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Reduction of Au(CN)$_2^-$ in Aqueous Solution. Formation of Nonmetallic Clusters and Colloidal Gold

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Au(CN)$_2^-$ is reduced by hydrated electrons and hydrogen atoms. Three primary reduction products, which are in protolytic equilibrium, are formed depending on pH: $Au(CN)_2^{2-} + 2H^+ \rightleftarrows Au(CN)_2H^- + H^+ \rightleftarrows Au(CN)_2H_2$. The absorption spectra of the three species, the pK values of their protolytic equilibria, and their rates of decay into $Au^0 + 2CN^-$ (or HCN) were measured by the method of pulse radiolysis. The absorption spectrum of the gold atom is also reported. The agglomeration of gold atoms yields intermediate clusters of nonmetallic gold and finally colloidal metal. Hydroxymethyl and 2,2-methylhydroxypropyl radicals can also reduce Au(CN)$_2^-$, although the specific rates are low. Gold atoms have strong reducing properties, the standard potential of the system Au^+/Au^0 being −1.5 V. Various organic radicals are reduced by Au^0. It is proposed that these reductions do not occur as simple electron-transfer reactions but through hydrolysis of intermediate organo–gold compounds.

Introduction

The investigation of extremely small particles of metals and semiconductors in aqueous solution has drawn increasing interest during the past ten years.[1] Such small particles have properties that change from those of the isolated atoms or molecules to the bulk materials with increasing size. In the case of silver, the "growing microelectrode" method has been applied to study optical and electrochemical properties of small particles: Ag atoms were generated in a silver salt solution by a short pulse of high-energy radiation and the subsequent agglomerations traced by recording the accompanying optical changes.[2] It was observed more recently that nonmetallic silver clusters formed in the reduction of aqueous Ag^+ solution containing polyphosphate are long lived and that chemical reactions of such clusters can be seen.[3]

In the present paper, the reduction of Au(CN)$_2^-$ by hydrated electrons and reducing organic radicals was investigated in order to determine whether free gold atoms in aqueous solution can be prepared and whether intermediate nometallic gold clusters can be detected during the agglomeration of the gold atoms, which finally leads to colloidal gold metal. It is shown that the reduction of Au(CN)$_2^-$ is a complex reaction that occurs through several intermediates, depending on the pH of the solution. A pulse radiolysis study of KAu(CN)$_2$ in aqueous solution has already been performed by Ghosh-Mazumdar and Hart.[4] They observed the absorption spectrum of a species resulting from the reaction of the hydrated electron with Au(CN)$_2^-$. A distinct structure has not yet been attributed to this species.

Experimental Section

Solutions of KAu(CN)$_2$ were prepared under argon to avoid contact with air. The pH was adjusted by adding KOH or HClO$_4$. Ionizing radiation produces hydrated electrons and hydroxyl radicals. The latter were scavenged by an alcohol or formate anion present in the solution. The organic radicals resulting from the scavenging reactions often have reducing properties, and it was hoped that they would contribute to the reduction of Au(CN)$_2^-$. The γ-irradiations were carried out with a ^{60}Co source. Usually, a dose rate of 1.3×10^5 rad/h was used.

Pulse radiolysis was carried out with 3.6-MeV electrons from a Van de Graaff generator. The duration of the pulse varied between 0.5 and 5 μs, depending on the desired dose. The transient signals of optical absorption and conductivity were processed and recorded simultaneously as described previously.[5] Depending on the time scale of the recording, either a dc[6] or an ac method[7] was used for the observation of transient conductivity.

The results are presented as specific absorptions ϵ and molar conductivities $\Delta\Lambda$ by dividing the absorbance and conductivity signals by the concentration of hydrated electrons or other reducing species generated and by the path length of the cell.

