Competitive Oxidation and Protonation of Aqueous Monomethylplatinum(II) Complexes: A Comparison of Oxidants

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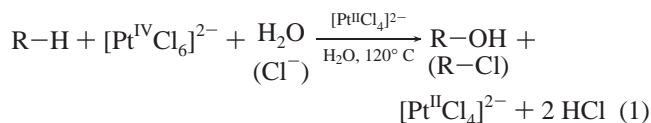
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$[Pt^{II}(CH_3)Cl_3]^{2-}$ (**1**), generated at 95 °C in situ from $Cs_2[Pt^{IV}(CH_3)_2Cl_4]$ in an aqueous solution of high chloride concentration and $[H^+] = 0.2$ M, undergoes competitive oxidation versus protonation (k_{ox}/k_{H+}) with several oxidants. A first-order dependence on oxidant concentration was determined for both $CuCl_2$ and $FeCl_3$ oxidations of **1**, and k_{ox}/k_{H+} was determined to be 191 ± 24 and 14 ± 3. $CuCl_2$ was shown to catalyze the oxidation of **1** by dioxygen; however, $[Pt^{II}Cl_4]^{2-}$ was also oxidized under these conditions. Anion **1**, generated in a mixture of platinum(II) salts, $[Cp_2Co^{III}]_2\{[Pt^{II}Cl_4] + \mathbf{1} + [Pt^{II}(CH_3)_2Cl_2] (\mathbf{4})\} \cdot x$NaCl (**5**), also undergoes competitive oxidation and protonation at room temperature in D_2O when in the presence of oxidants. Increasing chloride decreases the ratio k_{ox}/k_{H+} for **1** when $Na_2[Pt^{IV}Cl_6]$ is used as the oxidant, but when $CuCl_2$ is used as the oxidant, added chloride increases k_{ox}/k_{H+}. The one-electron oxidants, $Na_2[IrCl_6]$ and $(NH_4)_2[Ce(NO_3)_6]$, were also shown to oxidize **1**.

Introduction

Although the abundance and low cost of alkanes make them valuable chemical feedstocks, they have not been utilized to their full potential due to difficulties associated with their selective functionalization. About 35 years ago Shilov reported that oxidation of alkanes by an aqueous mixture of platinum-(II) and platinum(IV) salts at 120 °C gives the corresponding alcohols or alkyl chlorides with moderate selectivity (eq 1).[1] Mechanistic studies indicate that the catalysis involves three major steps, as shown in Scheme 1: (*i*) Pt(II) activates an alkane C−H bond to generate a Pt(II) alkyl; (*ii*) the Pt(II) alkyl is oxidized by hexachloroplatinate(IV) to a Pt(IV) alkyl; (*iii*) nucleophilic attack by water or chloride on the Pt(IV) alkyl affords the alcohol or alkyl chloride, respectively, and regenerates Pt(II).[2]
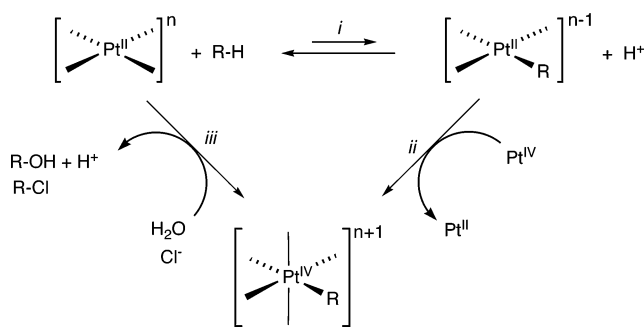
$$R-H + [Pt^{IV}Cl_6]^{2-} + H_2O \xrightarrow[H_2O, 120°\text{C}]{[Pt^{II}Cl_4]^{2-}} R-OH + (R-Cl)$$

$$(Cl^-) \qquad\qquad\qquad [Pt^{II}Cl_4]^{2-} + 2\ HCl \quad (1)$$

While the C−H activation step (*i*) is rate- and selectivity-limiting in the catalysis, the oxidation step (*ii*) provides the thermodynamic driving force for the reaction. Furthermore, since

Scheme 1

step (*i*) is highly reversible, oxidation of $[Pt^{II}-R]$ by $[Pt^{IV}Cl_6]^{2-}$ must be remarkably fast in order to compete with protonolysis. Studies on model complexes indicate that the oxidation step proceeds via a chloride-bridged intermediate, as shown in Scheme 2,[3] a common mechanism for Pt(II)−Pt(IV) redox reactions.[4] Isotopic labeling experiments have placed an upper limit on the rate of the self-exchange reaction between tetra-chloroplatinate(II) and hexachloroplatinate(IV)[5] that would be much too slow to compete with protonolysis. Nonetheless, two studies have demonstrated that the rate constant for oxidation of $[Pt^{II}-CH_3]$ is comparable to (at room temperature)[6] or much faster than (at 95 °C)[7] the competing protonolysis. The reasons for this great enhancement of reactivity are not entirely clear; possible factors include the lower oxidation potential of me-thylated Pt(II) complexes and/or the lower energy required for

(1) Goldshlegger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174−2175. Goldshlegger, N. F.; Eskova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1972**, *46*, 1353−1354. See also: Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: Dordrecht, 2000; pp 259−317.

