

# Catalytic hydroxylation using chloroplatinum compounds

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## Abstract

Using “PtCl<sub>4</sub>” as the Pt(IV) component in the mixture of aqueous chloroPt(II)/chloroPt(IV) compounds makes the “Shilov” functionalization of alkyl groups considerably faster and more chemoselective to alcohols, and adding hydrogen peroxide re-oxidizes the Pt(II) reduction product to Pt(IV). Run in this manner, the reaction system is long-lived and catalytic in platinum. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic hydroxylation; Chloroplatinum compounds; Shilov

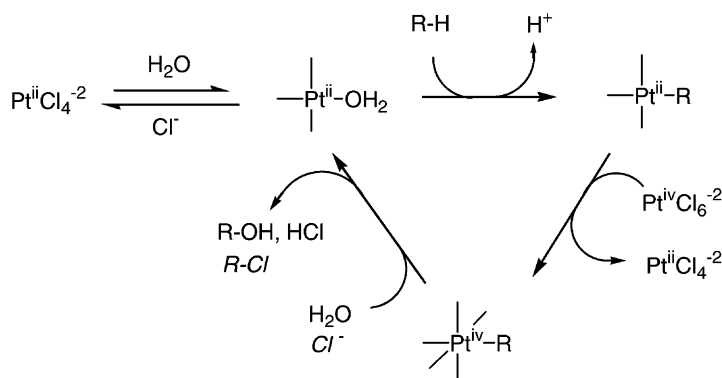
## 1. Introduction

Alkane functionalization by a combination of Pt(II) and Pt(IV) chlorides, often called the “Shilov” reaction, has fascinated chemists for many years (for reviews see Chapter VII of [1], [2,3] and Chapter V of [4]). Several researchers have established the key steps of the reaction mechanism [1–9] and identified conditions under which polyfunctional products are formed [2,3,10–12]. We were especially interested in reports that *n*-propanol is hydroxylated to form propane-1,3-diol [5,11,12] and *n*-butanol is functionalized to form tetrahydrofuran (THF) [12] because both of these products are monomers for commercially important polyethers and polyesters. However, most of these reports describe reactions that are stoichiometric in platinum, and devising useful catalytic “Shilov” systems has been challenging [2,3]. For the Pt(II)/Pt(IV)-chloride system, catalytic hydroxylation of toluenesulfonic acid [13], of alkanesulfonates [14], and of amino acids [15] is known, conversion of methane to methyl bisulfate has been reported for

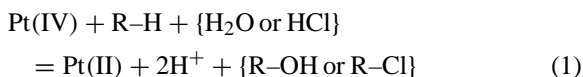
a reaction system based on a bipyrimidyl–platinum complex [16]. In the published reports, the syntheses of  $\alpha,\omega$  diols are stoichiometric in Pt(IV). Here we describe means of making the Pt(II)/Pt(IV)-chloride system catalytic in platinum for the conversion of *n*-propanol to diols.

We first summarize the important features of the mechanism of the typical reaction system, which uses chloroPt(II) and Pt(IV)Cl<sub>6</sub><sup>2-</sup> species (Scheme 1) [1–9]. The rate-determining step is the activation of a C–H bond by a chloroPt(II) center, which is believed to be Cl<sub>3</sub>Pt(OH<sub>2</sub>)<sup>-</sup> or Cl<sub>2</sub>Pt(OH<sub>2</sub>)<sub>2</sub> [1–9], and it is important to note that Cl<sub>4</sub>Pt<sup>2-</sup> itself apparently does not activate alkyl C–H bonds at useful rates under mild reaction conditions, e.g. aqueous solution at approximately 100 °C. (The challenge of modeling this key step, which may involve formal oxidative addition of the alkane C–H bond to the Pt center, has prompted the discovery of several remarkable activation/addition reactions described in [1,4,17–19]). After the C–H activation step, the first-formed Pt-alkyl intermediate reacts with Pt(IV)Cl<sub>6</sub><sup>2-</sup> to form a Pt(IV)-alkyl intermediate, which in turn reacts with nucleophilic chloride or water to form Pt(II), and the corresponding

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chloro- or hydroxy-functionalized organic product. The overall transformation is given in Eq. (1).