Results

Reaction of e^-_{aq} *with Au(CN)*$_2^-$. Figure 1 shows the changes in the specific absorption and the molar conductivity of a solution containing 1×10^{-5} M KAu(CN)$_2$ as functions of time after the pulse. The pH was 9.5, and the concentration of hydrated electrons (and protons) produced was 5×10^{-7} M. The solution also contained 0.1 M propanol-2 as OH scavenger:

$$OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2COH \qquad (1)$$

This reaction took place during the pulse. Immediately after the pulse, the 700-nm absorption of the hydrated electron was present (Figure 1b). It decayed with first-order kinetics, the rate constant being proportional to the concentration of KAu(CN)$_2$. A bimolecular rate constant of 1.1×10^{10} M^{-1} s^{-1} was obtained for the reaction of e^-_{aq} with Au(CN)$_2^-$, which agrees fairly well with the value of 8×10^9 M^{-1} s^{-1} reported previously.[4]

As the hydrated electron also has some absorption at 420 nm, an immediate absorption was present at this wavelength (Figure 1a). After the pulse, the absorption increased. This increase was first order, and its rate was equal to that of the 700-nm decay in Figure 1b. The absorption increase therefore is attributed to the first product of the reaction of e^-_{aq} with Au(CN)$_2^-$. To obtain the spectrum of this species, experiments were carried out with a solution of higher concentration i.e., $[Au(CN)_2^-] = 8 \times 10^{-4}$ M, in which the reaction was practically complete during the pulse. With the absorption increase being measured at various wavelengths immediately after the pulse, spectrum 0 in Figure 2 was obtained.

It is seen from Figure 1c that no change in conductivity occurred immediately after the pulse (for about 5 μs after the pulse, the measurement was distorted). During the pulse, hydrated electrons and protons are formed. At pH = 9.5, the protons rapidly react with OH^- ions during the pulse. After the pulse, one OH^- ion is substituted by an hydrated electron. As the two species have almost the same molar conductivity,[8] no conductivity change

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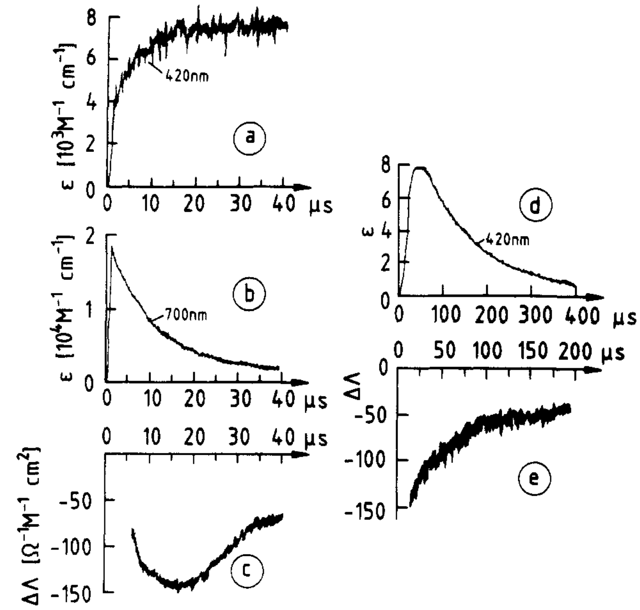

Figure 1. Optical absorption and conductivity curves. Conditions: $[\mathrm{Au(CN)_2^-}] = 1 \times 10^{-5}$ M; [propanol-2] = 0.1 M; dose, 5×10^{-7} M hydrated electrons/pulse.

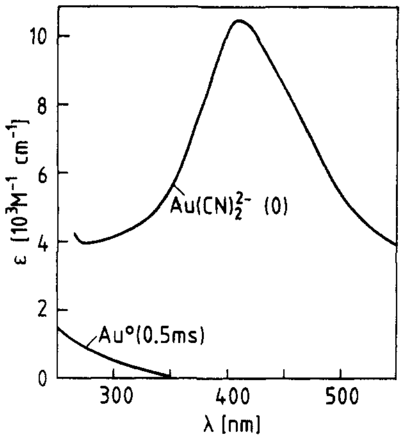

Figure 2. Absorption spectra of $\mathrm{Au(CN)_2^{2-}}$ (0) and $\mathrm{Au^0}$ (the latter was measured at 0.5 ms after the pulse). Dose: 2×10^{-7} M hydrated electrons/pulse.