(2) (a) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravskii, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729−733. (b) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004−3005. (c) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horvath, I. T.; Eller, K. *Organometallics* **1993**, *12*, 895−905. (d) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1994**, *13*, 755−756. (e) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75−91. (f) Hutson, A. C.; Lin, M.; Basickes, N.; Sen, A. *J. Organomet. Chem.* **1995**, *504*, 69−74.

(3) Scollard, J. D.; Day, M.; Labinger, J. A.; Bercaw, J. E. *Helv. Chim. Acta.* **2001**, *84*, 3247−3268.

(4) One-electron pathways are also known for some redox systems involving Pt(II) and/or Pt(IV). See: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic. Reactions*, 2nd ed.; John Wiley & Sons: New York, 1967; pp 494−497.

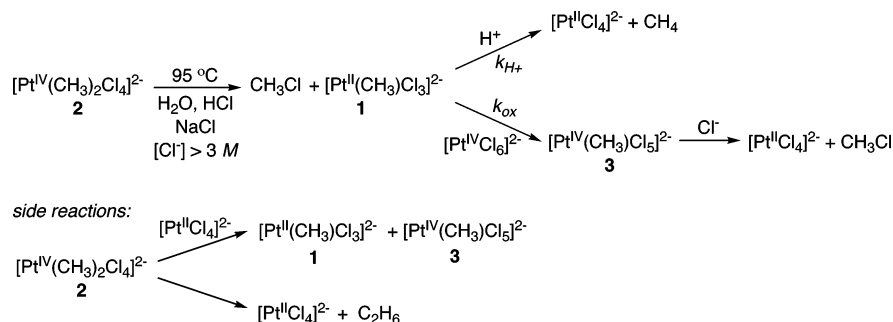(5) Rich, R. L.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 2608−2611.

(6) Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Catal. A* **1997**, *116*, 269−275.

(7) Zamashchikov, V. V.; Popov, V. G.; Litvinenko, S. L. *Russ. Chem. Bull.* **1993**, *42*, 352−358.

Scheme 2
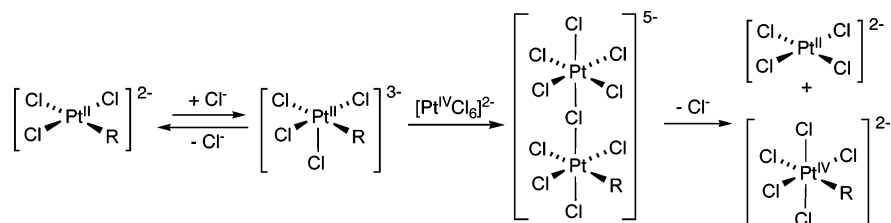
Scheme 3

formation of the five-coordinate species as a consequence of the greater *cis*- and *trans*-effects of a methyl ligand.[8]

A major practical limitation of the Shilov oxidation of alkanes is the use of $[Pt^{IV}Cl_6]^{2-}$ as a stoichiometric oxidant. Labeling studies indicate that this step occurs by electron transfer, not alkyl transfer, to Pt(IV); hence in principle it should be possible to substitute an inexpensive stoichiometric oxidant.[2e] There are strict constraints on suitable alternative oxidants; although they must be fast enough to oxidize [Pt^{II}−R] competitively with protonolysis, they must not rapidly oxidize inorganic Pt(II), i.e., $[Pt^{II}Cl_n(H_2O)_{4-n}]^{2-n}$, since that would deplete the species responsible for alkane activation. (Note that all inorganic ligands have been represented as chloride in schemes and structural formulas for simplicity; the species actually present will generally be a mixture of chloro/aquo complexes whose composition will vary with conditions.)

