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Oxidation of Zeise's Salt by $[PtCl_6]^{2-}$: A Mechanistic Model for Hydrocarbon Oxidation†

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Summary: Oxidation of $[PtCl_3(C_2H_4)]^-$ *by* $[PtCl_6]^{2-}$ *proceeds via a (β-hydroxyethyl)*Pt^{II} *intermediate; its oxidation to the (β-hydroxyethyl)*Pt^{IV} *product involves electron, not alkyl, transfer.*

Among a variety of organometallic approaches to C–H bond activation,[1] reactions with electrophilic metal centers such as Pt(II),[2–4] Pd(II),[5] and Hg(II)[6] currently appear to offer the best prospects for productive alkane functionalization. Our working mechanistic scheme for conversion of alkanes to alcohols and alkyl chlorides by aqueous solutions of $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ (eq 1) consists of electrophilic C–H activation to generate a platinum(II) alkyl, transformation to a platinum(IV) alkyl, and nucleophilic attack by water or chloride, displacing platinum(II) and generating the product alcohol or alkyl chloride.

$$\mathrm{RH} + [\mathrm{PtCl_6}]^{2-} + \mathrm{H_2O} \xrightarrow{[\mathrm{PtCl_4}]^{2-}} \mathrm{ROH} + [\mathrm{PtCl_4}]^{2-} + 2\mathrm{HCl} \tag{1}$$

$$\mathrm{RH} + [\mathrm{PtCl_6}]^{2-} \xrightarrow{[\mathrm{PtCl_4}]^{2-}} \mathrm{RCl} + [\mathrm{PtCl_4}]^{2-} + \mathrm{HCl}$$

Shilov has suggested that the second step might involve alkyl group transfer (eq 2b).[4] From a practical point of view, simple oxidation (eq 2a) would be preferable, as Pt(IV) would no longer be an obligatory stoichiometric oxidant. Since alkylplatinum(II) complexes such as 1 with

$$\underset{1}{[\mathrm{RPt^{II}Cl_3}]^{2-}} + [{}^*\mathrm{Pt^{IV}Cl_6}]^{2-}$$

$$\rightarrow \underset{2}{[\mathrm{RPt^{IV}Cl_5}]^{2-}} + [{}^*\mathrm{Pt^{II}Cl_4}]^{2-} \tag{2a}$$

$$\rightarrow \underset{2}{[\mathrm{R{}^*Pt^{IV}Cl_5}]^{2-}} + [\mathrm{Pt^{II}Cl_4}]^{2-} \tag{2b}$$

only chloro and/or aquo coligands are not stable,[7] we have investigated the oxidation of Zeise's salt, $[PtCl_3(C_2H_4)]^-$, in order to distinguish between these alternatives.

We have previously reported that $[PtCl_5(CH_2CH_2OH)]^{2-}$ (3), a postulated intermediate in the oxidation of ethanol to ethylene glycol, is obtained from oxidation of Zeise's salt with $[PtCl_6]^{2-}$ in water.[2,8] The kinetics are readily followed by ^1H NMR spectroscopy.[9] In the presence of excess$[PtCl_6]^{2-}$ at 45 °C, Zeise's salt transforms cleanly to 3 over several hours. The rate shows simple first-order dependence on $[PtCl_6]^{2-}$, but the dependence on Zeise's salt is more complex, exhibiting behavior suggesting an approach to equilibrium along the reaction pathway (Figure 1). The overall reaction is *not* reversible: a solution containing 3 and $[PtCl_4]^{2-}$ remains unchanged over the same time period. How then may the kinetics be explained?