It has been pointed out that Pt(IV), typically present as  $\text{Pt(IV)Cl}_6^{2-}$ , plays several roles in the reaction mixture. In addition to oxidizing the initial Pt-alkyl intermediate to the Pt(IV)-alkyl species and serving as the stoichiometric oxidant, it also suppresses the formation of metallic platinum by minimizing the disproportionation of Pt(II) (Eq. (2)) [20]. Metallic platinum promotes the oxidation of aliphatic alcohols to aldehydes or acids, thus, destroying our hoped-for products, and we recognized very early in our studies that metallic platinum must be excluded from the reaction system [20,21].



There is yet an additional role played by  $\text{Pt(IV)Cl}_6^{2-}$  in the reaction mixture: It apparently inhibits the alkyl C–H bond activation step [5]. The inhibition may result from  $\text{Pt(IV)Cl}_6^{2-}$  hydrolyzing to aquo-Pt(IV) compounds with release of chloride, and chloride in turn “ties up” the Pt(II) as the inactive  $\text{Cl}_4\text{Pt}^{2-}$  complex. Alternatively, inhibition may result from a direct reaction of  $\text{Pt(IV)Cl}_6^{2-}$  with Pt(II) to make chloro-bridged platinum clusters [22]. But regardless of the actual means by which  $\text{Pt(IV)Cl}_6^{2-}$  inhibits the C–H bond activation step, using excess  $\text{Pt(IV)Cl}_6^{2-}$  to suppress the formation of metallic platinum is not necessarily the best way to run the reaction system, and

some other non-inhibiting means of suppressing the formation of metallic platinum would be very useful.

## 2. Experimental

**Caution!** The combination of hydrogen peroxide with organic compounds can conceivably give rise to explosive organic peroxides or hydroperoxides. During the experiments conducted in this study, we observed no unexpected reaction activity, and we suspect that organic peroxy compounds were either never formed or were immediately decomposed by Pt(II)/Pt(IV). Nevertheless, we urge anyone performing similar experiments to take every precaution against the possible accumulation of explosive compounds.

Platinum compounds  $\text{Na}_2\text{PtCl}_6$ ,  $\text{Na}_2\text{PtCl}_4$ -hydrate, and “ $\text{PtCl}_4$ ” were obtained from Strem Chemicals Inc. The “ $\text{PtCl}_4$ ” contained some moisture, and some  $\text{PtCl}_5(\text{OH}_2)^-$  and  $\text{PtCl}_6^{2-}$  as well as several additional Pt(IV) complexes were evident in the  $^{195}\text{Pt}$  NMR spectra of aqueous solutions of “ $\text{PtCl}_4$ ”. *n*-Propanol, trifluoromethanesulfonic acid, and 30% aqueous hydrogen peroxide were obtained from Aldrich.

In a typical hydroxylation experiment, 3 ml water, 0.5 g trifluoromethanesulfonic acid, 0.07 g  $\text{Na}_2\text{PtCl}_4$ -hydrate, and 0.5 g “ $\text{PtCl}_4$ ” were added to a flask equipped with a condenser, then *n*-propanol was added in portions (initially 1 ml, a total of 4 ml over the duration of the experiment). The flask was heated to 92 °C and the mixture was then treated dropwise with 30% hydrogen peroxide (**Caution!**) at

a rate varying from approximately 0.7 to 2 drops/min, sufficient to keep the mixture from depositing metallic platinum. After approximately 15 h, the mixture was analyzed by  $^1\text{H}$  NMR and found to contain 1,3-propanediol (ca. 2.2 mmol) together with lesser amounts of 1,2-propanediol and acetic acid (ca. 0.8 mmol each), and much smaller amounts of several additional unidentified products. The amount of 1,3-propanediol corresponds to 1.3 turnovers of the entire Pt content, or about 0.09 turnovers/h; the total amount of organic products, 1,3-diol plus 1,2-diol plus acetic acid, corresponds to about 2.3 turnovers of the entire Pt content or 0.15 turnovers/h.

