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Low-Temperature Methane Chlorination with Aqueous Platinum Chlorides in the Presence of Chlorine

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Summary: The reaction of methane with chlorine in water at 125 °C in the presence of platinum chlorides results in the platinum-assisted formation of methyl chloride which is partially hydrolyzed in situ to methanol. Aqueous $Na_2[PtCl_4]$ reacts with chlorine at room temperature, resulting in $Na_2[PtCl_6]$, which is the major species in solution even at 125 °C.

Although low-temperature activation of methane by transition-metal complexes has been demonstrated,[1] homogeneous catalytic conversion of methane under mild conditions still remains a formidable challenge. Chlorination is an important process for the functionalization of methane because the chlorinated products are used as solvents and chemical intermediates.[2] Methane is usually chlorinated at high temperatures or at room temperature using ultraviolet irradiation to a mixture of the four chloromethanes. While heterogeneous catalytic chlorination of methane has been studied,[3–8] no homogeneous liquid-phase transition-metal catalysts are known for the chlorination. The stoichiometric reaction of methane with aqueous platinum chlorides leading to methyl chloride and/or methanol was reported by Shilov and co-workers;[9–11] however, the reaction is frequently accompanied by the concomitant formation of metallic platinum, leading to sporadic results. The peculiar reactivity of the aqueous platinum system was also noted by Labinger and Bercaw[12] and by Sen[13] on the functionalization of unactivated C–H bonds in ethanol and aliphatic carboxylic acids, respectively. It has been suggested that a Pt(II) species is responsible for the activation of carbon–hydrogen bonds.[9–13] We report that aqueous platinum chlorides can be used as catalysts for the homogeneous catalytic chlorination of methane between 100 and 125 °C in water to give methyl chloride, which is partly hydrolyzed in situ to methanol.

Our initial experiments were designed to gain mechanistic information on the reaction of methane with platinum chlorides[9–11] by using high-pressure NMR.[14] A solution of Na_2PtCl_4 (0.16 mmol) and Na_2PtCl_6 (1.2 mmol) in D_2O (3 mL) was placed in a transparent 10-mm sapphire NMR tube[15] (5 mL) under N_2 and charged with methane (300–1500 psi, 1.7–8.5 mmol) at room temperature. Since initial high-pressure NMR showed almost identical results at 25 and 125 °C probe temperatures, further experiments were performed by heating the lower third of the tube, covered with aluminum foil, in an oil bath at 125 °C for variable times. The tube was then cooled to room temperature, and NMR spectra were recorded. A typical ^{13}C NMR spectrum, recorded after heating a solution of platinum chlorides under 400 psi of $^{13}CH_4$ (99% isotope purity) at 125 °C for 7 h, shows the presence of CH_3Cl, CH_3OD, $CH_2(OD)_2$, HCOOD, CO_2, and unreacted CH_4 (Figure 1). Neither H/D exchange between D_2O and methane nor C–H for D exchange in the organic products was observed. It should be emphasized that no signals due to platinum complexes containing a hydrocarbon ligand (e.g. methyl, hydroxymethyl, etc.) were observed, and this is not surprising if we assume that C–H activation is the rate-limiting step. Visual inspection of the tube revealed the presence of a metallic platinum ring just above the liquid phase. This suggested that the decomposition of a platinum chloride species may have occurred at the liquid/gas interphase or in the gas phase, resulting in the formation of the metallic platinum ring and free chlorine.[16]

If the aqueous solutions of platinum chlorides decompose at these higher temperatures, the free chlorine formed could be responsible for the platinum-assisted chlorination of methane to methyl chloride, which, in turn, could be hydrolyzed in situ to methanol. Accordingly, when a solution of Na_2PtCl_4 (0.16 mmol) and Na_2PtCl_6 (1.2 mmol) in D_2O (3 mL) is charged with 72 psi of Cl_2 and 396 psi of $^{13}CH_4$ and heated in the dark at 125 °C for 1 h, the selective conversion of methane to methyl chloride and methanol was observed (Figure 2A–D), with *no formation of metallic platinum.*[17] When the solution is heated for another 3 h, the slow formation of CH_2Cl_2, $CH_2(OD)_2$, HCOOD, and CO_2 was observed (Figure 2E).[18] ^{195}Pt

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[16] It should be noted that several platinum chloride complexes are known to decompose to metallic platinum and chlorine upon heating; see for example: Schweizer, A. J.; Kerr, G. T. *Inorg. Chem.* **1978**, *17*, 2326–2327.