occurs. However, the conductivity decreased after the pulse, i.e., when the hydrated electrons reacted with $\mathrm{Au(CN)_2^-}$ ions. If the reaction

$$\mathrm{e^-_{aq} + Au(CN)_2^- \rightarrow Au(CN)_2^{2-}} \qquad (2)$$

takes place, the molar conductivity change is $-\Delta(\mathrm{e^-_{aq}}) - \Delta(\mathrm{Au(CN)_2^-}) + \Delta(\mathrm{Au(CN)_2^{2-}})$. With $\Delta(\mathrm{e^-_{aq}}) = 190\ \mathrm{cm^2\ \Omega^{-1}\ M^{-1}}$[8] and assuming the difference between the two anions as $30\ \mathrm{cm^2\ \Omega^{-1}\ M^{-1}}$, the drop in conductivity at the end of reaction 2 would be $160\ \mathrm{cm^2\ \Omega^{-1}\ M^{-1}}$. However, as the reaction proceeds, the conductivity starts to increase again and ΔΛ reaches zero at longer times (Figure 1c,e). This indicates that during and after reaction 2 a second process occurs in which $\mathrm{OH^-}$ ions are produced. These phenomena are understood in terms of the decay

$$\mathrm{Au(CN)_2^{2-} \rightarrow Au^0 + 2CN^-} \qquad (3)$$

followed by

$$\mathrm{CN^- + H_2O \rightarrow HCN + OH^-} \qquad (3a)$$

taking into account that HCN is half dissociated at the pH in the experiments of Figure 1. The decay of the absorption of $\mathrm{Au(CN)_2^{2-}}$ (Figure 1d) followed first-order kinetics, the rate constant being $6.7 \times 10^3\ \mathrm{s^{-1}}$. From this, one calculates a half-life of 1×10^{-4} s of $\mathrm{Au(CN)_2^{2-}}$ with respect to its decay, according to eq 3. At wavelengths below 350 nm, the absorption did not decay to zero. The long-lived rest absorption is attributed to the free gold atom formed. The spectrum of $\mathrm{Au^0}$ as measured 0.5 ms after the pulse is also shown in Figure 2.

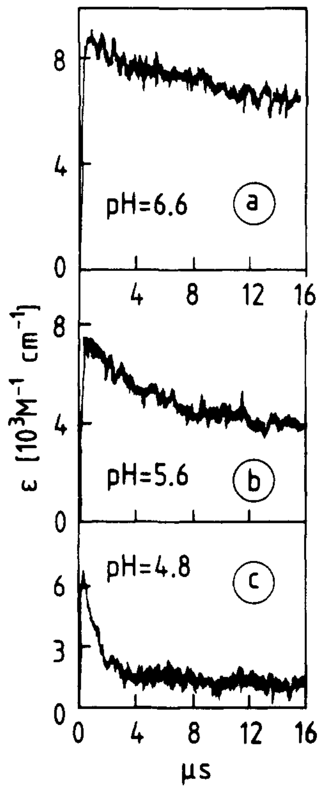

Figure 3. Absorbance at 420 nm as a function of time at various pH values. Conditions: solution, 8×10^{-4} M $\mathrm{Au(CN)_2^-}$ and 0.1 M propanol-2; hydrated electron production per pulse, 1×10^{-7} M.

Experiments were also performed with $\mathrm{N_2O}$ solutions containing propanol-2. Under these circumstances hydrated electrons are scavenged and additional OH radicals formed, which in turn produce organic radicals according to eq 1:

$$\mathrm{N_2O + e^-_{aq} + H_2O \rightarrow N_2 + OH^- + OH} \qquad (4)$$

Only these organic radicals are the possible reactants under these conditions. No changes in absorption or conductivity were detected. It has to be concluded that $\mathrm{(CH_3)_2COH}$ radicals do not react with $\mathrm{Au(CN)_2^-}$ under the conditions of pulse radiolysis.

Protonation of $\mathrm{Au(CN)_2^{2-}}$. Figure 3 shows typical absorption versus time curves obtained with slightly acidic solutions. $\mathrm{KAu(CN)_2}$ was present at 8×10^{-4} M to ascertain that $\mathrm{Au(CN)_2^{2-}}$ was formed during the pulse. The dose was kept low to produce only 1×10^{-7} M hydrated electrons (and protons) to avoid significant changes in the pH of the solution. It is seen that the absorption signal immediately after the pulse decreased with decreasing pH and that its decay after the pulse became faster. The immediate change in conductivity at pH = 6.6 was $300\ \mathrm{cm^2\ \Omega^{-1}\ M^{-1}}$, which corresponds to the formation of a proton during the pulse. However, this conductivity signal became smaller as the pH decreased. Figure 4, curve a, shows the signal intensity as a function of pH. The S-shaped curve is typical for a protolytic equilibrium.

