Reduction of Pt(II) by H₂: Effects of Citrate and NaOH and Reaction Mechanism

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Aqueous solutions of Pt(II) (aged $PtCl_4^{2-}$ solutions) are reduced by hydrogen in the absence of a stabilizer and in the presence of stabilizing sodium citrate or/and sodium hydroxide. The rate of reduction is measured optically and conductometrically, and the colloidal nanoparticles, which are finally formed, are studied by high-resolution electron microscopy. In dilute solutions, the rate of reduction is proportional to the square of the Pt(II) concentration. In the presence of citrate and NaOH, the reduction occurs more slowly. A mechanism, in which intermediate free Pt atoms do not appear, is discussed. Monovalent platinum is postulated as the first intermediate, and an autocatalytic contribution to the reduction occurs in two steps: formation of a hydroxilated precursor and reduction of the latter. Depending on the concentration of the stabilizing additives, colloids consisting of polyhedra of different shape (cubic, tetrahedral, and triculent octahedral) are formed. Stabilization by citrate plus NaOH yields particularly long lifetimes of the colloidal solutions.

Introduction

Colloidal platinum in aqueous solution is readily prepared by chemical reduction of Pt(II) and Pt(IV) compounds. Rampino and Nord reported in 1941 that platinum hydroxide, which is made by boiling a $PtCl_4^{2-}$ solution in the presence of the required amount of NaOH, is reduced by hydrogen gas to yield an efficient hydrogenation catalyst.¹ The reduction by hydrogen was more recently applied again, using an aged PtCl₄²⁻ solution that contained mainly PtCl₂(H₂O)₂: in the presence of polyacrylate or polyphosphate, nicely facetted 5-10 nm nanoparticles were obtained.^{2,3} The reduction of $PtCl_6^{2-}$ by citrate in boiling water was introduced by Turkevich⁴ and has, ever since, been applied in many laboratories. This method yields small particles of about 3 nm in size, which exhibit many catalytic effects. However, it has more recently been recognized that these particles contain a certain contribution of a higher valence state of platinum. This manifests itself in the destabilization they undergo upon exposure to hydrogen gas and the formation of colored Chini complexes upon the exposure to CO.⁵ Studies on the interaction of these particles with reducing free radicals have also shown that some kind of higher oxidation state is present.6

In the present work, some features of the H_2 reduction of Pt(II) are investigated, and the nature of the nanoparticles formed is studied by electron microscopy. It was found that the reduction by H_2 at ambient temperature in the presence of sodium citrate yields Pt sols of particularly long lifetime. Citrate is not the reducing agent in these experiments; it acts solely as a stabilizer. A similar study on the capping action of citrate has recently been performed in the case of silver reduction.⁷ In addition, the effect of NaOH is studied. NaOH causes changes in the structure of the starting Pt(II) material and also decreases the rate of reduction.

Experimental Section

As has previously been described, the reduction of a freshly prepared PtCl₄²⁻ solution occurs much more slowly than that of an aged solution.² A 10⁻² M K₂PtCl₄ (99.99%, Aldrich) stock solution was prepared and aged for at least 2 days. This solution was then diluted to obtain the desired concentration. The reduction occurred in a glass vessel, which had sidearms carrying an optical cuvette (optical path given on the ordinate axis of the spectra) and a homemade conductivity cell (glassy carbon electrodes; 3-mm diameter; 5-mm distance; cell constant of 1.23 cm⁻¹). Absorption and conductivity measurements could therefore be made without bringing the solution into contact with air. The vessel was also equipped with a septum; solution could therefore be removed or substances added via a syringe. The solution was first bubbled with argon and then very vigorously flushed with hydrogen for 90 s. The vessel then was closed and, immediately afterward, the first spectrum or conductivity measurement was recorded. Depending on the composition of the solution, the formation of the colloid lasted an hour or up to several days. During this time, the vessel was slightly shaken to secure saturation of the solution with hydrogen. The volume of the vessel was 150 mL, and the volume of the solution 20-50 mL. Considering the much higher H₂ concentration in the gas than in the liquid phase, there was always a vast excess of hydrogen in the reacting system.