[17] Only a trace amount of CH_3Cl is observed when 73 mmol of Cl_2 in 100 mL of water under 400 psi of CH_4 pressure is heated at 140 °C for 7 h in a 250-mL Teflon-lined autoclave.

[18] While CH_2Cl_2 is probably due to the chlorination of CH_3Cl, the other products could have formed either via the chlorination of methanol followed by hydrolysis (as epichlorohydrins are not stable in water) or by platinum-assisted oxidation. The reaction of methanol (27 mmol) with chlorine (45 mmol) in 99 mL of water at 125 °C for 4 h yields 10% $CH_2(OH)_2$, 6% HCOOH, and 2% CO_2. When the same reaction is performed in the presence of platinum chlorides, a trace amount of CH_3Cl is also formed.

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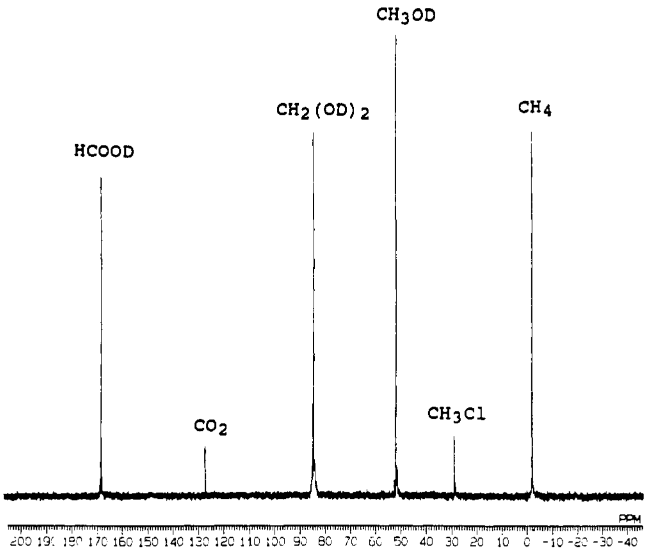


Figure 1. ^{13}C NMR spectrum of a solution containing 0.16 mmol of Na_2PtCl_4 and 1.2 mmol of Na_2PtCl_6 in 3 mL of D_2O under 400 psi of $^{13}CH_4$ after heating to 125 °C for 7 h.

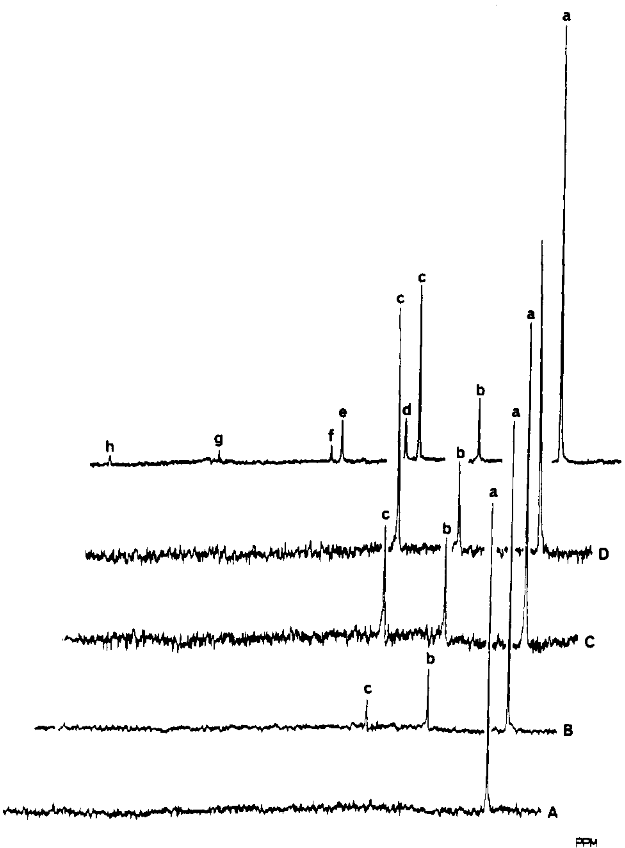
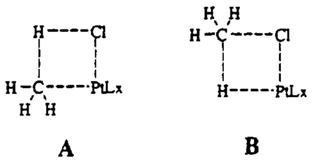


Figure 2. High-pressure ^{13}C NMR spectra of a solution containing 0.16 mmol of Na_2PtCl_4 and 1.2 mmol of Na_2PtCl_6 in 3 mL of D_2O: (A) after pressurization with 82 psi of Cl_2 and 396 psi of $^{13}CH_4$; (B–E) with heating to 125 °C for 15, 30, 60, and 240 min, respectively. Peak assignments are as follows: (a) CH_4, (b) CH_3Cl, (c) CH_3OD, (d) CH_2Cl_2, (e) $CH_2(OD)_2$, (f) $DOCH_2OCH_2OD$, (g) CO_2, and (h) HCOOD.

