The hydrolysis of gold(I) in aqueous acetonitrile solutions

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The hydrolysis and subsequent decomposition of gold(I) in aqueous solutions with acetonitrile were found not to yield the expected disproportionation products gold(0) and gold(III) in a ratio of 2:1, but more than 98% gold(0), and also oxygen when acetonitrile from the gold(I) stock solution was removed first. The pH dependence of the reaction rate is attributed to a hydrolysis equilibrium established before the redox decomposition. The species [Au(CH$_3$CN)(OH)] and Au(OH) were identified by alkalimetric titrations and numerical analysis, with the logarithms of their formation constants being 10.7 and 10.2 respectively. These species seem to be sources of the OH$^\bullet$ radical, which explains the oxygen formation in the absence of acetonitrile, and an alteration of its UV spectrum when it is left in the reaction mixture. The high complex stability of gold(I) with hydroxide ions means that it is one of the most acidic univalent cations, similar to HgCH$_3{}^+$. The known relativistic contraction of the 6s orbital in gold(I) may account for this unusual property.

Univalent cations normally do not undergo detectable hydrolysis in aqueous solution. Known exceptions are Ag$^+$ and HgCH$_3{}^+$ with pK_a values of 12 and 3.5 respectively.[1] The corresponding values for the chemically similar Cu$^+$ and Au$^+$, which also could undergo hydrolysis, are not known. Stabilization of Cu$^+$(aq) has never been accomplished due to the disproportionation reaction that takes place readily at all pH values; Au$^+$ is also known to be unstable in aqueous solution, especially under alkaline conditions. The disproportionation to Au and Au^{III} is generally believed to be favoured in alkaline solutions because of the stability of gold(III) oxo and hydroxo species,[2] but the decomposition of hydrated Au$^+$ has actually never been studied. Gold(I) solutions in mixtures of acetonitrile and dilute mineral acids, however, have been used to obtain an estimate of the Au$^+$–Au standard redox potential.[3,4] Gadet and Pouradier[5] demonstrated the hydrolysis of AuCl$_2{}^-$ at pH values below 7, meaning that Au$^+$ should be somewhat acidic. The stability (log β$_{11}$ = 19.6) of [Au(OH)(mpt)] (mpt = *N*-methylpyridine-2-thione) found by Szvircsev[6] also supports this hypothesis. It was thought to be possible, therefore, that the hydrolysis of Au$^+$ in slightly acidic water–acetonitrile mixtures would be observable.

A main problem in this study was posed by the prediction that the disproportionation should yield protons by the irreversible hydrolysis of Au^{III}. Also, the way hydrated Au$^+$ disproportionates has never been elucidated. While only one-electron steps are needed to convert Cu$^+$ into the disproportionation products, for Au$^+$ a two-electron step is required, or Au^{2+} must be an intermediate, its existence in dilute aqueous solutions being questionable. Assuming Au^{2+} is never formed in the reaction, a two-electron acceptor should occur as an intermediate in the reaction. For these reasons, the decomposition of Au$^+$ in aqueous solution was studied in advance to the hydrolysis.

Experimental

Reagents

All reagents were analytical grade or better (Merck or Fluka), except for AuO$_3$SCF$_3$ solution in acetonitrile, which was produced by electrolysis[7] of 99.999% gold wire (Johnson Matthey). Water of triply distilled quality was obtained from a Millipore water-purification unit which was fed with deionized water.