In another similar demonstration, 1.4 mmol 1,3-propanediol, 0.5 mmol 1,2-propanediol and 0.5 mmol acetic acid were the major products obtained by adding hydrogen peroxide dropwise to a hot aqueous solution initially charged with *n*-propanol, trifluoromethanesulfonic acid and 0.55 mmol  $\text{Na}_2\text{Pt(II)Cl}_4$ .

The  $^{195}\text{Pt}$  NMR signals ( $\text{D}_2\text{O}$ ,  $\text{Pt(IV)Cl}_6^{2-}$  reference) of  $\text{Pt(IV)Cl}_6^{2-}$  (0 ppm),  $\text{Pt(IV)Cl}_5(\text{OH}_2)^-$  (497 ppm) and *cis*- and *trans*- $\text{Pt(IV)Cl}_4(\text{OH}_2)_2$  (986 and 918 ppm, respectively) were each split by ca. 0.2 ppm according to the isotopomeric distribution of  $^{35}\text{Cl}/^{37}\text{Cl}$ . The relative intensity of each component fits well to the calculated statistical ratios, confirming the assignments [24,26]. The  $^{195}\text{Pt}$  NMR spectrum of a stock solution of commercial  $\text{Na}_2\text{Pt(II)Cl}_4$ -hydrate had a dominant peak at  $-1626$  ppm ( $\text{Cl}_4\text{Pt(II)}^{2-}$ ) with weaker peaks at  $-1190$  and  $0$  ppm ( $\text{Cl}_3\text{Pt(II)(OH}_2)^-$  and  $\text{Pt(IV)Cl}_6^{2-}$ , respectively) [23–25]. The  $^{195}\text{Pt}$  NMR spectrum of a stock solution of commercial “ $\text{Pt(IV)Cl}_4$ ” had dominant peaks at 986 and 497 ppm (*cis*- $\text{Pt(IV)Cl}_4(\text{OH}_2)_2$  and  $\text{Pt(IV)Cl}_5(\text{OH}_2)^-$ , respectively) with a weak peak at  $0$  ( $\text{Pt(IV)Cl}_6^{2-}$ ) and weak unassigned peaks (not observably split by isotopomeric chloride distribution) at 848, 886, 1111, 1316, 1492 and 1596 ppm. When solutions of  $\text{Cl}_4\text{Pt(II)}^{2-}$  were treated with  $\text{H}_2\text{O}_2$  or when aqueous mixtures of  $\text{Cl}_4\text{Pt(II)}^{2-}$  and “ $\text{Pt(IV)Cl}_4$ ” were heated, the peak assigned to  $\text{Cl}_4\text{Pt(II)}^{2-}$  weakened, the peak assigned to  $\text{Cl}_3\text{Pt(II)(OH}_2)^-$  became stronger, as did peaks assigned to  $\text{Pt(IV)Cl}_6^{2-}$  and  $\text{Pt(IV)Cl}_5(\text{OH}_2)^-$ . Additional unassigned (unsplit)  $^{195}\text{Pt}$  NMR signals at  $-1325$ ,  $-1003$ ,  $-819$ ,  $-644$ ,  $-518$ , 1169, 1402, 1531, 1828, 1997 and 2230 ppm were observed in solutions of  $\text{Cl}_4\text{Pt(II)}^{2-}$  treated with  $\text{H}_2\text{O}_2$  or in heated aqueous mixtures of  $\text{Cl}_4\text{Pt(II)}^{2-}$  and “ $\text{Pt(IV)Cl}_4$ ”.

