

Homogeneous Palladium(II) Mediated Oxidation of Methane

SELECTIVE FUNCTIONALISATION UNDER MILD CONDITIONS

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A metal catalysed, electrophilic approach to methane oxidation is discussed. This involves the oxidation of methane to the corresponding methyl ester in trifluoroacetic acid; the oxidant is hydrogen peroxide and the catalyst is the palladium(II) ion. The latter species activates methane by the electrophilic cleavage of a C-H bond, and then acts as a two-electron oxidant towards the resultant metal-bound methyl group. The hydrogen peroxide reoxidises palladium(0) back to palladium(II).

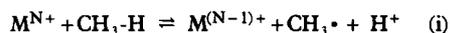
Methane is the most abundant and the least reactive member of the hydrocarbon family. Thus, the selective functionalisation, preferably catalytic, of methane under mild conditions is one of the most challenging chemical problems, in addition to being of great practical importance. Among the various functionalisation possibilities, oxidative functionalisation is of special interest, since several commercially important organic chemicals (methanol, formaldehyde and formic acid) are nominally related to methane through oxidation steps.

The number of reported methods for the selective, low temperature (at about 100°C or below) functionalisation of methane is very limited indeed. For example, the radical initiated chlorination of methane is very non-selective and invariably leads to multiple chlorinations (1) (chlorination, however, is more specific in the presence of superacids (2)). Among transition metal mediated procedures, the only one that gives good yield involves PtCl₄²⁻ catalysed oxidation of methane by PtCl₆²⁻ in water at 120°C, which leads to the formation of equal amounts of methanol and methyl chloride (3).

The oxidative functionalisation of methane through direct reaction with molecular oxygen in homogeneous media at low to moderate

temperatures is not a practical procedure for two principal reasons. The interaction of triplet oxygen with a singlet organic molecule is associated with a high activation energy barrier due to the requirement of a "spin-flip". In addition, the auto-oxidation of alkanes is usually a chain reaction and is very non-specific in nature (4). In view of the above problems, it is attractive to consider metal mediated pathways for the oxidative functionalisation of methane. One role of the metal would be to stabilise unstable organic intermediates by binding to them. Specific reaction pathways may be promoted in this manner.

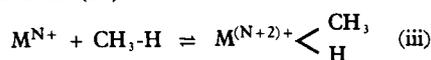
Three basic modes of interaction of a metal with methane may be envisaged. The first involves the metal as a 1e⁻ oxidant as shown in Equations (i) and (ii), (5).



Sometimes, as shown in Equation (ii), an auxiliary ligand on the metal may assist in the 1e⁻ oxidation step, as is observed with the enzyme cytochrome P₄₅₀ (6, 7) and, perhaps, methane mono-oxygenases (8). Unfortunately, the methyl radical thus generated will participate in a multitude of reaction pathways. Only when severe steric restraints are present, as in an enzyme pocket, is any degree of

specificity expected. In addition to the problem of reaction specificity, $1e^-$ oxidation of methane is particularly unfavourable from a thermodynamic standpoint (see Table I) and, therefore, the generation of methyl radicals requires the use of rather strong oxidants and/or high temperatures (9).

The two common modes of interaction of a metal with methane that do not lead to the formation of radicals are oxidative addition, Equation (iii), and electrophilic displacement, Equation (iv). In recent years, Bergman, Graham and others have demonstrated that methane can participate in oxidative addition reactions (10).

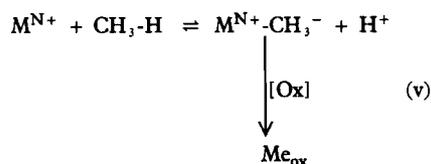


However, a problem associated with this reaction is that the relative weakness of the metal-carbon bond often makes the oxidative addition step thermodynamically unfavourable (11). A common way to circumvent this problem is to generate a high-energy, coordinatively unsaturated species (usually by photochemical means) which then reacts with the CH_3-H bond in a "downhill" process. Unfortunately, the presence of the highly reactive metal species precludes the simultaneous presence of most oxidising reagents capable of functionalising the bound methyl group in the oxidative addition product. Thus, it is difficult to construct a "one pot" catalytic procedure for the oxidative functionalisation of methane that is based on Equation (iii).