The samples were observed in a high-resolution transmision electron microscope, Phillips 12, operating at 120 kV, as described previously.⁷

Results

Kinetic Measurements. An aged solution containing Pt(II) mainly as $PtCl_2(H_2O)_2$ has a UV absorption that increases toward shorter wavelengths,² with an absorption coefficient at 200 nm of $1.24 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$. Colloidal platinum exhibits

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Figure 1. 200-nm absorption of Pt(II) (aged $PtCl_4^{2-}$) as a function of time at various initial Pt(II) concentrations. The quantity "Pt(II) concentration times optical path length" was kept constant. The absorbance at the completion of the reduction was 0.45. No stabilizer was added.

less absorption at this wavelength. Thus, the course of the reaction can be monitored by recording the decrease in the 200nm absorption as a function of time. In Figure 1, several initial concentrations of Pt(II) were used; the solutions did not contain a stabilizer. All solutions had the same initial absorbance of 1.24, as optical cells of different path length were used, so that the quantity "initial concentration times path length" was kept constant. Thus, the curves represent the relative Pt(II) contration as a function of time. If the rate of reduction were proportional to the Pt(II) concentration, then all points would lie on a single curve. However, it can be seen that the negative slope of the curves becomes greater with increasing Pt(II) concentration. At the lower concentrations shown in the figure, the rate is proportional to the square of the concentration; this indicates a complex mechanism of reduction. At the higher concentrations, the order with respect to the Pt(II) concentration is even higher.

Moreover, the various curves are almost straight lines over a wide range of concentrations without a significant induction period. With increasing time, the Pt(II) concentration decreases, and the curves should therefore have a smaller slope (because of the above-mentioned higher order), which is not the case. This indicates an increase in specific rate with time along a curve, i.e., an autocatalytic contribution to the reduction. No precipitation of the colloid formed took place during the measurements. During aging of the colloids for several days, a black precipitate appeared, which could initially be repeptised, but which became insoluble at longer aging times.

The change in the 200-nm absorbance is equal to the decrease in the Pt(II) absorption plus an increase due to the absorption of the final product. If the absorption spectrum of the product is the same at all times, then the change in the 200-nm absorbance is truly a measure of the rate of Pt(II) consumption. In fact, the absorption of colloidal platinum in the visible region developed at about the same time as the Pt(II) absorption disappeared. A more reliable method for measuring the reaction rate, which does not depend on the nature of the product, consists of recording the conductivity of the solution as a function of time. Hydrogen ions and chloride anions are formed during the reduction



Figure 2. Semilog plot of the relative concentration of Pt(II) vs time as derived from conductivity measurements (\bigcirc). The initial concentration was 2.0 × 10⁻⁴ M. The dotted second-order curve (\bullet) was calculated from the early part (40% conversion) of the experimental curve. No stabilizer was added.

$$PtCl_{2}(H_{2}O)_{2} + H_{2} \rightarrow Pt + 2 Cl^{-} + 2 H^{+} + 2 H_{2}O \quad (1)$$

The relative Pt(II) concentration is equal to $(C_{\infty} - C_t)/C_{\infty}$ – C_{0}), where C_{0} and C_{∞} are the respective conductivities at time t = 0 and at the end of reaction. The conductivity measurements corroborated the above conclusions about the order of the reaction rate with respect to the initial Pt(II) concentration. The conductivity curves yielded more detailed information, as shown in Figure 2. At about 40% conversion, the negative slope of the curve becomes noticeably larger, which indicates an increase in the specific rate. Toward the end of reaction, the slope finally decreases continuously. Assuming that the reaction rate is proportional to the square of the Pt(II) concentration (on the basis of the optical measurements in Figure 1), the pointed curve in Figure 2 was calculated by extending the experimental curve at 40% conversion. The faster decrease of the experimental curve is attributed to an autocatalytic contribution to the reaction rate, similar to the autocatalytic effect that has been reported for the reduction of an iridium(I) complex by H₂.⁸ It has to be pointed out that the presentation in Figure 2 does not quantitatively describe the autocatalytic contribution, as the choice of the point of extension of the experimental curve at 40% is rather ambiguous.