These results are understood in terms of the protonation of the first reaction product:

$$\mathrm{H^+ + Au(CN)_2^{2-} \rightleftarrows Au(CN)_2H^-} \qquad (5)$$

This equilibrium is established within the pulse, the predominant reaction in the forward direction being $\mathrm{Au(CN)_2^{2-} + H_2O \rightarrow Au(CN)_2H^- + OH^-}$. The p$K$ of the equilibrium of eq 5 is 5.9 (see arrow in Figure 4).

The decay at the highest pH in Figure 3 is attributed to the unprotonated species (reaction 3), which is the major species present at this pH. With decreasing pH, the decay is also due

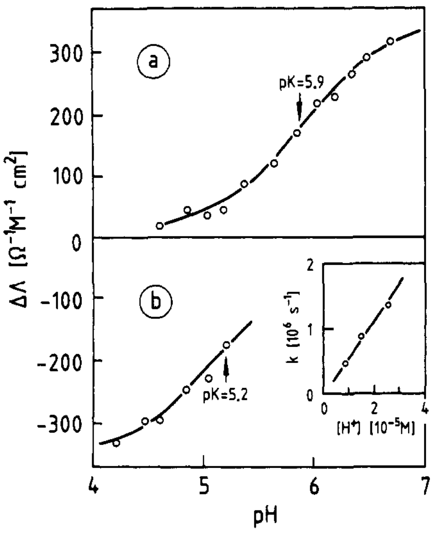

Figure 4. Molar conductivity change at 4 μs (curve a) and at 20 μs (curve b) after the pulse as functions of pH. Solution as in Figure 3. Inset: pseudo-first-order rate constant of the second protonation step at various H^+ concentrations.

to the decay of the protonated product. However, a new process also started to occur as the conductivity after the pulse decreased and ΔΛ even reached negative values. This indicates that an additional proton was picked up as the following equilibrium was established:

$$H^+ + Au(CN)_2H^- \rightleftarrows Au(CN)_2H_2 \qquad (6)$$

Curve b in Figure 4, where the conductivity after 20 μs is plotted vs pH, shows this effect. As the doubly protonated product has no absorption at 420 nm, the uptake of the proton after the pulse is mainly responsible for the decay of the absorption. The inset of Figure 4 shows the rate constant of the first-order decay of the 420-nm absorption at higher H^+ concentrations in Figure 3. A bimolecular rate constant of 5.9×10^{10} M^{-1} s^{-1} for the forward reaction of the equilibrium of eq 6 was obtained from this plot. The absorption remaining after the fast decay (Figure 3c) is due to the singly protonated form after the establishment of equilibrium 6. A pK value of 5.2 for the equilibrium of eq 6 was obtained as indicated by the arrow on curve b in Figure 4.

Absorption Spectra and Reduction by H Atoms. The absorption spectrum of $Au(CN)_2^{2-}$ (Figure 2) resembles that of the reduction product observed previously.[4] The absorption spectrum of the free gold atom in aqueous solution (Figure 2) seems to have been reported here for the first time. The absorption spectrum of $Au(CN)_2H^-$ was obtained by measuring the absorbance at various wavelengths immediately after the pulse of an 8×10^{-4} M $KAu(CN)_2$ solution at pH = 4.8. Both the reaction of e^-_{aq} (eq 2) and the first protonation (eq 5) occur during the pulse under these conditions. A small percentage of the hydrated electrons formed reacts with H^+ ions to form H atoms. However, as is shown below, these H atoms also rapidly reduce $Au(CN)_2^-$. The spectrum of $Au(CN)_2H^-$ obtained resembles very much that of $Au(CN)_2^{2-}$, the maximum appearing at 430 nm. However, the specific absorbance is only 6.0×10^3 M^{-1} cm^{-1} as compared to 1.0×10^4 M^{-1} cm^{-1} for $Au(CN)_2^{2-}$.