A variety of alternative oxidants, including chlorine,[9] hydrogen peroxide,[10] peroxydisulfate,[11] and the anode of an electrochemical cell[12] have been used with limited success. The most interesting examples are Wacker-like systems that use catalytic amounts of an oxidant that can in turn be reoxidized by dioxygen, making the latter the stoichiometric oxidant; significant numbers of turnovers have been achieved with both Cu^{II}-Cl$_2$[13] and a polyoxometalate.[14] All of the above still fall far short of what would be required for practical application, due in large part to catalyst inactivation, usually by deposition of metallic platinum. A bipyrimidine platinum(II) complex has been found to catalyze oxidation of methane to methyl bisulfate in high yield, using sulfuric acid as the oxidant and solvent;[15]

while it does not suffer from catalyst inactivation by deposition of metallic platinum, it still falls short of a practical process.[16]

A systematic approach toward replacing Pt(IV) with a more practical oxidant would be facilitated if we better understood how various oxidants function in the actual oxidation step; such information is difficult to glean from overall performance of a complex catalytic system. While, as noted above, the presumed Pt(II) alkyl that undergoes oxidation in the Shilov system is highly unstable to protonolysis, methods[6,7] that were developed for generating this species in situ and assessing its reactivity toward $[Pt^{IV}Cl_6]^{2-}$ may be readily extended to other oxidants. We report here the results of these studies.

Results and Discussion

Competitive Oxidation and Protonation at Elevated Temperature: Cu-Mediated Oxidation by O$_2$. Zamashchikov and co-workers determined the relative rates of protonolysis and oxidation of $[Pt^{II}(CH_3)Cl_3]^{2-}$ (**1**) by means of the system shown in Scheme 3[7] Here nucleophilic attack of chloride on the *di*methyl complex $[Pt^{IV}(CH_3)_2Cl_4]^{2-}$ (**2**) generates **1** (along with an equivalent of methyl chloride), which is competitively protonated to generate methane and $[Pt^{II}Cl_4]^{2-}$ and oxidized by $[Pt^{IV}Cl_6]^{2-}$ to monomethyl $[Pt^{IV}(CH_3)Cl_5]^{2-}$ (**3**). Complex **3** is unstable under the reaction conditions, undergoing nucleophilic attack by chloride (step (*iii*) of the overall Shilov mechanism) to generate an additional equivalent of CH$_3$Cl and $[Pt^{II}Cl_4]^{2-}$.

As shown in Scheme 3, there are two side reactions. Nucleophilic attack by $[Pt^{II}Cl_4]^{2-}$ on **2** generates **1** and **3**; however, this has no net effect on the final product distribution. Also, some ethane is reductively eliminated from **2**, but this is sufficiently slow relative to nucleophilic attack that only a very small amount of ethane (<5%) is generated. Hence the ratio of second-order rate constants for oxidation and protonation (k_{ox}/k_{H+}) could be determined from the relative yields of products along with the stoichiometry of reagents used and was found to be 18.4 ± 0.5.

(8) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; John Wiley & Sons: New York, 1967; pp 375−382.

(9) Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8−10.

(10) Devries, N.; Roe, D. C.; Thorn, D. L. *J. Mol. Catal. A* **2002**, *189*, 17−22.

(11) Basickes, N.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 13111−13112.

(12) Freund, M. S.; Labinger, J. A.; Lewis, N. S.; Bercaw, J. E. *J. Mol. Catal.* **1994**, *87*, L11−L16.

(13) Lin, M.; Shen, C.; Garcia-Zayas, E. A.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 1000−1001.

(14) Bar-Nahum, I.; Khenkin, A. M.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 10236−10237.

(15) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564.

(16) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514.

Table 1. k_{ox}/k_{H+} for a Variety of Oxidants Reacting with $[Pt^{II}(CH_3)Cl_3]^{2-}$ (1) at Constant $[H^+]^a$

entry	oxidant	k_{ox}/k_{H+}
1	$Na_2Pt^{IV}Cl_6$	20 ± 4
2	$Cu^{II}Cl_2$	191 ± 24
3	$O_2/Cu^{II}Cl_2{}^b$	173 ± 35
4	$Fe^{III}Cl_3$	14 ± 3
5	$Na_3[H_3PMo_9V_3O_{40}]^c$	15 ± 3
6	$Br_2{}^c$	210 ± 40

^{a} Except as noted, $[Cs_2Pt^{IV}(CH_3)_2Cl_4] = 0.002$ M; $[H^+] = 0.2$ M; [oxidant] ≥ 0.02 M; $[Cl^-] = 4$ M. ^{b} $[H^+] = 2$ M. ^{c} $[Cu^{II}Cl_2] = 0.001$ M, under excess O_2 (1 atm); $[H^+] = 0.02$ M. ^{d} $[Cl^-] = 3$ M. ^{e} [oxidant] = 0.01 M.
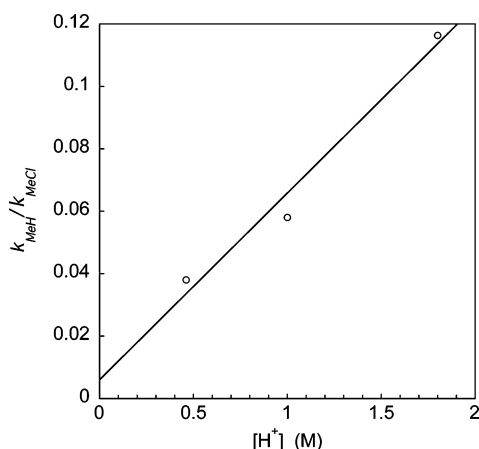
Figure 1. Dependence of k_{MeH}/k_{MeCl} on $[H^+]$ ($[Cu^{2+}] = 0.05$ M, $[Cl^-] = 4$ M).