The electrophilic displacement (heterolytic cleavage) pathway, Equation (iv) (3, 12, 13), is generally more favourable than the corresponding oxidative addition reaction for two reasons (11). First, the low reactivity of methane vis-à-vis most metal compounds is due, at least in part, to the absence of low-lying unoccupied orbitals. Hence, the transition state often involves the promotion of electrons into antibonding orbitals. Accordingly, the reactivity of methane is expected to be highest towards species having low-lying unoccupied orbitals, – that is to elec-

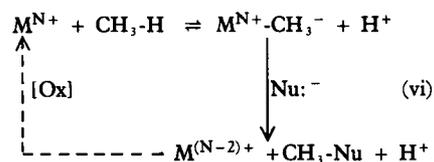
trophiles. Second, the electrophilic displacement reaction is not as severely limited as is oxidative addition by the thermodynamic constraint associated with the weakness of the M-C bonds, since the driving force for processes such as Equation (iv) can be favourably influenced by the stabilisation of the leaving group, H^+ . For example, it has been shown that the analogous heterolytic cleavage of H_2 by metal ions such as Cu^{2+} , Ag^+ and Hg^{2+} is favoured by the presence of bases which serve to stabilise the released H^+ ion (14). Moreover, the recent reports of the addition of CH_4 across a $Zr=NR$ bond may be an example of base assisted heterolytic cleavage of an alkane C-H bond (15).

Our general scheme for oxidative functionalisation of methane is outlined in Equation (v) and is based on an initial electrophilic displacement step (12(a), (b)). The $2e^-$ oxidant could be the metal itself or a separate reagent.

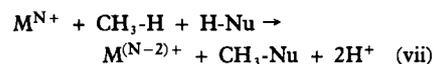


Ox = $2e^-$ oxidant, Me_{ox} = oxidised organic product

If the metal acts both as the electrophile and oxidant, then the above scheme may be modified in the following way, Equation (vi). The overall reaction is shown in Equation (vii). If the final reduced metal species



Ox = $2e^-$ oxidant, Nu: $^-$ = nucleophile



can be reoxidised back (either chemically or electrochemically) then a catalytic cycle would ensue. Note that the steps involved in Equations (v) and (vi) are not totally unprecedented since Shilov and others have reported the following

Table III
Promotion Energies and Electron Affinities for Selected Metal Ions (17)

Ion	Promotion energy*, eV	Electron affinity, eV
Rh(I)	1.6	7.31
Ir(I)	2.4	7.95
Pd(III)	3.05	18.56
Pt(III)	3.39	19.42
Cu(I)	8.25	7.72
Ag(I)	9.94	7.59
Zn(II)	17.1	17.96
Cd(II)	16.6	16.9
Hg(II)	12.8	18.75

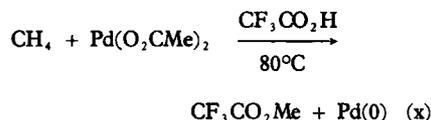
* $nd^x \rightarrow nd^{x-1}(n+1)p^1$

of radicals). For example, the Pd(II) mediated $2e^-$ oxidation of olefins and arenes is well-known (18). In addition, Pd metal can be readily oxidised back to Pd(II) using several different co-oxidants, such as Cu(II) + O₂ and RONO, and this forms the basis of several practical Pd(II) catalysed oxidation processes, such as, the Wacker process and the Pd(II) catalysed oxalate synthesis (19).

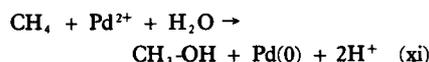
In our own work we chose to focus on the reactivity of the Pd(II) ion based on the arguments presented above (12). The initial problem involved the choice of the proper complex and the solvent, and Pd(II) in CF₃CO₂H was chosen for the following reasons: the CF₃CO₂⁻ ion is a relatively poor base and M-O₂CCF₃ bonds are known to be quite labile (20). Therefore, the Pd(II) species present in the above system is expected to be labile and highly electrophilic. In this context, it is noteworthy that the electrophilic metallation of arenes by Ti(O₂CCF₃)₃ occurs readily under mild conditions, while the corresponding acetate derivative is unreactive (21). Also of note is the observation of facile electrophilic cleavage of the allylic C-H bonds of olefins by Pd(O₂CCF₃)₂ in CF₃CO₂H (22).

When CH₄ (at 800 psi) was heated in the presence of Pd(O₂CMe)₂ in CF₃CO₂H at 80°C, a yield of approximately 60 per cent of CF₃CO₂Me together with precipitated Pd metal was observed, Equation (x) (12(a), (b)).