Experiments were also performed with solutions having pH = 3.0. Under these circumstances, most of the hydrated electrons react with hydrogen ions to yield H atoms. The solution contained 3.6×10^{-5} M $KAu(CN)_2$ and 5×10^{-3} M *tert*-butyl alcohol as OH radicals scavenger. As the reaction of H atoms with *tert*-butyl alcohol is relatively slow ($k = 1 \times 10^5$ M^{-1} s^{-1} (ref 9)) one could expect that the H atoms would be able to react with $Au(CN)_2^-$ provided that this reaction is fast. In fact, one observed a buildup of absorbance at 260 nm. The half-life of this buildup was proportional to the $KAu(CN)_2$ concentration. The absorption is attributed to $Au(CN)_2H_2$:

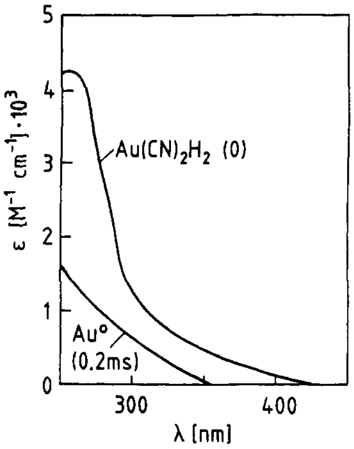

Figure 5. Absorption spectra of the intermediates at 0 and 0.2 ms in a pulsed solution of pH = 3.0, containing 3.6×10^{-5} M $KAu(CN)_2$ and 5×10^{-3} M *tert*-butyl alcohol.

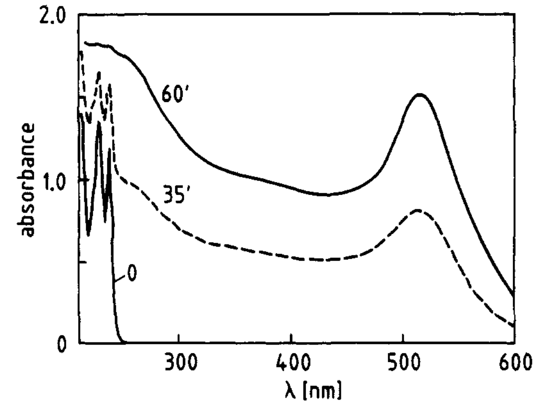

Figure 6. Absorption spectrum of a 4.2×10^{-4} M $KAu(CN)_2$ solution before and after γ-irradiation (30 and 70 min). Conditions: Dose rate, 1.3×10^5 rad/h; 0.1 M propanol-2.

$$H + Au(CN)_2^- \xrightarrow{H^+} Au(CN)_2H_2 \qquad (7)$$

A rate constant of 1.4×10^{10} M^{-1} s^{-1} was obtained. The doubly protonated species was found to decay with 5.3×10^4 s^{-1} (corresponding half-life, 13 μs). The spectrum of $Au(CN)_2H_2$ is shown in Figure 5. It is substantially different from those of $Au(CN)_2^{2-}$ and $Au(CN)_2H^-$ as there is practically no extension into the visible. After the decay of the doubly protonated species, the spectrum of Au^0 remained (also shown in Figure 5).

Gold Atom-Radical Reactions. Two species are present in the pulsed solutions after the decay of the primary reduction products: gold atoms resulting from this decay and free radicals formed by the attack of OH radicals on the added organic compound. At the low doses of 10^{-7}–10^{-6} M radical production per pulse, these organic radicals live many milliseconds with respect to their mutual deactivation. The question arises whether the gold atoms are able to react with the radicals. In previous studies on the radiolytic reduction of metal ions, such as Ni^{2+},[10] Cd^{2+},[11] and Pb^{2+},[12] such interactions have been detected. For example, Ni^+ ions form Ni–C bonds with 1-hydroxyalkyl radicals, and these nickel–organic compounds are then hydrolyzed.[10]

Both γ-irradiations and pulse radiolysis experiments were carried out to study such reactions. γ-Irradiation of $KAu(CN)_2$

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TABLE I: *G* Values[a] of $Au(CN)_2^-$ Disappearance (or Gold Formation) in γ-Irradiated 8×10^{-4} M $KAu(CN)_2$ Solutions Containing Various OH Scavengers (0.1 M) under Various Gases

H scavenger	pH	Ar	N_2O
propanol-2	natural	3.4	3.2
methanol	natural	1.8	1.4
NaCOOH	natural	0.2	<0.1
tert-butyl alcohol	natural	0	0
propanol-2	13	2.2	0.41
methanol	13	1.9	0.30

[a] Number of molecules consumed (or gold atoms formed) per 100 eV absorbed radiation energy.