In Figure 3, the 200-nm absorption of Pt(II) in a 2.0×10^{-4} M solution was measured as a function of time in the absence and presence of 4.0×10^{-4} M sodium citrate. A strong retarding effect of citrate can be recognized. The absorption spectrum of PtCl₂(H₂O)₂ is not changed upon the addition of sodium citrate to the solution. It is therefore concluded that PtCl₂(H₂O)₂ is still the reaction partner of H₂. The colloidal particles formed in the presence of citrate are stable for weeks and months. In our former study, polyacrylate was found to be a good stabilizer;² however, a comparison revealed that citrate exerts a stronger protecting effect.

In the experiments of Figures 4 and 5, the effect of NaOH was investigated. When NaOH is added to a Pt(II) solution, the spectrum of PtCl₂(H₂O)₂ is changed: an absorption band at 214 nm grows in with increasing NaOH concentration until the molar Pt(II)/NaOH ratio is 1:1 ($\epsilon_{214} = 9.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). An additional increase in NaOH concentration does not lead to a further increase in the intensity of this band. It is concluded that a well-defined species, such as PtCl(OH)(H₂O)₂ or



Figure 3. Concentration vs time curves for the reduction of 2.0×10^{-4} M PtCl₂(H₂O)₂ in the absence and presence of 4.0×10^{-4} M citrate. The final absorption spectra were identical with that in the inset of Figure 5.



Figure 4. Absorption spectra. (a) Aged 5.0×10^{-4} M PtCl₄²⁻ solution [containing mainly PtCl₂(H₂O)₂]. (b) After addition of 1.0×10^{-3} M NaOH to solution in a. (c) After aging of solution in b for 30 h.

 $PtCl_2(OH)(H_2O)^-$, is formed upon the addition of NaOH, which we call the first product of hydrolysis. This product, however, is not stable upon further addition of NaOH: the 214-nm band decreases within 1–2 days, the final product of hydrolysis showing a nonstructured increase in absorption toward the shorter UV wavelengths. This can be seen from Figure 4. The final hydrolysis product probably is platinum hydroxide.

In Figure 5, the absorption spectrum of a 5.0×10^{-4} M Pt-(II) solution containing 1.0×0^{-3} M NaOH is shown at various times of exposure to H₂. A comparison with the reduction of 5.0×10^{-4} M Pt(II) in the absence of NaOH in Figure 1 shows that NaOH drastically decreases the rate of reaction. In Figure 6, the absorbancies at 214 nm [Pt(II) species] and at 280 nm (Pt nanoparticles) are plotted as functions of the reaction time. Although there is a decrease in the 214-nm absorption of the Pt(II) species right at the beginning, the 280-nm absorption of nanoparticles does not start before ca. 40 h. Under the conditions of Figure 5, the reaction obviously occurs in two steps: (1) transformation of the first hydrolysis product (which is not reduced by H₂) into a second hydrolysis product, as described in Figure 4, and (2) reduction of the latter to yield colloidal platinum. The final colloid has an aborption spectrum with a UV maximum. This spectrum agrees with the calculated one,⁹



Figure 5. Absorption spectrum of a solution containing 5.0×10^{-4} M aged PtCl₄^{2–} and 1.0×10^{-3} NaOH at different times of exposure to hydrogen. The full UV-vis spectrum of the final colloid is shown in the inset.



Figure 6. Absorbancies at 214 nm [initially present Pt(II) complex] and at 280 nm (final platinum colloid) as functions of time. The solution initially contained 5.0×10^{-4} M Pt(II) and 5.0×10^{-4} M NaOH.

as has previously been discussed in detail² (inset of Figure 5). Upon aging of the colloidal solution formed, the spectrum becomes flatter as the particles aggregate. This effect can be largely avoided by subsequent addition of 2.0×10^{-4} M stabilizer (either citrate or polyacrylate) to the solution.

In the experiment of Figure 7, the processes of precursor formation and reduction of the precursor are separated. A 5.0 $\times 10^{-4}$ M Pt(II) plus 1.0×10^{-3} M NaOH solution was aged under argon for 2 days. Hydrogen was then added, and the absorption spectrum determined at various times afterward. One can see that the formation of the colloid in the aged solution requires about 1 h. The rate of reduction still is much slower than that of reduction of 5.0×10^{-4} M Pt(II) in the absence of NaOH (see Figure 1).