### 3. Results and discussion

The mechanism by which this reaction operates, as outlined earlier, places stringent requirements on the reaction system. In particular, it appears necessary for both Pt(II) and Pt(IV) to be present in the reaction system: The Pt(II) performs the initial alkane C–H bond activation, and the Pt(IV) suppresses metallic Pt formation and oxidizes alkylplatinum intermediates. If the role of the Pt(IV) had been strictly limited to oxidizing alkylplatinum intermediates, it would be useful to seek another oxidant for this purpose, and  $\text{CuCl}_2$  and  $\text{CuCl}_2/\text{O}_2$  are attractive candidates [14,15]. However, in order for us to have an indefinitely long-lived catalytic reaction system we need to prevent the formation of metallic platinum, short- and long-term. For this purpose either strongly-binding ligand/substrate [15], or substantial amounts of Pt(IV) to force the reverse of the reaction in Eq. (2), appears to be required. Therefore, we sought some means of having a substantial amount of Pt(IV) present yet avoiding the inhibition observed for  $\text{Pt(IV)Cl}_6^{2-}$ .

We reasoned that this might be accomplished if we used “ $\text{PtCl}_4$ ” for the Pt(IV) component instead of  $\text{Pt(IV)Cl}_6^{2-}$ , based on the expectation that “ $\text{PtCl}_4$ ” might accept chloride instead of release chloride. We hoped to observe improvements in three inter-related aspects.

First, by accepting chloride, the Pt(IV) population should increase the rate of C–H bond activation by increasing the amounts of  $\text{Cl}_3\text{Pt(OH}_2)^-$  and/or  $\text{Cl}_2\text{Pt(OH}_2)_2$  relative to  $\text{Cl}_4\text{Pt}^{2-}$ , i.e. by accepting chloride from the solution and the Pt(II) population, the Pt(IV) population should promote the functionalization reaction rather than inhibit it.

Second, a chloride-accepting Pt(IV) population should scavenge nucleophilic chloride, thus, diminish the amount of chloroorganic products and improve the selectivity for alcohols or ethers.

Third, if the chloride-accepting Pt(IV) population promotes the desired reaction and improves the desired selectivity, we are free to use as large a concentration of Pt(IV) as necessary to entirely suppress the formation of metallic platinum.

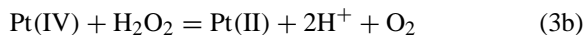
As hoped, all three aspects were improved by the use of “ $\text{PtCl}_4$ ” for the Pt(IV) component instead of  $\text{Pt(IV)Cl}_6^{2-}$ .

- (i) In a side-by-side comparison, an aqueous solution prepared with 0.05 M Na<sub>2</sub>Pt(II)Cl<sub>4</sub>, 0.50 M “PtCl<sub>4</sub>”, and 0.58 M *n*-propanol initially formed polyfunctional products (mostly 3-chloro-1-propanol and 1,3-propanediol) approximately 10 times faster at 100 °C than an aqueous solution prepared with 0.05 M Na<sub>2</sub>Pt(II)Cl<sub>4</sub>, 0.50 M Na<sub>2</sub>PtCl<sub>6</sub>, and 0.58 M *n*-propanol.
- (ii) The polyfunctional products obtained in the initial stages of these reactions (5–10% conversion of *n*-propanol or approximately 0.5 to 1 turnover of the initial amount of Pt(II)) had noticeably less (ca. 50% versus 70%) chloropropanol when “PtCl<sub>4</sub>” was used for the Pt(IV) component than when Na<sub>2</sub>PtCl<sub>6</sub> was used.
- (iii) A solution prepared with 0.05 M Na<sub>2</sub>PtCl<sub>4</sub>, 0.20 M “PtCl<sub>4</sub>” and 0.02 M *n*-propanol did not form an observable deposit of metallic platinum within 2 days at 98 °C, whereas similar solutions prepared with 0.10 M Na<sub>2</sub>PtCl<sub>4</sub>, 0.15 M “PtCl<sub>4</sub>”, and 0.02 M *n*-propanol did deposit metallic platinum during this time. Thus, the solution prepared in (i) having 0.5 M “PtCl<sub>4</sub>” and 0.05 M Cl<sub>4</sub>Pt<sup>2-</sup> contains Pt(IV) well in excess of the amount required for the long-term suppression of metallic platinum by Pt(II)-disproportionation, yet is quite active for the functionalization of *n*-propanol.