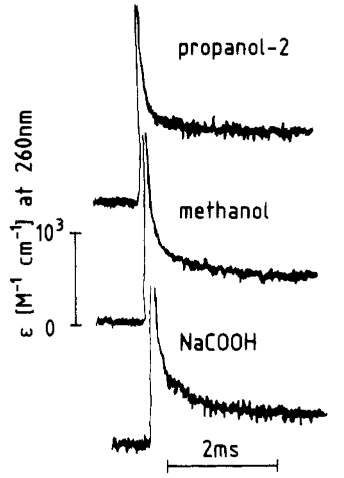

Figure 7. Absorption at 260 nm of Au^0 as a function of time in solutions containing various OH radical scavengers. Radicals of 1.5×10^{-6} M concentration were generated in one pulse.

solutions leads to the formation of red colloidal gold. Figure 6 shows a typical example. The band at 520 nm is attributed to the surface plasmon absorption of metallic gold particles formed upon irradiation. One also recognizes two sharp bands at 229 and 238 nm that decrease in intensity. They belong to the $Au(CN)_2^-$ complex. Assuming an unstructed absorption of the colloidal gold in this wavelength range that could readily be subtracted from the absorptions of the sharp bands, one could calculate the rate of disappearance of $Au(CN)_2^-$. Table I gives the yields for this disappearance in solutions containing different OH scavengers. The rate of disappearance of $Au(CN)_2^-$ is equal to the rate of the formation of gold atoms. The experiments were performed with argon-saturated solutions containing the organic OH scavenger, in which e^-_{aq} and H atoms react with $Au(CN)_2^-$, and with N_2O-saturated solutions, where only the organic radicals react with the gold complex. One should also keep in mind that the 1-hydroxyalkyl radicals are protolytically dissociated at pH = 13.[13]

If the organic radicals efficiently reduced $Au(CN)_2^-$, the Au^0 yield should amount to 6 atoms/100 eV. A glance at the table shows that this is not the case. If the radicals do not react with the Au^0 atoms, which are formed by the hydrated electrons, the yield should be equal to 2.7 − 0.8 = 1.9, i.e., the difference in the yields of e^-_{aq} and the molecular H_2O_2 that is also formed in irradiated aqueous solutions. H_2O_2 oxidizes one Au^0 atom

$$H_2O_2 + Au^0 \rightarrow Au^+ + OH^- + OH \qquad (8)$$

the OH radical formed being scavenged by the organic additive.

In order to observe the decay of the gold atoms due to their reaction with the organic radicals generated simultaneously, the pulse radiolysis experiments of Figure 7 were carried out. The solution contained $KAu(CN)_2$ at 8×10^{-4} M and had pH = 4.6. The primary processes producing Au^0 atoms occurred here with a half-life of 20 μs. In the beginning of the curves in Figure 7, one recognizes the final part of this fast decrease in the absorption of $Au(CN)_2^-$ (whose absorption straight after the pulse is so high that it cannot be shown on the ordinate scale of Figure 7). After this decay is over, an additional decay occurs that ends in a long-lived absorption at times >1 s. This second decay is of second order as it becomes faster with increasing dose in the pulse. It is important to note that the height of the final absorption depends on the nature of the organic additive. It is highest for propanol-2 and lowest for sodium formate. The effect is understood in terms of reactions of the Au^0 atoms with organic radicals leading to the reoxidation of Au^0. The *G* values for surviving gold atoms, as calculated from the long-lived rest absorptions in Figure 7, are 2.7 for propanol-2, 1.3 for methanol, and 0.4 atoms/100 eV for NaCOOH. They agree fairly well with the values of gold formation in the γ-irradiation experiments (Table I).

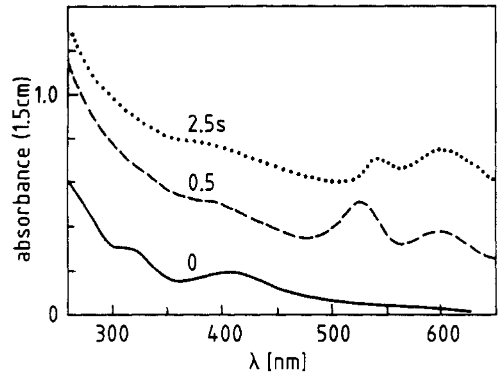

Figure 8. Irradiation of a solution containing 1.7×10^{-4} M $KAu(CN)_2$ and 0.1 M sodium formate with a pulse train during 0.5 s. Absorption spectrum is at different elapsed times.