The effects of citrate and NaOH were also combined by reducing aged Pt(II) solutions that contained both additives. It turned out that platinum sols of especially long lifetime, which contain nicely shaped nanoparticles with a rather narrow size distribution, are formed under these conditions.

Electron Microscopy. The particles are polyhedra, similar to those that are formed in the presence of polyacrylate as a stabilizer.^{2,3} Typical examples are shown in Figure 8. In the absence of citrate (Figure 8, left), relatively large particles with



Figure 7. Absorption spectrum at various times after exposure to H₂. The solution contained 5.0×10^{-4} M Pt(II) and 1.0×10^{-3} M NaOH; it was aged under argon for 2 days before the exposure to hydrogen.

a narrow size distribution are present. Closer inspection shows that they consist of two populations, i.e., cubes and truncated octahedra, the latter being a bit larger. Tetrahedra are practically absent. In the presence of citrate, the particles are smaller, and tetrahedra appear more frequently with increasing citrate concentration. The explanation for this phenomenon has already been given for polyacrylate stabilized particles:³ tetrahydra are formed first, which then grow into cubes or truncated octahedra, unless their growth is hampered by adsorbed stabilizer. Note that a very small citrate concentration (6×10^{-5} M in Figure 8, middle) exerts a significant effect on the particle properties, a further increase in citrate concentration by almost one order of magnitude (5×10^{-4} M in Figure 8, right) having little additional effect. It thus seems that the coverage of the particles by citrate is nearly complete already at the lower concentration.

No significant differences in the size or shape of the particles were observed, when they were formed in the presence or absence of NaOH. The main effect of NaOH consists in a better stabilization of the particles. This might be due to a lesser extent of protonation of citrate in the presence of NaOH, the citrate thus acting as a better stabilizer.

It was observed that the particles were larger and had a more uniform distribution in size and shape when they were formed at a higher initial Pt(II) concentration. This can be seen from Figure 9, in which Pt(II) was reduced at two concentrations, the citrate concentration being 2.0×10^{-4} M in both cases.

Discussion

Considerations of the Mechanism of Reduction. If the first step of the reduction consisted of the interaction of H₂ with *one* molecule of the Pt(II) compound, as indicated by eq 1, then a free platinum atom would be formed. However, one calculates that the reaction is highly endoergic, with $\Delta G = 3.4 \text{ eV}$, using the known free enthalpies of formation of the species involved in eq 1.¹⁰ The reason for this endoergicity is the high free enthalpy of formation of 5.4 eV of the free Pt atom. It is therefore concluded that free Pt atoms do not appear as intermediates in colloid formation. Another reaction route could lead to PtH as the first reduction product.

$$PtCl_2(H_2O)_2 + 1.5H_2 \rightarrow PtH + 2Cl^- + 2H^+ + 2H_2O$$
 (2)

Using a Pt-H bond energy of 3.47 eV,¹¹ one calculates ΔG =2.03 eV; we again exclude this reaction path because of the high endoergicity involved.

The second-order behavior of the reaction (Figure 1) entices one to postulate the involvement of *two* molecules of $PtCl_2$ -(H₂O)₂ in the first reduction event.

$$H_{2} + PtCl_{2}(H_{2}O)_{2} \rightleftharpoons [H_{2} - PtCl_{2}(H_{2}O)_{2}]$$

$$(3a)$$

$$PtCl_{2}(H_{2}O)_{2} + [H_{2} - PtCl_{2}(H_{2}O)_{2}] \rightarrow$$

$$2Pt^{+} + 4Cl^{-} + 4H_{2}O + 2H^{+} (3b)$$

$$H_2 + 2PtCl_2(H_2O)_2 \rightarrow 2Pt^+ + 4Cl^- + 4H_2O + 2H^+$$
 (4)

