+)-diethyl tartrate.

6. Formation of a C—C bond from CO and CO_2

a) Synthesis of ethylene glycol from CO + H_2

By using rhodium cluster catalysts for the synthesis of ethylene glycol from CO and H_2, the required pressure is sufficiently low for practical requirements (see, for example, Ref. 29).

b) Formation of a C—C bond from CO_2

A review of reactions and achievements in the field of CO_2 fixation by metal complexes has been published.[30]

7. Isomerisation of methylformate to acetic acid, and the carbonylation of methyl acetate catalysed by platinum phosphide complexes

For a commercially viable route to acetic acid and acetic anhydride from methanol, there is now the possibility of using platinum phosphide complexes in place of rhodium complexes and iodine.[31] The process is conducted in the presence of a Lewis acid.

8. Low-temperature dehydration of alcohols

The low-temperature dehydration of alcohols has been achieved by a carbene route without the use of a Brönsted or Lewis acid. A palladium-molybdenum cluster with eight nuclei was used as catalyst.[32]

9. Catalytic preparation of ozone

A new catalytic preparation of ozone has been reported.[33]

$$3H_2O_2 \xrightarrow{V(V),\ CF_3COOH} O_3 + 3H_2O.$$

The reaction, carried out at 20 °C, has a half-life of 1 min. The homogenous catalytic system, based on vanadium(V) complexes, is effective for the oxidation of alkanes and perfluoroalkenes with H_2O_2 at room temperature.[34]

10. The development of new approaches to complex metal catalysts

a) Biomimetic

This research is based on the principles of biocatalysis, and devoted to the synthesis of enzyme models. A E Shilov and co-workers are the leading Soviet chemists in this field. By way of an example, one can cite the effective oxidation of hydrocarbons with Fe(III)-, Mn(III)-, Cr(III)- and Ru(III)-porphyrin complexes as models of the cytochrome P-450 enzyme. These complex porphyrin catalysts are suitable for the hydroxylation of alkanes to alcohols.[35] If molecular oxygen is used as oxidant in the presence of a metalloporphyrin, then a reductant is required in the catalytic cycle; an electrochemical system[36,37] or metallic zinc[38–40] may serve this purpose. An oxo-compound, such as PhIO, H_2O_2, NaOCl, $KHSO_5$, or XeO_3[35] may be used in place of the oxygen-reductant couple. The system $Fe(ClO_4)_2-H_2O_2$ is effective for the hydroxylation of alkanes.[41]

b) Giant palladium clusters as catalysts for the oxidation of olefins and alcohols

There is a review devoted to the synthesis, structure, and catalytic activity of giant palladium clusters, and to the mechanism of catalysis by such compounds.[42]

c) Transition metal polyhydrides

This potentially interesting class of complex metal catalysts has the composition $[MH_xP_y]$, where P is a tertiary phosphine.[43] Such complexes serve as effective hydrogen reservoirs, and show a tendency to form free coordination sites through the facile reductive elimination or transfer of coordinated hydrogen. Interest in the chemistry of these complexes has widened with the recent finding that hydrogen may be coordinated in the polyhydride complex in the form of a non-dissociated molecule. The catalytic behaviour of polyhydrides is especially noteworthy. Thus, they hydrogenate arenes and ethers, and are involved in C—C bond activation.[23]

11. Some examples of the industrial use of homogenous complex metal catalysts

The industrial use of complex metal catalysis is unquestionably extensive. By way of example, the companies, Rhône-Poulenc and Ruhrchemie, have used the water-soluble rhodium complex, $[P(m\text{-}C_6H_4SO_3Na)_3]_3(CO)RhH$, for the hydroformylation of propylene.[44–46] This catalyst has a number of advantages over the water-insoluble analog, $(PPh_3)_3(CO)RhH$, which has been used in this process by the Union Carbide company since 1973. The higher stability of the water-soluble catalyst, even under a high pressure of CO, and the higher selectivity for formation of the linear aldehyde, n-butanal, are notable advantages.

One should also note the possible industrial application of a catalytic system containing a water-soluble rhodium complex and a surface-active compound in a 2-phase system comprising organic substrate/product and water.[45] A most notable feature of hydroformylation with this system is the extremely high selectivity for the linear aldehyde. Thus, a new type of catalytic process, designated 'micellar metal complex catalysis' has been revealed. This has been discussed in Ref. 47. Evidently, this field of research is of great potential. Thus, by using micellar metal complex catalysis in the oxidation of cumene to cumyl hydroperoxide, one can achieve 98% selectivity at 20% conversion and a high rate of reaction under mild conditions.[48] We consider that catalysis in micelles is a particular case of a more general phenomenon — that of catalysis in structured

media, such as normal and reverse micelles, liquid crystalline phases, films, etc. It is anticipated that metal complex catalysis in structured media will significantly increase the selectivity of catalysts.

It has been reported[49] that the Degussa company have discovered a process for epoxidation of olefins with H_2O_2, in which Mn-, Mo- and W-porphyrin catalysts or platinum chelate complexes have been used as catalyst.

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