In our hands, heating an aqueous solution of $Cs_2[Pt^{IV}(CH_3)_2Cl_4]$ (0.002 M) containing greater than 3 M chloride concentration at 95 °C for 9 days resulted in complete disappearance of $[Pt^{IV}(CH_3)_2Cl_4]^{2-}$ and generation of 1 equiv of methane, as determined by GC-MS. Under these reaction conditions CH_3Cl substantially decomposes (to CH_3OH) and cannot be accurately quantified; nonetheless the extent of competing oxidation (when an oxidant is present) can be calculated from the reduction in methane yield. Assuming the reaction is first-order in both oxidant and **1**, as is the case for $Na_2[Pt^{IV}Cl_6]$, the ratios of the "observed" rate constants for formation of CH_3Cl versus methane (k_{MeCl}/k_{MeH}) and the second-order rate constants for oxidation versus protonation (k_{ox}/k_{H+}) are found using eqs 2 and 3, respectively, where n is the number of moles of the corresponding species.[7]

$$\frac{k_{MeCl}}{k_{MeH}} = \frac{2n_{Cs_2Pt^{IV}(CH_3)_2Cl_4} - n_{EtH} - n_{MeH}}{n_{MeH}} \quad (2)$$

$$\frac{k_{ox}}{k_{H+}} = \frac{1}{2}\left(\frac{k_{MeCl}}{k_{MeH}} - 1\right)\frac{[H^+]}{[ox]} \quad (3)$$

The results for several different oxidants are shown in Table 1; that for $Na_2[Pt^{IV}Cl_6]$, 20 ± 4, is within experimental error of the previously reported value. As noted above, the calculation assumes first-order dependence on reagent concentration. Protonolysis was shown to be first-order in $[H^+]$ (for $CuCl_2$ as oxidant), as shown in Figure 1, while oxidation was shown to be first-order in oxidant for both $CuCl_2$ and $FeCl_3$, as shown in Figure 2.

The rapid oxidation by $CuCl_2$ is particularly striking. Oxidation of platinum(II) complexes by copper(II) halides could in principle proceed via either one- or two-electron mechanisms,

as shown in Scheme 4. In (*a*) an initial two-electron oxidation is followed by comproportionation of copper(0) and copper(II), while in (*b*) initial (rate-determining) one-electron oxidation generates $[Pt^{III}(CH_3)]$, which undergoes fast one-electron oxidation by a second Cu(II). The first-order dependence on [Cu(II)] could be consistent with either of these possibilities. For the all-inorganic analogue, for which the thermodynamics lie in the opposite direction ($[PtCl_6]^{2-}$ oxidizes Cu(I)), a one-electron route was proposed on the basis of kinetics;[17] but in fact, the kinetics could be consistent with the two-electron path as well. In a later study on oxidation of (N,C)-ligated Pt(II) complexes by CuX_2 the authors also preferred alternative (*b*), though not decisively so.[18]

The three oxidants Cu^{II}, Fe^{III}, and $Na_3[H_3PMo_9V_3O_{40}]$ are all capable of reoxidation by O_2 under certain conditions. (Bromine, the most reactive oxidant, would not be useful in a catalytic system because it is known to oxidize $[Pt^{II}Cl_4]^{2-}$.[19]) As noted above, efficient catalytic oxidation of substrates such as ethanesulfonic acid has been achieved with a $Pt/Cu/O_2$ system; in that case catalyst deactivation apparently does *not* involve Pt metal deposition.[13] That finding implies that (as in the Wacker process) reoxidation of Cu^I by O_2 is fast relative to other steps. Indeed, when **1** is generated from $[Pt^{IV}(CH_3)_2Cl_4]^{2-}$ (**2**) under an atmosphere of dioxygen in the presence of only half an equivalent of $CuCl_2$ (entry 3, Table 1), the same rate constant ratio is observed (within experimental error) as with excess $CuCl_2$ (entry 2, Table 1). A similar result could not be obtained with $FeCl_3$, as k_{ox}/k_{H+} varied from run to run when only half an equivalent of $FeCl_3$ was used under an atmosphere of dioxygen.