Colloidal particles are then formed via dismutation and coalescence reactions of Pt⁺. Nothing seems to be known about the thermodynamic and electrochemical properties of the monovalent state of platinum. The free enthalpy of formation of Pt⁺_{aq} can be calculated as follows, by making a resonable guess of the free enthalpy of its hydration: Platinum appears before gold in the periodic table, and its molar volume is 11% smaller than that of gold. We thus conclude that Pt⁺ is smaller than Au⁺, and that its free enthalpy of hydration, ΔG_{hydr} , therefore is more negative than that of Au⁺. The free hydration enthalpy of the latter is calculated as -6.3 eV from known thermodynamic data;¹² thus, it does not seem unreasonable to



zero

6 × 10⁻⁵ M [citrate]

 5×10^{-4} M

Figure 8. Electron micrographs of Pt particles formed at different concentrations of citrate, 5.0×10^{-4} M Pt(II), and 7.0×10^{-4} M NaOH.



5×10⁻⁴ M Pt

1×10⁻⁴ M Pt

Figure 9. Electron micrographs of particles formed at different initial Pt(II) concentrations and 2.0×10^{-4} M citrate.

assume a value of -7.0 eV for the free enthalpy of hydration of Pt⁺. The combination of this value with known thermodynamic data allows one to calculate the free enthalpy of the redox system

$$Pt_m \rightleftharpoons Pt_{aq}^+ + e^- \tag{5}$$

on the standard electrochemical scale, $eE^{\circ} = \Delta G_{\rm f}^{\circ}({\rm Pt^+}_{\rm g}) - W_{\rm h} + \Delta G_{\rm hydr}({\rm Pt^+})$ (g, gas phase; aq, solution; m, bulk metal; $W_{\rm h} = 4.5 \, {\rm eV}$, work function of the standard hydrogen electrode). With $\Delta G_{\rm f}^{\circ}({\rm Pt^+}_{\rm g}) = 14.3 \, {\rm eV^{10}}$ and $\Delta G_{\rm hydr}({\rm Pt^+}) = -7.0 \, {\rm eV}$, the free enthalpy of the equilibrium in eq 5 is $+2.8 \, {\rm eV}$. With this value, one calculates that the overall reaction 4 has $\Delta G = 1.0 \, {\rm eV}$ under standard conditions and is practically thermoneutral at pH = 7 and dilute solution $(10^{-3} \, {\rm M})$. It thus seems plausible, although not proven by direct experiment, that the colloid is formed through the monovalent state of platinum. Moreover, it is conceivable that ${\rm Pt}_2^{2+}$ is directly formed in reaction 4, i.e., a species analogous to ${\rm Pd}_2^{2+}$, which was observed in the radiolytic reduction of the homologous ion ${\rm Pd}({\rm II})$.¹³ Dismutation and coalescence reactions of ${\rm Pt}^+$ (or ${\rm Pt}_2^{2+}$) may finally lead to metallic nanoparticles.

We can finally examine a reaction path, in which Pt_2 appears as the first product of reduction.

$$2PtCl_{2}(H_{2}O)_{2} + 2H_{2} \rightarrow Pt_{2} + 4Cl^{-} + 4H^{+} + 4H_{2}O \quad (6)$$

Using a bond strength of 3.70 eV for Pt_2 ,¹¹ one obtains $\Delta G = 3.1$ eV, i.e., a high endoergicity. Thus, Pt^+ formation, as discussed above, seems to be the reaction route with the lowest energy barrier.

The atoms of some other precious metals, such as iridium, have large free enthalpies of formation, too. It seems probable that reduction by H_2 also does not proceed through intermediate free atoms, as has been postulated.⁸

The autocatalytic behavior of the reduction of Pt(II) can be understood in the facilitation of reaction 2 on the surface of the colloidal particles, Pt_n , which are formed in the early stages of reaction

$$Pt_n + x/2 H_2 \rightleftharpoons Pt_n - xH \tag{7}$$

 $Pt_n - xH + PtCl_2(H_2O)_2 \rightarrow$ $Pt_{n+1} - (x-2)H + 2H^+ + 2Cl^- + 2H_2O$ (8)

where $Pt_n - xH$ [or $Pt_n - (x - 2)H$] are particles carrying x (or

x - 2) chemisorbed H atoms. On the other hand, monovalent platinum may be formed

$$Pt_{n}-H + PtCl_{2}(H_{2}O)_{2} \rightarrow Pt_{n+1}^{+} + H^{+} + 2Cl^{-} + 2H_{2}O \quad (9)$$

or

$$Pt_n - H + PtCl_2(H_2O)_2 \rightarrow Pt_n + H^+ + Pt^+ + 2Cl^- + 2H_2O$$
(10)

