

Oxidation of Methane Using Homogeneous Platinum Catalysts

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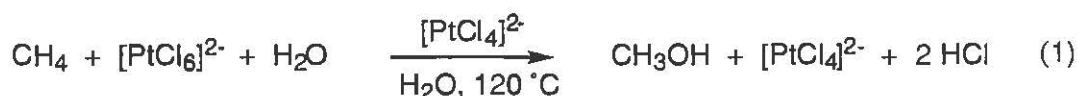
Literature Seminar

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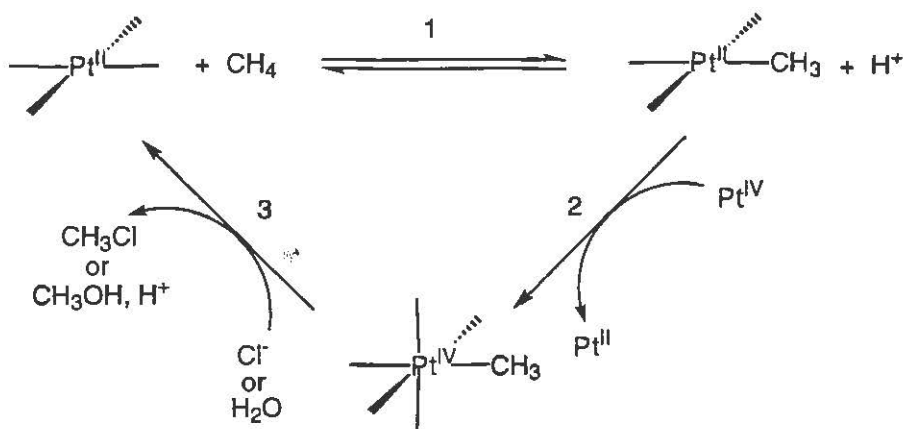
At the present rate of consumption, the known reserves of petroleum should last approximately eighty years.¹ There is roughly an equal quantity of natural gas, of which the major component is methane. The conversion of methane into useful organic compounds has proven to be quite elusive due to the low kinetic activity of methane. There has been much interest in designing complexes that can break a C-H bond and catalytically functionalize methane.²

In 1972, the facile conversion of methane to methanol and methyl chloride at low temperature (100 °C) was reported by A. E. Shilov and coworkers.³ This reaction was performed in an acidic aqueous solution of hexachloroplatinate ($K_2[PtCl_6]$) and tetrachloroplatinate ($K_2[PtCl_4]$). Since then several groups have investigated Shilov's system.⁴⁻⁸ This seminar surveys these developments.

The platinum catalyzed alkane oxidation involves the net oxidation of methane to methanol by hexachloroplatinate(IV) (eq. 1). This transformation is proposed to proceed via



three basic steps.⁴ The first step involves the electrophilic activation of a C-H bond by Pt(II) to give a methyl-platinum(II) intermediate.^{3,9-10} This is followed by a two-electron oxidation of the methyl-platinum(II) to give a methyl-platinum(IV) complex.¹¹ The Pt(IV) intermediate reductively eliminates MeX (X = OH, Cl) to regenerate Pt(II).¹²⁻¹³ The reductive elimination from Pt(IV) in the final step proceeds through a nucleophilic attack at the methyl group by water or chloride.



Scheme 1

As shown in Scheme 1, this system is not catalytic with respect to the hexachloroplatinate(IV). Oxygen will, however, react with $\text{Pt}^{\text{II}}\text{Cl}_4^{2-}$ in an acidic solution to slowly produce water and $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$. The addition of a small amount of a heteropolyacid, $\text{Na}_8\text{HPMo}_6\text{V}_6\text{O}_{40}$ (HPA-6), increases the rate of oxidation by more than tenfold.¹⁴ Although multiple turnovers can be observed with HPA-6, the catalyst is degraded to give products which will catalyze the unselective oxidation of methane.

The most significant recent advance in this area is the use of a new catalyst for the oxidation of methane to methyl bisulfate with high yields. The catalyst, dichloro(κ^2 -[2,2'-bipyrimidyl])platinum(II) (Figure 1), catalyzes the formation of methyl bisulfate from methane in 102% H_2SO_4 at 220 °C.¹⁵ The formation of a methyl bisulfate intermediate effectively protects the methyl group from further oxidation (Scheme 2). The methyl bisulfate can be readily converted to methanol by the addition of water. The system was reported to have a 72% one-pass yield with 81% selectivity based on methane.

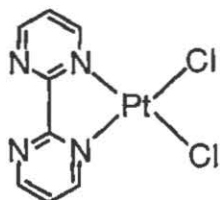
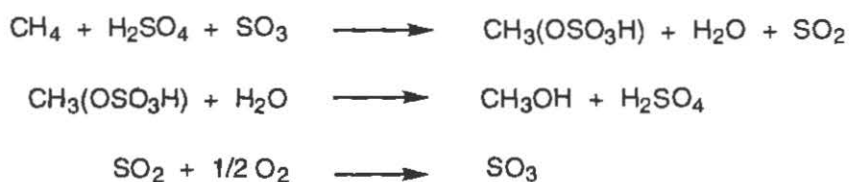


Figure 1



Scheme 2

These advances make the development of a selective, high-yield catalytic system for alkane functionalization a realistic goal.¹⁶ With a basic understanding of the three steps in Shilov's original mechanistic hypothesis and the new bipyrimidine platinum catalyst, a commercial system may soon be viable.

References

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