As for the polyoxometalate ($Na_3[H_3PMo_9V_3O_{40}]$), it is known to be reoxidizable by dioxygen; however, it is also difficult to obtain as a pure trivanadium species;[20] furthermore, it proved to be partially insoluble under our reaction conditions, so it was not tested in the presence of dioxygen. It is encouraging though that stoichiometric oxidation of **1** could be observed, at a rate close to that of $[Pt^{IV}Cl_6]^{2-}$ (Table 1).

One likely mode of catalyst inactivation with the $CuCl_2/O_2$ system is suggested by the observation that $Cs_2[Pt^{IV}Cl_6]$ crystallizes out of solution during the course of this reaction, indicating oxidation of $[Pt^{II}Cl_4]^{2-}$. That would not be effected by either $CuCl_2$ (the reverse reaction takes place: see above) or O_2 alone. Presumably, peroxidic species (possibly free peroxide or some sort of copper–peroxide complex) formed during the reoxidation of copper(I) with dioxygen[21] are responsible. Because in the accepted mechanism $[Pt^{II}Cl_4]^{2-}$ is required for C–H activation, such a process would gradually remove a crucial component of the system and shut down the catalytic reaction.

Competitive Oxidation and Protonation at Room Temperature: Chloride Effects. The above probe generates the key intermediate $[Pt^{II}(CH_3)Cl_3]^{2-}$ (**1**) by reaction of $[Pt^{IV}(CH_3)_2Cl_4]^{2-}$ (**2**) with chloride and, hence, requires high $[Cl^-]$. This may be problematic in several regards. First, since excess chloride inhibits the C–H activation step in the Shilov system,[1] the

(17) Moodley, K. G.; Nicol, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 239–243.

(18) van Beek, J. A. M.; van Koten, G.; Wehman-Ooyevaar, I. C. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 883–893.

(19) Preetz, W.; Rimkus, G. *Z. Naturforsch, B: Chem. Sci.* **1983**, *38B*, 442–445.

(20) Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171–198.

(21) (a) Henry, P. M. *Inorg. Chem.* **1966**, *5*, 668–669. (b) Jhaveri, A. S.; Sharma, M. M. *Chem. Eng. Sci.* **1967**, *22*, 1–6. (c) Gray, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 56–62. (d) Stevanato, R.; Argese, E.; Viglino, P. *Inorg. Chim. Acta.* **1984**, *92*, 177–180. (e) Goldstein, S.; Czapski, G. *Inorg. Chem.* **1985**, *24*, 1087–1092.

Figure 2. Dependence of k_{MeCl}/k_{MeH} on $[Cu^{2+}]$ (left) and $[Fe^{3+}]$ (right) ($[H^+] = 2$ M, $[Cl^-] = 4$ M).

Scheme 4

Scheme 5

chloride level for this experiment differs significantly from that of the "real" reaction, potentially affecting the platinum speciation in solution. Second, the rate at which **1** is oxidized is likely to be $[Cl^-]$-dependent in the mechanism of Scheme 2. Finally, the chloride concentration affects the oxidation potential of a variety of oxidants,[22] including some of those examined here.

We have previously reported an alternate route to transient **1** that does not require excess Cl^-.[6] Reduction of $Na_2[Pt^{IV}(CH_3)-Cl_5]$ with cobaltocene in tetrahydrofuran (THF) precipitates a mixture of cobaltocenium salts of $[Pt^{II}(CH_3)Cl_3]^{2-}$ (**1**), $[Pt^{II}(CH_3)_2Cl_2]^{2-}$ (**4**), and $[Pt^{II}Cl_4]^{2-}$ (along with some NaCl), which upon addition to a solution of $Na_2[Pt^{IV}Cl_6]$ in D_2O exhibits competitive protonolysis and oxidation of **1**; the relative rates can be determined from the yield of $[Pt^{IV}(CH_3)Cl_5]^{2-}$ (**3**) (Scheme 5). In that earlier study, carried out under a limited range of acid and oxidant concentrations, it appeared that **4** was completely oxidized to $[Pt^{IV}(CH_3)_2Cl_4]^{2-}$ (**2**) (which is stable under the reaction conditions), even at low levels of $[Pt^{IV}Cl_6]^{2-}$, indicating that $[Pt^{II}Cl_4]^{2-}$ is also capable of effecting oxidation of **4**, presumably with formation of Pt^0. The rate constant ratio for oxidation versus deuterolysis (k_{ox}/k_{D+}) at 22 °C was estimated at approximately 2.55; using an independent determination of

the isotope effect ($k_{H+}/k_{D+} \approx 9$)[23] gave $k_{ox}/k_{H+} \approx 0.3$, around 2 orders of magnitude lower than at 95 °C.[6]