No deuterium incorporation into CF₃CO₂Me was observed when Pd(O₂CCH₃)₂ was replaced by Pd(O₂CCD₃)₂,



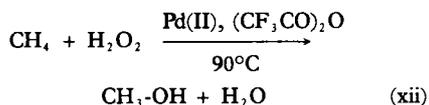
indicating that the MeCO₂⁻ group did not participate in the product formation through a decarboxylation step. Since the ester can be hydrolysed to the corresponding alcohol, the overall reaction can be written as follows:



Further information concerning the mechanism of the Pd(II) oxidation of hydrocarbons was obtained through the study of arene oxidations (12(a), (b)) which were also performed at 80°C using Pd(O₂CMe)₂ in CF₃CO₂H. Under these conditions, the monotrifluoroacetoxylation of 1 equivalent of *p*-dimethoxybenzene proceeded to completion in 1 hour. Furthermore, comparative experiments indicated the following relative oxidation rates: *p*-dimethoxybenzene (1), *p*-xylene (0.1), toluene (0.02) and benzene (0). For *p*-xylene and toluene, attack on the ring rather than the benzylic position accounted for over 97 per cent and over 90 per cent, respectively, of the monotrifluoroacetate esters obtained. The two conclusions that can be drawn from our

observations on Pd(II) oxidations (12(a), (b)) are that (a) radical pathways are not involved, since the weak benzylic C-H bonds were not attacked to any significant extent and (b) the enhanced rate of oxidation with electron-rich arenes is consistent with an electrophilic displacement pathway, as shown in Equations (iv) and (vi). The latter conclusion was further supported by the observation that the trifluoroacetoxylation of anisole proceeded to yield para and ortho products in a 3:1 ratio with almost no meta isomer formed.

In order to make the oxidation of methane catalytic in Pd(II), it is necessary to have a co-oxidant that is capable of reoxidising the Pd(0) formed at the end of the stoichiometric oxidation step, see Equation (vi). Hydrogen peroxide is one such co-oxidant. Thus, peroxytrifluoroacetic acid, generated from H₂O₂ and (CF₃CO)₂O, was found to oxidise methane specifically to CF₃CO₂Me, with the Pd(II) ion acting as the catalyst, see Figure 1(12c). The reaction shown in Equation (xi) can therefore be rewritten as follows:



The purpose of having an excess of trifluoroacetic anhydride is to remove the water generated, thereby preventing the hydrolysis of the ester to the more easily oxidised methanol. Ready further oxidation (eventually to CO₂ and H₂O) of the primary products is a persistent problem in the area of selective oxidation of alkanes. As is evident from Figure 1, our strategy works to a certain extent; however, at long reaction times, further oxidation of CF₃CO₂CH₃ does occur. Significantly, this latter oxidation step is also catalysed by Pd(II) since CF₃CO₂CH₃ was found to be stable in the reaction mixture in the absence of the metal.

The following observations seem to indicate that an electrophilic, rather than radical, mechanism also operates for the catalytic oxidation of methane. The oxidation of *cis* and *trans* 1,2-dimethylcyclohexane to the corresponding

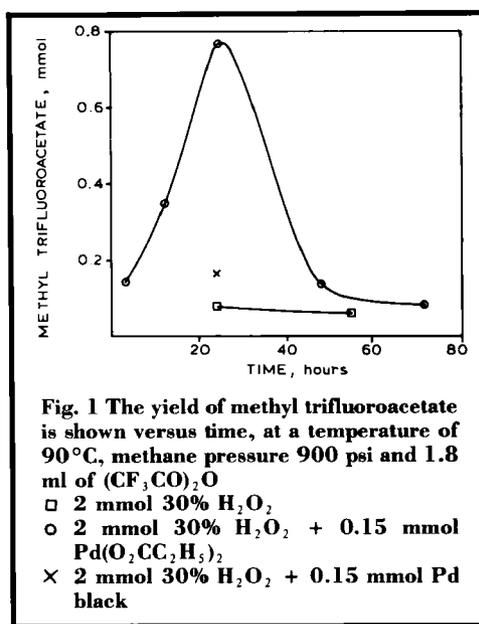


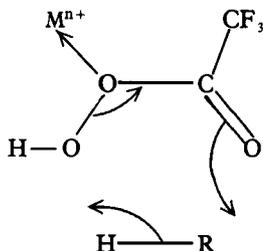
Fig. 1 The yield of methyl trifluoroacetate is shown versus time, at a temperature of 90°C, methane pressure 900 psi and 1.8 ml of (CF₃CO)₂O
 □ 2 mmol 30% H₂O₂
 ○ 2 mmol 30% H₂O₂ + 0.15 mmol Pd(O₂CC₂H₅)₂
 × 2 mmol 30% H₂O₂ + 0.15 mmol Pd black