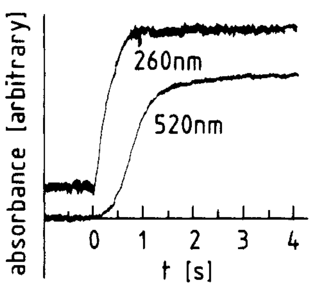

Figure 9. Buildup of the 260- and 520-nm absorptions during application of a pulse train. Solution as in Figure 8.

Agglomeration of Gold Particles. Although the yield of residual gold atoms in the experiments of Figure 7 was low, substantial gold concentrations could be produced by applying many pulses in the form of a train, in which each pulse generated 10^{-5} M hydrated electrons. The interval between the pulses was 3×10^{-3} s corresponding to a frequency of 333 s^{-1}. Under these conditions, a total irradiation time of 0.5 s was sufficient to reduce all the $Au(CN)_2^-$ ions initially present in a 1.7×10^{-4} M solution containing formate anions and having pH = 9. The absorption spectrum after this 0.5-s irradiation is shown in Figure 8 (spectrum 0). It is significantly different from that of colloidal gold metal (Figure 6) as the main absorptions are in the UV. These absorptions are attributed to gold clusters that do not yet possess metal character. The spectrum changed with time after application of the 0.5-s pulse train. After 0.5 s of thermal growth, the maximum at 520 nm of gold metal was present, and after 2.5 s, a maximum at 600 nm appeared. The solution had a blue color after this time, which indicates that very large gold particles must have been formed. The rate of transformation of the clusters to colloidal metal particles increased with the increasing ionic strength of the solution. The agglomeration process is also demonstrated in Figure 9, where the increase in absorbance at 260 and 520 nm with time after the beginning of the pulse train is shown. As expected, the 260-nm absorption started to increase immediately while that at 520 nm began in an S-shaped manner.

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Discussion

The reaction of the hydrated electron with $Au(CN)_2^-$ does not yield a gold atom immediately. First, $Au(CN)_2^{2-}$ or one of its protonated forms, $Au(CN)_2H^-$ or $Au(CN)_2H_2$, is produced, which then decays to form Au^0. Such a delayed release of ligands from a central metal atom whose charge is suddenly changed has been observed in many other cases.[14]

The standard redox potential of the system $Au(CN)_2^-/Au(CN)_2^{2-}$ is -0.6 V.[15] The reaction of the hydrated electron whose potential is -2.9 V has a lot of driving force and is, therefore, practically diffusion controlled. The 1-hydroxyalkyl radicals, which were formed simultaneously in solutions containing an alcohol as OH scavenger, should in principle also be able to reduce $Au(CN)_2^-$ as their redox potentials are more negative than -0.6 V.[16] In fact, the results of the γ-irradiation experiments indicate that at least CH_2OH and $(CH_3)_2COOH$ radicals reduce $Au(CN)_2^-$ (Table I). The low yields, however, indicate that the rates of these reductions are not high. No reduction of $Au(CN)_2^-$ could be observed in the pulse experiments where the radical concentration is much higher than in γ-radiolysis. It can be said from the absence of reaction under these conditions that the rate constants of the radical–$Au(CN)_2^-$ reactions are smaller than 10^6 M^{-1} s^{-1}.

It was shown in the experiments of Figure 7 that Au^0 atoms can reduce organic radicals. This can be understood in terms of a rather negative standard potential of the system Au^+/Au^0, where Au^0 is a free gold atom in solution. The standard potential of the compact gold electrode is +1.68 V. By subtracting $\Delta G_{subl}(Au)/e = 3.15$ V,[17] the free energy of sublimation of gold divided by the elementary charge, from the potential of the metal electrode, one obtains a value of -1.47 V for the potential of the Au^+/Au^0 system (this value should still be corrected by the free hydration energy of Au^0, which is not known; it can, however, be assumed that this hydration energy does not exceed 0.1 eV, the value for the hydration of other atoms such as Kr or Xe). One can thus expect the gold atom in aqueous solution to be a strong reducing agent as was found for the silver atom in the earlier work.[18]