On repeating those experiments, we find the results are not quite so straightforward as previously reported. In the first place, deuterolysis is competitive with oxidation for *both* **1** and **4**, as shown in Scheme 5: increasing the amount of acid (by adding D_2SO_4) results in a reduction of the yields of both **2** and **3**. Since **2** was used as an internal standard for NMR quantitation, the assumption that its yield was invariant introduced some error. Second, the yields are not as reproducible as suggested by the earlier limited study. This is not too surprising because of the way the experiment is (necessarily) performed: the solid mixture of Pt(II) salts is dissolved directly in the solution with which it reacts, probably causing the local concentrations of reagents to change drastically and irreproducibly as the solid dissolves. From an extensive series of experiments measuring the amounts of **2** and **3** generated, rate constant ratios for oxidation versus deuterolysis (k_{ox}/k_{D+}) at 22 °C were determined to be 7.7 ± 0.9 for **1** and 14 ± 2 for **4**. This translates into a k_{ox}/k_{H+} of about 0.9 for **1**. (Tabular results for the specific experiments are provided in the Supporting Information.)

The difference between the two findings suggest that the k_{ox}/k_{H+} value determined by this method is only accurate to within a factor of 3 or so, but it is clearly significantly lower than that obtained at 95 °C with high chloride concentrations. Previously, this was attributed to the large temperature difference between the two studies; however, the large difference in chloride concentration between the two studies could also affect k_{ox}/k_{H+}, if the kinetic order in chloride for oxidation and protonation differ. Under the same conditions but with 3.0 M added chloride, k_{ox}/k_{D+} was determined to be 3.5 ± 0.4 for **1** and 5.0 ± 0.9 for **4**. Thus there is a chloride dependence on the ratio, with k_{ox}/k_{H+} for **1** about 0.4 under high chloride (vis-à-vis 0.9 at low chloride concentration) at 22 °C.

An analogous determination of k_{ox}/k_{H+} and its dependence on chloride concentration for $CuCl_2$ is complicated by the effect of paramagnetic copper(II), which makes it difficult to integrate

(22) Latimer, W. M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2 ed.; Prentice Hall: New York, 1952. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley & Sons: New York, 1999.

(23) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961−5976.

Table 2. Ability of Cu(II) Salts to Oxidize [Pt^{IV}(CH$_3$)Cl$_3$]$^{2-}$ (1) to [Pt^{II}(CH$_3$)Cl$_5$]$^{2-}$ (3) under Different Conditions^a

entry	oxidant	added Cl$^-$	added H$^+$	3 formed (>35%)
1	Cu^{II}Cl$_2$			yes
2	Cu^{II}Cl$_2$		0.35 N D$_2$SO$_4$	no
3	Cu^{II}Cl$_2$	3 M	0.35 N D$_2$SO$_4$	yes
4	Cu^{II}Br$_2$			yes
5	Cu^{II}X$_2$^{b}			no

^{a} [Pt^{II}(CH$_3$)Cl$_3$]$^{2-}$ = 0.005 M. [Cu^{II}] = 0.24 M. ^{b} X = perchlorate, triflate, acetate, sulfate.

^{1}H NMR peaks in the spectrum; hence only qualitative results can be obtained (Table 2). It is clear that some additional halide (there is always a small amount of chloride present in these experiments, as the precipitated mixed cobaltocenium/Pt(II) salts contain some NaCl) is needed for the oxidation even in the absence of added acid, and quite high [Cl$^-$] is needed to compete at low pH. This requirement for relatively high chloride concentration could be due to the role of bridging halide, if an inner-sphere oxidation mechanism (Schemes 2, 4a) is followed. It is also well known that Cu(II) is a stronger oxidant at higher halide concentrations and further that one-electron oxidations are favored in the presence of chloride or bromide.[24] Substantial oxidation of [Pt^{II}(CH$_3$)$_2$Cl$_2$]$^{2-}$ (4) to [Pt^{IV}(CH$_3$)$_2$Cl$_4$]$^{2-}$ (2) was observed in all these experiments, confirming that oxidation of 4 is more facile than oxidation of [Pt^{II}(CH$_3$)Cl$_3$]$^{2-}$ (1) to [Pt^{IV}(CH$_3$)Cl$_5$]$^{2-}$ (3).

To test the possibility of a one-electron pathway (such as that depicted in Scheme 4b) for oxidation of [Pt^{II}(CH$_3$)Cl$_3$]$^{2-}$ (1), Na$_2$[Ir^{IV}Cl$_6$] and (NH$_4$)$_2$[Ce^{IV}(NO$_3$)$_6$] were examined. These are known one-electron oxidants, which could not be tested by the high-temperature route (Na$_2$[IrCl$_6$] because it directly oxidizes methane;[25] Ce(IV) because at high chloride concentrations it oxidizes chloride[22]). Indeed, addition of the mixed Pt-(II) salts to a D$_2$O solution containing an excess of either Na$_2$[IrCl$_6$] or (NH$_4$)$_2$[Ce(NO$_3$)$_6$] resulted in significant oxidation of both 1 and [Pt^{II}(CH$_3$)$_2$Cl$_2$]$^{2-}$ (4), indicating that a one-electron oxidation pathway can be rapid for these oxidants and, by extension, may be plausible for Cu(II) and Fe(III) as well. Finally, Na$_3$[H$_3$PMo$_9$V$_3$O$_{40}$], bromine, and hydrogen peroxide also were shown to oxidize 1 (and 4) in D$_2$O at room temperature in the absence of added chloride.