While we can rationalize these improvements by the mechanistic reasoning given above, there may well be entirely different factors not yet recognized. It is clear that these reaction mixtures are far more complex than suggested in Scheme 1. From <sup>195</sup>Pt NMR studies of several mixtures representative of different stages in these reactions, we have observed a total of 23 signals, of which we have been able to assign only Pt(IV)Cl<sub>6</sub><sup>2-</sup>, Pt(IV)Cl<sub>5</sub>(OH<sub>2</sub>)<sup>-</sup>, *cis*- and *trans*-Pt(IV)Cl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>, Cl<sub>4</sub>Pt(II)<sup>2-</sup>, and Cl<sub>3</sub>Pt(II)(OH<sub>2</sub>)<sup>-</sup> [23–25]. Consistent with the reasoning outlined above, combining “PtCl<sub>4</sub>” with Cl<sub>4</sub>Pt(II)<sup>2-</sup> does increase the intensity of the “Cl<sub>3</sub>Pt(II)(OH<sub>2</sub>)<sup>-</sup>” signal (–1190 ppm) at the expense of the Cl<sub>4</sub>Pt(II)<sup>2-</sup> signal (–1626 ppm), but also changes the relative populations of other species as well.

The use of “PtCl<sub>4</sub>” instead of Pt(IV)Cl<sub>6</sub><sup>2-</sup> for the Pt(IV) component improves several aspects of the

reaction, but there remains the need for a stoichiometric oxidant. The Pt(IV) population can serve as the stoichiometric oxidant but by doing so, the concentration of Pt(IV) necessarily decreases while the concentration of Pt(II) necessarily increases during the course of the reaction (Eq. (1)). Without an oxidant to convert Pt(II) back to Pt(IV), eventually the concentration of Pt(II) builds up to the point that disproportionation (Eq. (2)) occurs, metallic platinum is formed, and alcohols are converted to aldehydes and/or acids. We found that added hydrogen peroxide oxidizes Pt(II) to Pt(IV) [25,26], simplistically according to Eq. (3a). Although inefficient in H<sub>2</sub>O<sub>2</sub>, if excess hydrogen peroxide is used the oxidation of Pt(II) occurs at an adequate rate at around 90–100 °C if the reaction solution is strongly acidic (ca. 1 M trifluoromethanesulfonic acid). We initially feared that excess hydrogen peroxide would oxidize all the Pt(II) to Pt(IV) and by doing so it would stop the C–H activation reaction (which requires Pt(II)). But excess hydrogen peroxide appears to be removed by decomposition to O<sub>2</sub> (“catalase reaction”), so the functionalization process, and necessarily the C–H activation step, is not quenched by modest excess hydrogen peroxide. It is possible that hydrogen peroxide may convert some Pt(IV) back to Pt(II) according to Eq. (3b), thus, maintaining a small “steady-state” population of Pt(II) in the presence of a much greater population of Pt(IV), which is a suitable mixture for the “Shilov” hydroxylation process.



In a typical experiment, a flask was charged with water, trifluoromethanesulfonic acid, chloroplatinum compound (Na<sub>2</sub>PtCl<sub>4</sub>-hydrate, “PtCl<sub>4</sub>” or both; Cl:Pt ratio nominally 4:1), and *n*-propanol. The heated mixture was treated dropwise with 30% hydrogen peroxide (**Caution!**) at a rate sufficient to keep the mixture from depositing metallic platinum. After several hours, the mixture contained 1,3-propanediol together with lesser amounts of 1,2-propanediol and acetic acid (approximate ratios 2.8:1:1, see Section 2) and much smaller amounts of several additional unidentified products. While substantially diluted during the course of the experiment by the addition of aqueous hydrogen peroxide, the mixture was

still active when the process was interrupted. To the best of our knowledge, the reaction could have been continued indefinitely, but owing to the potential hazards of mixing hydrogen peroxide with organic compounds we chose to terminate the demonstrations soon after true catalytic turnover in platinum had been achieved. Chloropropanol was not a major product in the “steady-state” catalytic process, although it was observed as a significant product in the initial “transient” stages of the reaction of chloroPt(II)/Pt(IV) compounds with *n*-propanol.