The overall conversion involves two processes: conversion of a π-ethylene to a β-hydroxyethyl ligand and oxidation of Pt(II) to Pt(IV). In principle they might occur in either order (eqs 3 and 4); only the latter would serve as a model for eq 2. Sen has argued for the former, on the

$$[\mathrm{PtCl_3(C_2H_4)}]^- + [\mathrm{PtCl_6}]^{2-} \overset{K}{\rightleftarrows} [\mathrm{PtCl_5(C_2H_4)}]^- + [\mathrm{PtCl_4}]^{2-}$$

$$[\mathrm{PtCl_5(C_2H_4)}]^- + \mathrm{H_2O} \overset{k}{\rightarrow} [\mathrm{PtCl_5(CH_2CH_2OH)}]^{2-} + \mathrm{H^+} \tag{3}$$

$$[\mathrm{PtCl_3(C_2H_4)}]^- + \mathrm{H_2O} \overset{K}{\rightleftarrows} [\mathrm{PtCl_3(CH_2CH_2OH)}]^{2-} + \mathrm{H^+}$$

$$[\mathrm{PtCl_3(CH_2CH_2OH)}]^{2-} + [\mathrm{PtCl_6}]^{2-} \overset{k}{\rightarrow} [\mathrm{PtCl_5(CH_2CH_2OH)}]^{2-} + [\mathrm{PtCl_4}]^{2-} \tag{4}$$

grounds that no (β-hydroxyethyl)platinum(II) species can

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(1) See, for example: Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; Wiley-Interscience: New York, 1989; and references therein.

(2) (a) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990,** *112,* 5628. (b) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horváth, I. T.; Eller, K. *Organometallics* **1993,** *12,* 895. (c) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993,** *115,* 3004.

(3) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992,** *114,* 6385 and references cited therein.

(4) Kushch, K. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *New J. Chem.* **1983,** *7,* 729.

(5) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991,** *113,* 700 and references cited therein.

(6) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Löffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993,** *259,* 340.

(7) Reduction of $[CH_3PtCl_5]^{2-}$ with Sn(II) or Cr(II) results in immediate liberation of CH_4. Substituted alkylplatinum(II) complexes are of course well-known; oxidation of $(CH_3)PtCl(tmeda)$ with $[PtCl_6]^{2-}$ gives $(CH_3)PtCl_3(tmeda)$. However, the absence of alkyl transfer in this model system does not necessarily extend to the alkane activating complexes that contain no such stabilizing ligands.

(8) Halpern and Jewsbury earlier reported oxidation of Zeise's salt to a mixture of $[PtCl_5(CH_2CH_2X)]^{2-}$ (X = Cl, OH), by chlorine: Halpern, J.; Jewsbury, R. A. *J. Organomet. Chem.* **1979,** *181,* 223.

(9) Typical reaction conditions were as follows: 0.014 M Zeise's salt, 0.14–0.56 M $[PtCl_6]^{2-}$ in D_2O, with ionic strength adjusted to 3 M with $NaClO_4$. Reactions were carried out at 45 °C and followed by ^1H NMR spectroscopy; the mass balance of reactants and products was always ≥95%.

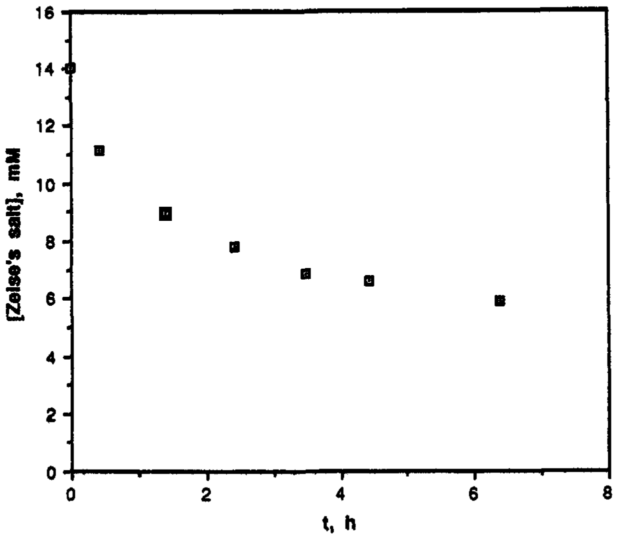

Figure 1. Concentration of Zeise's salt vs time. Initial concentrations and conditions: Zeise's salt, 0.014 M; $[PtCl_6]^{2-}$, 0.14 M; 45 °C in D_2O; μ = 3 M.