tertiary alcohols by peroxytrifluoroacetic acid was previously shown to proceed by complete retention of configuration (23). The addition of the Pd(II) ion to the system does not appear to alter the mechanism since, when *p*-xylene was used as the substrate, the ratio of esters derived from the attack on the ring versus the benzylic position was >100:1. Therefore, a radical pathway is not involved since the weak benzylic C-H bonds were not broken.

Since the catalytic cycle presumably combines the reaction shown in Equation (x), with a step involving the reoxidation of Pd(0) to Pd(II) by peroxytrifluoroacetic acid, it should be possible to initiate the catalytic cycle starting with Pd(0). The addition of "palladium black" to peroxytrifluoroacetic acid did result in an enhanced yield of CF₃CO₂CH₃; nevertheless, the effect was much less than that observed with Pd(O₂CC₂H₅)₂, as shown in Figure 1. This observation does not necessarily rule out the above catalytic cycle since, in several catalytic oxidations involving the Pd(II)/(0)/(II) cycle, it has been observed that once Pd(0) is allowed to aggregate, it cannot be easily re-oxidised to Pd(II) (24).

An alternative explanation for the catalytic

effect of the Pd(II) ion encompasses attack by an incipient OH⁺ ion and proceeds through the following transition state (25). Under this scenario, the



Pd(II) ion promotes the reaction by coordination to the α -oxygen atom, thereby further polarising the O-O bond (26). Other metal ions should also have a similar effect. The substitution of Pd(O₂CC₂H₅)₂ by either Pb(O₂CCH₃)₄, Fe(O₂CCH₃)₂ or

Co(O₂C-CF₃)₂ however, (27) resulted in a yield of CF₃CO₂CH₃ that is either similar to, or only marginally higher, than that observed with peroxytrifluoroacetic acid alone.

In conclusion, the selective transition metal catalysed, oxidation of methane through an electrophilic pathway under mild conditions has been demonstrated.

Note that the electrophilic oxidation of methane in superacid media is known (28). In the latter case, the methanol formed is protected from further oxidation by protonation to the methyloxonium ion.

Acknowledgment

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Platinum 1991

During 1990 the supply of platinum to the Western World increased to 3.73 million ounces, while demand rose by 5.5 per cent to a record 3.66 million ounces, due to increased usage for automobile emission control catalysts, by the chemical and petroleum industries, and for the production of jewellery. These are just a few of the many facts contained in "Platinum 1991", a 64 page comprehensive review of the platinum industry recently published by Johnson Matthey.

Sales of platinum and palladium by the U.S.S.R. increased by 27 and 12 per cent, respectively, compared to the previous year. Almost 20 per cent of platinum and over half the palladium supply comes from that country, although it is not known what part of the shipments represents current mine production and what was withdrawn from stock.

Demand for rhodium rose by 20 per cent during 1990, the increase being due entirely to purchases by the car manufacturers, and included some inventory building. Supply did not match demand, and a significant price increase resulted. On the South African Bushveld Igneous Complex, the source of almost 75 per cent of the Western World's supply of platinum, the platinum:rhodium ratio in the generally

mined Merensky reef is 19:1, but in the UG2 seam it is 6:1, thus more rhodium will become available as mining of the latter increases.

There are indications that fuel cells may become the next major application for platinum. In fuel cells, platinum catalyst coatings on the electrodes promote the combination of hydrogen and oxygen ions and thus the generation of electricity. During 1990 Toshiba and Fuji Electric in Japan, and International Fuel Cells in the U.S.A. decided to start the commercial production of fuel cell electricity generators. It is predicted that their commercialisation will make a significant impact on the demand for platinum, as the versatility of fuel cells for producing "clean" power becomes more widely appreciated, and as economies of scale reduce manufacturing costs.

Readers of *Platinum Metals Review* who do not have access to this survey and who believe that they would benefit from a better understanding of the platinum market, and many of the factors that influence it, are invited to request a free copy of "Platinum 1991" from the author: Mr. Jeremy S. Coombes, Johnson Matthey P.L.C., New Garden House, 78 Hatton Garden, London EC1N 8JP, England.