Reactions 8 and 9 would lead to an increase in particle size, whereas reaction 10 would lead to the formation of new nuclei. It is also conceivable (on the basis of the high positive potential of the redox system in eq 5) that monovalent platinum is reduced by hydrogen.

$$\operatorname{Pt}_{n+1}^{+} + \operatorname{H}_{2} \to \operatorname{H}-\operatorname{Pt}_{n+1}^{+} + \operatorname{H}^{+}$$
(11)

Note that reactions 9 and 11 constitute the growth steps of a chain mechanism for the autocatalytic reduction of Pt(II). This case is possibly fulfilled at high PtCl₂(H₂O)₂ concentrations, for which the order of reaction becomes higher (Figure 1); the growth of the nuclei would become faster, which would explain why larger particles are formed at the higher Pt(II) concentration in Figure 9.

Effect of NaOH. The most startling effect of NaOH consists of the decrease in the rate of reaction by at least an order of magnitude. For example, whereas it takes about $^{1}/_{4}$ h for complete reduction of a 5.0×10^{-4} M Pt(II) solution, about 60 h are required when 1.0×10^{-3} M NaOH is present. In both cases, the final particles have about the same size (~12 nm). However, they have a more narrow size distribution in the presence of NaOH, and the high content of cubic structures is of interest from a preparative point of view. The stability of the particles is also different in the two cases. The particles are more strongly agglomerated when formed in the absence of NaOH, the solution having a dark color; in the presence of NaOH, the solution color is yellow-brown, and the spectrum agrees with the theoretical spectrum of well-separated particles (inset of Figure 5).

As has already mentioned by Rapino and Nord,¹ platinum hydroxide is formed in the reaction of NaOH with $PtCl_4^{2-}$. Our findings indicate that this reaction occurs at ambient temperature in two steps. The first product is formed practically instantaneously. It is, however, nonreactive toward hydrogen. As mentioned above, we tentatively attribute it to the structure $PtCl(OH)(H_2O)_2^-$; its charge possibly prevents it from forming

the dimeric complex of eq 3a. The conversion to the final hydroxide, possibly being $Pt(OH)_2(H_2O)_2$, requires almost 2 days. This hydroxide is believed to be reduced by H₂, a process still much slower than the reduction non-hydroxilated Pt(II).

Effect of Citrate. Citrate is a good stabilizer of the colloidal particles produced in the H_2 reduction of Pt(II). The reduction occurs significantly more slowly in the presence of this stabilizer. Because the structure of the Pt(II) compound present is not changed by citrate, the decrease in the reaction rate cannot be explained by a change in the structure of the Pt(II) compound. With increasing citrate concentration, the size of the particles decreases, i.e., more particles are formed. This is understood in terms of adsorbed citrate retarding the growth of the particles. A similar effect of polyacrylate has previously been found.³ From a practical point of view, citrate has the advantage of stabilizing the particles more efficiently than polyacrylate, especially at higher Pt(II) concentrations.

Final Remarks

The reduction of aged $PtCl_4^{2-}$ by hydrogen in the presence of citrate is a useful method for the preparation of colloidal platinum. The particles formed do not have the shortcomings mentioned above when they are formed via the reduction by citrate. The reduction by H_2 is a complex phenomenon. In the present work, some ideas about this complexity are expressed. It may be mentioned that $PdCl_4^{2-}$ can also be reduced by hydrogen to yield colloidal particles, and the mechanism seems to be quite similar. The particles prepared in the present work are also used to synthesize bi- and trimetallic structures in combination with other metals and to investigate fast electronic processes in femtosecond laser experiments, as we have recently reported for other systems.¹⁴

Acknowledgment. The authors thank Prof. D. Meisel for valuable discussions and Mrs. U. Bloek for assistance in the

electron microscope measurements. The work described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Contribution No. 4205 NDRL from the Notre Dame Radiation Laboratory.

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