NMR of this solution has shown a strong resonance at ca. 0 ppm due to $[PtCl_6]^{2-}$ and a low-intensity resonance at ca. −1625 ppm indicating minute amounts of $[PtCl_4]^{2-}$. This suggests that equilibrium 1 operates in the aqueous platinum chloride system under chlorine. As expected, when a solution of 0.45 mmol of Na_2PtCl_4 in 0.5 mL of D_2O is charged with 45 psi of Cl_2 in the dark at room temperature, ^{195}Pt NMR shows one resonance for Na_2PtCl_6. We are currently studying this equilibrium in more detail. However, preliminary data suggest that, under 45 psi of Cl_2 at 125 °C, equilibrium 1 lies far to the right, as the only species observed by NMR is Na_2PtCl_6. Furthermore, when Na_2PtCl_6 (0.45 mol/L) or the mixture of Na_2PtCl_4 (0.05 mol/L) and Na_2PtCl_6 (0.40 mol/L) is pretreated with Cl_2 (85 psi) at 125 °C for 2 h[19] and then 300 psi of CH_4 is added, the conversions of methane after 2 h at 125 °C are practically the same.

$$Na_2PtCl_4 + Cl_2 \rightleftharpoons Na_2PtCl_6 \qquad (1)$$

Chart I



Finally, in order to slow down the hydrolysis of methyl chloride[21] as well as the reaction of methanol with aqueous chlorine, we have performed the chlorination of methane at lower temperatures. When a solution of Na_2PtCl_4 (0.8 mmol) and Na_2PtCl_6 (4.9 mmol) in H_2O (20 mL) is charged with 82 psi of Cl_2 and 400 psi of CH_4 and this mixture is heated in a 250-mL Teflon-lined autoclave at 100 °C for 12 h, the formation of methyl chloride (2.3 mmol) and trace amounts of methanol was observed. Metallic platinum was not observed, indicating again that the chlorine stabilizes the system. Although the amount of CH_3Cl formed is less then the total amount of platinum chlorides, it is definitively higher than that of the Pt(II) species. If we assume that methane is activated by a Pt(II) species, as proposed by several groups,[9–13] the reaction is catalytic with a turnover number of 0.24 turnovers/h. However, if we consider that the ^{195}Pt NMR shows that the concentration of Pt(II) is reduced at least by 1/100, then the turnover number is not less than 24 turnovers/h.

Our results show that C–H bond activation is irreversible in the aqueous platinum system because neither H/D exchange between D_2O and methane was observed nor was deuterium incorporation into the products. Although radical mechanisms cannot be ruled out entirely at this time,[22] methane is probably activated by an electrophilic platinum center and the reaction could proceed through a four-centered transition state proposed previously by several groups and shown in Chart I. Once formed, a

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[19] When solutions of (a) Na_2PtCl_6 (0.45 mol/L), (b) Na_2PtCl_4 (0.45 mol/L), or (c) the mixture of Na_2PtCl_4 (0.05 mol/L) and Na_2PtCl_6 (0.40 mol/L) are *not pretreated with chlorine* but pressurized successively with chlorine and methane and then heated immediately to 125 °C, the relative reactivities of the three solutions toward methane conversion are 1, 7.8, and 5.8, respectively. These results suggest that several equilibria operate in a aqueous platinum chloride system under chlorine and that the establishment of stable equilibrium, including reaction 1, requires a longer time. This is in accord with previous reports which show that *aging* of aqueous platinum chloride solutions can significantly alter their reactivity[20] and thus their catalytic activity.

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[21] CH_3Cl hydrolyzes rapidly to CH_3OD in D_2O at 125 °C without any platinum species present.

[22] We do not believe that methane is activated by Cl radicals formed from chlorine, as the reactions were performed in the dark and at temperatures that are too low for radical formation. However, we cannot rule out that a platinum species could be formed and serve as a radical initiator.

MePt^{II} intermediate could conceivably react directly with Cl_2 but more likely with $[PtCl_6]^{2-}$, which has a far higher concentration under catalytic conditions. The role of chlorine remains to be fully elucidated, but its role in influencing the Pt(II)/Pt(IV) equilibrium and stabilizing the system would seem to be of fundamental importance.

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