Clearly, the addition of hydrogen peroxide maintains the catalytic activity of the system and prevents the formation of metallic platinum. While we rationalize this by the assumption that hydrogen peroxide is reoxidizing Pt(II) to Pt(IV), it is possible that peroxide is also more directly involved in the oxidation/hydroxylation of the organic substrate(s), as is known for “Fenton” reactions (see, Chapter X in [1] and references therein). The fact that the major organic product is 1,3-propanediol suggests that “Shilov” Pt-based hydroxylation is still the dominant process even in the presence of hydrogen peroxide. The minor products, especially acetic acid and 1,2-propanediol, may conceivably arise from “Fenton” radical hydroxylation. But we note that in non-catalytic, anaerobic reaction mixtures containing propane, propanol and chloroPt compounds alone without added hydrogen peroxide, small amounts of acetic acid do appear, so there is at least one pathway to acetic acid which does not involve peroxide-derived hydroxyl radicals.

It is difficult to compare these results with previously described catalytic systems, because the conditions and substrates employed are quite different. Sen and co-workers [14] recently described using dioxygen directly at elevated temperature and pressure as the stoichiometric oxidant in a “Shilov” hydroxylation process. For the hydroxylation of alkanesulfonates in the presence of  $\text{CuCl}_2$ , they report platinum turnover rates up to  $13 \text{ h}^{-1}$  at  $160^\circ\text{C}$ ; in the absence of copper chloride their turnover rates were lower, from less than 1 to about 3 turnovers/h at  $160^\circ\text{C}$ , and inhibition by chloride (added as  $\text{NaCl}$  or  $\text{HCl}$ ) was apparent. ( $\text{CuCl}_2$  in water is known to accept chloride, see for example [27], and in addition to facilitating reoxidation it may activate the chloroPt(II) species in a similar manner as  $\text{PtCl}_4$ .)

From the reported Arrhenius activation energies (27.4 and  $31.6 \text{ kcal/mol}$ ), their reaction system would have run about 370- to 940-fold slower at  $92^\circ\text{C}$  than at  $160^\circ\text{C}$ , which extrapolates to platinum turnover rates no greater than  $0.04 \text{ h}^{-1}$  at  $92^\circ\text{C}$ . Under our conditions we observe turnover rates of about  $0.09 \text{ h}^{-1}$  (forming 1,3-propane diol) to  $0.15 \text{ h}^{-1}$  (all products) at  $92^\circ\text{C}$ . For the electrocatalytic hydroxylation of *p*-toluenesulfonic acid described by Freund et al. [13], short-term turnover rates in platinum approaching  $0.4 \text{ h}^{-1}$  were observed at  $120^\circ\text{C}$ , but the authors note the system could not function for extended periods owing to the irreversible formation of Pt(0). Thus, while consumption of  $\text{H}_2\text{O}_2$  is extravagant, once we extrapolate to a common temperature we find the present  $\text{Cl}_4\text{Pt(II)}^{2-}/\text{Pt(IV)Cl}_4/\text{H}_2\text{O}_2$  system catalytically hydroxylates *n*-propanol to 1,3-propanediol with as high a turnover rate in platinum as is presently known for any hydroxylation substrate or reaction medium.

#### 4. Summary and conclusions

Even if, as we believe, the approach we take here to make a catalytic “Shilov” hydroxylation system offers significant improvement in turnover rates and chemoselectivity, the process is far from commercial viability for synthesizing polymer intermediates. The turnover in platinum is still much too slow, hydrogen peroxide is an expensive oxidant to use for this purpose even if none were lost to “catalase reaction,” and the formation of both 1,2- and 1,3-propanediol is disadvantageous. But, if means can be found to use air as the stoichiometric oxidant in the catalytic synthesis of diols, to increase the platinum turnover rate several hundred-fold, and to improve the regioselectivity of polyfunctionalization, “Shilov” hydroxylation may become a useful industrial processes for converting alkane feedstock into polymer intermediates.

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