The reduction power of gold atoms makes it understandable that they can reduce organic radicals, although many of these radicals are strong reducing agents themselves. In the reduction of a carbon-centered radical, a water molecule is involved, the reaction occurring through the hydrolysis of an intermediate organo–gold compound. We formulate this for the hydroxymethyl radical:

$$Au^0 + CH_2OH \rightarrow AuCH_2OH \qquad (9)$$

$$AuCH_2OH + H_2O \rightarrow Au^+ + CH_3OH + OH^- \qquad (9a)$$

The radical–gold atom reactions have to compete with radical–radical deactivation. The efficiency of reoxidation of gold atoms therefore depends on the ratio of the rate constants of these competing processes. The fact that radical–gold reactions do occur shows that the specific rates of such reactions must be of the order 10^9 M^{-1} s^{-1}.

The gold yields in the γ-radiolysis experiments (Table I) are the result of a very complex reaction mechanism: In argon-containing solution, Au^0 is formed via reaction of e^-_{aq} (eq 2 and 3). Additional Au^0 atoms may be formed by reduction of $Au(CN)_2^-$ by organic radicals. On the other hand, as these reactions are very slow, the organic radicals may also oxidize Au^0 atoms formed. In N_2O-containing solution, only organic radicals are formed, which may reduce $Au(CN)_2^-$, but again, reoxidation and the loss of radicals via self-reaction will influence the yield. Finally, when the irradiation is carried out with solutions at pH = 13, one is dealing with the base forms of the 1-hydroxyalkyl radicals that are generally stronger reducing and may have reactivities toward both $Au(CN)_2^-$ and Au^0 different from those of the neutral radicals.

Keeping in mind these various factors, we come to the following interpretation of the gold yields in the γ-radiolysis experiments of Table I:

In the case of methanol and N_2O, gold is formed, which shows that CH_2OH radicals can reduce $Au(CN)_2^-$. However, the yield is not high (1.4 atoms/100 eV). In the presence of argon, the yield (1.8 atoms/100 eV) is close to expectation if only e^-_{aq} contributes to the gold formation. Both observations are best understood in terms of both reduction of $Au(CN)_2^-$ and oxidation of Au^0 by CH_2OH taking place, the two effects counterbalancing in the case of the argon-containing solution. In the case of propanol-2 and N_2O, a relatively good yield (3.2 atoms/100 eV) is observed, indicating that $(CH_3)_2COH$ radicals can reduce $Au(CN)_2^-$. However, as the maximum yield of 6 atoms/100 eV is not reached, a partial reoxidation of gold atoms must be postulated, although the self-reaction of the radicals may be the more important factor. In the case of the argon-containing solution, a slightly higher yield (3.4 atoms/100 eV) is obtained, again indicating that reduction of $Au(CN)_2^-$ occurs more frequently than reoxidation of gold atoms.

The low yields in alkaline solutions of propanol-2 and methanol in the presence of N_2O are difficult to interpret unambiguously. It seems that the base forms of the 1-hydroxyalkyl radicals are almost nonreactive toward both $Au(CN)_2^-$ and Au^0.

In the cases of *tert*-butyl alcohol and formate, extremely low yields are observed. The *tert*-butyl alcohol radical, having less reducing power than 1-hydroxyalkyl radicals, probably cannot reduce $Au(CN)_2^-$ at all. On the other hand, it is very efficient oxidizing gold atoms formed in the $e^-_{aq} + Au(CN)_2^-$ reaction. The CO_2^- radical, formed in formate-containing solution, has a strong negative reduction potential (-2.0 V). One would, therefore, expect a more efficient reduction of $Au(CN)_2^-$, although the electrostatic repulsion between the two species may be unfavorable. Further, CO_2^- can also accept an electron from a strong reducing donor,[19] which would explain why practically no gold is formed in the argon-containing solution.

Registry No. $Au(CN)_2^-$, 14950-87-9; Au, 7440-57-5; $Au(CN)_2^{2-}$, 121675-40-9; $Au(CN)_2H^-$, 121675-41-0; $Au(CN)_2H_2$, 121675-42-1; N_2O, 10024-97-2; hydrogen atoms, 12385-13-6; propanol-2, 67-63-0; methanol, 67-56-1; *t*-butanol, 75-65-0; formate, 71-47-6.

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