be observed when Zeise's salt is exposed to high pH in the absence of Pt(IV) and that oxidation of $CH_3{}^{13}CH_2OH$ leads to scrambling of label in the product 2-chloroethanol.[10] However, these observations are not inconsistent with eq 4, if the first equilibrium is rapid and lies far to the left. In fact, we can rule out eq 3 by the observation that the rate is unaffected by the addition of excess $[PtCl_4]^{2-}$.[11] In contrast, the reaction *is* slowed dramatically at low pH, exhibiting inverse first-order dependence on $[H^+]$.[12] The kinetics of reactions starting at pH 7 are in good agreement with the rate law predicted by eq 4.[13]

Since the oxidation of Zeise's salt to 3 can thus serve as a model for the second step of the alkane oxidation process, we can use it to test whether alkyl group transfer between Pt centers is involved. Isotopically enriched ^{195}Pt (97.3%) was dissolved in aqua regia, converted to $Na_2{}^{195}PtCl_6$, and used to oxidize ordinary Zeise's salt. The ^1H NMR spectrum of the resulting 3 showed ^{195}Pt satellites of *normal* intensity (~33% of total peak area) for the Pt–CH_2CH_2OH signal, demonstrating that the hydroxyethyl group does *not* transfer to the Pt(IV) center during oxidation.[14] The oxidation step in the alkane oxidation mechanism must therefore follow eq 2a rather than eq 2b and probably involves an inner-sphere two-electron transfer accompanied by Cl^- transfer, as found in similar systems.[15] There is accordingly no inherent mechanistic reason why Pt(IV) could not be replaced by another suitable oxidant, so long as it is capable of oxidizing the alkylplatinum(II) intermediate to alkylplatinum(IV) *without* fully oxidizing $[PtCl_x(H_2O)_{4-x}]^{2-x}$ to Pt(IV). Indeed, we have found that alkane oxidation may be carried out electrochemically, thus becoming catalytic in platinum, although only a limited number of turnovers have been achieved.[16]

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[10] Sen, A., personal communication. The label scrambling was also reported in ref 2b.

[11] An alternate formulation in which the first step is irreversible and the second reversible can also be excluded. Regiospecifically deuterated 3 was prepared by oxidative addition[2b] of ICD_2CH_2OH to $[PtCl_4]^{2-}$. The resulting $[PtCl_5(CD_2CH_2OH)]^{2-}$ does not interconvert with its regioisomer $[PtCl_5(CH_2CD_2OH)]^{2-}$ to any measurable (by ^1H NMR) degree, over a period of 8 h at 45 °C.

[12] At pH <1 reaction at 45 °C is too slow; kinetics were studied at 85 °C, where 3 is not observed but goes directly on to final products $HOCH_2CH_2OH$ and $HOCH_2CH_2Cl$. We have been unable to find a buffer system to maintain a constant higher pH level that does not interfere with formation of 3.

[13] Equation 4 predicts $dz/dt = -kKz[PtCl_6{}^{2-}]/[H^+]$ where z = [Zeise's salt]. Substituting $[H^+] = z_0 - z$ and integrating gives $\ln(z/z_0) - (z/z_0) + 1 = -kK[PtCl_6{}^{2-}]t$; plots of the left-hand side of this equation vs t give good straight lines.

[14] The satellite signals of 3 do *slowly* increase, over a period of days, if the reaction solution is allowed to stand at room temperature. Separate experiments demonstrate that this exchange is due to transfer of alkyl between 3 and $[^{195}PtCl_4]^{2-}$, not $[^{195}PtCl_6]^{2-}$.

[15] Mason, W. R. *Coord. Chem. Rev.* **1972**, *7*, 241. We do not observe a positive dependence on $[Cl^-]$, as is commonly the case in such reactions. The exact coordination environment of all species at all times is not known; complexes such as 3 may well contain some combination of chloro and aquo ligands,[2b] although for simplicity they are represented as all chloro.

[16] Freund, M. S.; Labinger, J. A.; Lewis, N. S.; Bercaw, J. E. *J. Mol. Catal.*, in press.