Conclusions

The competitive oxidation and protonation of the monomethylplatinum(II) salt (1) involved in the Shilov system was studied in order to gain insight into the possibility of using an inexpensive stoichiometric oxidant for the replacement of Na$_2$[Pt^{IV}Cl$_6$]. When Na$_2$[Pt^{IV}Cl$_6$] is used as the oxidant, chloride has been shown to decrease the ratio of oxidation to protonation of 1, while high temperatures have been shown to increase the ratio of oxidation to protonation. This implies that oxidation has a considerably higher activation energy than does protonolysis. The chloride dependence of k_{ox}/k_{H+} is modest and may represent either inhibition of oxidation or acceleration of protonolysis (or both) by chloride. From the mechanism of Scheme 2, oxidation is expected to be accelerated by chloride, but this could be balanced by a similar effect on protonolysis.[26] Shifting the speciation equilibrium could then favor more highly

chlorinated species that are harder to oxidize. In any case, the conditions of the "real" Shilov system (low chloride concentrations, temperatures of about 120 °C) highly favor oxidation by Pt(IV) over protonation, and any alternative oxidant must also compete quite efficiently with protonation.

Ideally, the Shilov oxidation of alkanes would be performed under an atmosphere of oxygen with an oxidant that could oxidize 1, generating a reduced form that could be reoxidized by dioxygen. To this end, a variety of oxidants were shown to oxidize 1, including CuCl$_2$, FeCl$_3$, and Na$_3$[H$_3$PMo$_9$V$_3$O$_{40}$], all of which could potentially be reoxidized by dioxygen. CuCl$_2$ was actually shown to oxidize 1 catalytically in the presence of excess dioxygen; however under these conditions, the catalyst in the Shilov system, [Pt^{II}Cl$_4$]$^{2-}$, is also oxidized. This could prove problematic for the use of CuCl$_2$ as a catalytic co-oxidant for the Shilov system.

Both CuCl$_2$ and FeCl$_3$ oxidize 1 with a first-order dependence on oxidant. The oxidation of 1 by copper(II) was shown to be highly dependent on the counteranion—only chloride and bromide proved competent—and oxidations by CuCl$_2$ are highly dependent on chloride concentration. In contrast to the case of Na$_2$Pt^{IV}Cl$_6$, decreasing the chloride concentration decreases the rate at which CuCl$_2$ oxidizes 1.

At this time we cannot determine whether oxidation by Cu-(II) goes via a one- or a two-electron pathway. The fact that one-electron oxidants such as Na$_2$Ir^{IV}Cl$_6$ and (NH$_4$)$_2$Ce^{IV}(NO$_3$)$_6$ rapidly oxidize 1 implies the former is quite reasonable, but the kinetics could be consistent with either, and the [Cl$^-$] dependence might reflect the effect of chloride concentration on the one-electron oxidation potential of copper(II) or the chloride requirement of a bridged intermediate in a two-electron pathway.

Experimental Section

General Considerations. Platinum salts were obtained from Strem. Anhydrous lithium chloride was purchased from Aldrich. Hydrochloric acid (aq, 6.25 M) was purchased from VWR. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Cesium dimethyltetrachloroplatinate(IV)[1] and Na$_3$[H$_3$PMo$_9$V$_3$O$_{40}$][27] were prepared according to literature procedures. NMR spectra were acquired on a Varian Mercury 300 (^{1}H, 299.8 MHz) spectrometer at 23 °C. NMR shifts were referenced relative to internal solvent: 4.80 (s) (deuterium oxide) and 2.50 (m) (dimethyl sulfoxide-d_6). GC-MS data were collected using a Hewlett-Packard 5890 gas chromatograph with a HP-PLOT Q column and a Hewlett-Packard 5973 mass spectrometer.

Oxidation versus Protonolysis of Monomethylplatinum(II) Complex (1) at Elevated Temperature. To determine the baseline methane yield, a solution of 1.94 g of anhydrous lithium chloride in about 8 mL of deionized water was cooled to room temperature, and 34.8 mg of Cs$_2$[Pt^{IV}(CH$_3$)$_2$Cl$_4$] added. This solution was then injected into the reaction vessel using a plastic syringe with a Teflon needle and washed in with additional deionized water to give a total of 17 mL of solution in the reaction vessel. The reaction vessel consisted of a round-bottom flask with a small stir bar sealed inside. The only opening to the flask was a stopcock with a short (1.5 cm) hose adaptor on the other side. The total internal volume of the flask was about 31 mL. The solution was then degassed and filled with helium. With the stopcock open and connected via a rubber hose to a helium source and a mercury bubbler, the flask was heated to 368 K. Then, 7.0 mL of 6.25 M hydrochloric acid (aq) was

(24) Malyszko, J.; Kaczor, M. *J. Chem. Educ.* **2003**, *80*, 1048–1050.

(25) Control experiments revealed that under these conditions Na$_2$[Ir^{IV}Cl$_6$] oxidizes methane in the absence of platinum. There is precedent for iridium(IV) oxidation of alkanes. See: Shilov, A. E. *Activation of Saturated Hydrocarbons with Transition Metal Complexes*; D. Reidel: Dordrecht, The Netherlands, 1984; pp 66–67.

(26) For a previous indication of the possible involvement of chloride in the protonolysis of platinum(II) methyl species, see: Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966–4968.

(27) Grate, J. H.; Hamm, D. R.; Saxton, R. J. International Patent Application Publication Number WO 91/13681, 1991.

injected into the flask through the hose connected to the stopcock, using a plastic syringe with a Teflon needle. The stopcock was sealed, and the rubber hose was removed. The hose adapter on the stopcock was then capped with a rubber septum held down by copper wire. Using a syringe, the capped hose adapter was then filled with silicon oil in order to minimize exchange of gases between the air and the head space of the reaction vessel during sampling. The air in the capped hose adapter was drained with a needle as it was being filled with silicon oil. Then 200 μL of argon at 1 atm, for use as an internal standard, was added to the head space inside the vessel via syringe. The reaction was stirred at 368 K for 9 days, at which point consumption of **2** was complete as determined by the completion of methane generation. A 50 μL sample of the head space gas was injected into the GC-MS for analysis of argon, methane, ethane, carbon dioxide, and methyl chloride. (In a separate experiment, methyl chloride was found to decompose under the reaction conditions in the absence of $Cs_2[Pt(CH_3)_2Cl_4]$, while methane, ethane, and carbon dioxide were stable.) The final volume of solution in the vessel was measured at 368 K using a graduated cylinder in order to determine the exact concentrations of reagents.

For determination of relative rates, the desired amount of appropriate oxidant was added to the solution before heating, and the reaction carried out as above. Some reactions were carried out under an atmosphere of dioxygen instead of helium. The crystals that deposited at the end of the reaction using $CuCl_2$ and dioxygen were identified as $Cs_2[Pt^{IV}Cl_6]$ by matching the X-ray crystallographic unit cell parameters to published values.

Oxidation versus Protonolysis of Monomethylplatinum(II) Complex (1) at Room Temperature. The solid mixture of cobaltocenium salts containing **1** was prepared as previously described.[6] A solution containing the desired amounts of oxidant, lithium chloride, and (in some cases) D_2SO_4 in 1.0 mL of D_2O

was added to 20 mg of the solid mixture with vigorous stirring. The reaction was stirred for 20 min before being centrifuged. The supernatant was then transferred to an NMR tube for analysis by ^1H NMR spectroscopy. Quantification was achieved using the signals of either added sodium *p*-toluenesulfonate or THF (present in the solid mixture) as internal standard; separate experiments showed that the amount of THF relative to sodium *p*-toluenesulfonate remained the same under all reaction conditions tested. k_{ox}/k_{D+} was determined for **4** and for **1** using eqs 4 and 5, respectively. $[1]_0$ and $[4]_0$ represent the initial concentrations of the respective platinum(II) species in solution. This was determined from the reaction in which **5** was dissolved in D_2O with 0.12 M $[Na_2Pt^{IV}Cl_6]$ because in this reaction both **1** and **4** were completely oxidized. The concentrations of the methylplatinum(IV) species were determined by ^1H NMR spectroscopy at the end of the reaction.

$$\textbf{4}: \frac{k_{ox}}{k_{D+}} = \frac{[\textbf{2}]}{[\textbf{4}]_0 - [\textbf{2}]} \frac{[D^+]}{[ox]} \tag{4}$$

$$\textbf{1}: \frac{k_{ox}}{k_{D+}} = \frac{[\textbf{3}]}{([\textbf{1}]_0 + [\textbf{4}]_0) - [\textbf{3}] - [\textbf{2}]} \frac{[D^+]}{[ox]} \tag{5}$$

Supporting Information Available: Detailed tabular results of room-temperature experiments are available free of charge via the Internet at http://pubs.acs.org.