Decomposition experiments

Gold trifluoromethanesulfonate in acetonitrile (0.01 mol dm^{-3}) was added to 0.1 mol dm^{-3} aqueous NaClO$_4$ solutions of various pH values, adjusted using HClO$_4$ or NaOH, so that the gold(I) concentration was around 10^{-3} mol dm^{-3} at the beginning. It was measured then periodically by voltammetric scans with a Metrohm 628-10 rotating gold-disc electrode connected to an AMEL 553 potentiostat and a 568 function generator. The reference electrode was a Ag–AgCl half cell in 0.01 mol dm^{-3} KCl. When the reduction current step had dropped to the background value it was assumed that the reaction had finished. The most acidic solutions of pH ⩽ 2 were refluxed for 1 h the day after the start of the experiment, because there was still a current signal of Au$^+$ present at that time. Upon this treatment the reaction was complete. The precipitate was collected on a 0.2 μm Teflon filter. It was then treated with 6 mol dm^{-3} hydrochloric acid in order to dissolve gold(III) compounds as chloro complexes, mainly AuCl$_4{}^-$. This procedure was repeated three times, the solutions were pooled and brought to a defined volume in a graduated flask. The residue then was treated with *aqua regia*, in order to dissolve metallic gold, which was also converted into gold(III) chloro complexes. The *aqua regia* solution was boiled to remove chlorine and nitrogen dioxide, and also brought to a defined volume. Both solutions were analysed with a Kontron Uvikon 820 double-beam spectrophotometer at 313 nm. From the results the fractions of Au^0 and Au^{III} were calculated.

Hydrogen peroxide detection was tried with saturated oxo-titanium(IV) sulfate in 1.5 mol dm^{-3} sulfuric acid which was added quickly to a solution from a decomposition experiment at pH 12 (see above). The gold powder was filtered off subsequently, and the absorbance was read at 410 nm.[8] A calibration was carried out with four dilute hydrogen peroxide solutions of different concentrations. The concentration of the hydrogen peroxide stock solution for the calibration was determined by iodometric titration. The detection limit of the oxo-titanium method found with the calibration was 5 × 10^{-6} mol dm^{-3}.

The following method was applied for oxygen detection. A micro Clark cell (volume ≈ 10 mm^3) was assembled from a 10 mm glass tube, a 1 mm gold wire, a 10 mm^2 silver disc and epoxy resin. The silver disc was covered with AgCl by anodic oxidation in 2 mol dm^{-3} HCl. The cell was filled with 0.1 mol dm^{-3} KCl and sealed with a Teflon membrane. The cell was connected to an AMEL 553 potentiostat and the current signal was fed to a strip-chart recorder. The system was calibrated using argon- and air-saturated water respectively.[8]

Titration procedure

Aqueous trifluoromethanesulfonic acid was mixed in a 10 cm³ round flask with AuO_3SCF_3 in acetonitrile. The weight of the flask and mixture was determined, and the flask was slowly evacuated to 2 kPa under rotation. The flask cooled rapidly because of acetonitrile evaporation. After a variable time of some minutes, atmospheric pressure was restored and the flask allowed to warm to room temperature. The acetonitrile content of the solution was determined from the volume of the initially added acetonitrile, the density of acetonitrile and the weight loss. The weight loss in the first 10 min was rapid and never exceeded the total amount of acetonitrile in the sample; only after longer times, a slow loss of further mass by water evaporation was detectable. For experiments with constant acetonitrile concentration, suitable amounts of acetonitrile were added to compensate for excessive loss. The solution then was mixed with water and electrolyte ($NaClO_4$) and finally brought to a defined volume (10 cm³) and an ionic strength of $I = 0.1$ mol dm⁻³ in the thermostatted Metrohm titration vessel (Haake thermostat, set to 25 °C). The mixture was titrated under computer control with 0.1 mol dm⁻³ NaOH from a Metrohm 665 precision motor burette, total volume 1 cm³, resolution 1 mm³. The pH was read from an Ingold glass electrode with an internal Ag–AgCl reference electrode by an Orion model 720 digital pH meter. Twelve curves with acetonitrile concentrations from 0.05 to 4.39 mol dm⁻³ and a gold(I) concentration from 6×10^{-4} to 8×10^{-4} mol dm⁻³ were recorded. Another four curves with a constant acetonitrile concentration of 0.91 mol dm⁻³ and total gold(I) concentrations from 5×10^{-4} to 5×10^{-3} mol dm⁻³ completed the titrations.

The electrode was calibrated every day by titration of 0.01 mol dm⁻³ CF_3SO_3H in 0.09 mol dm⁻³ $NaClO_4$. From the resulting curve, 30 points before and after neutralization were used to calculate K_w and the standard potential $E^{\circ\prime}$ of the electrode, assuming a slope of 59.16 mV pH⁻¹ at 25 °C. The log K_w value ranged between -13.75 and -13.82. Acetonitrile concentrations above 0.5 mol dm⁻³ changed $E^{\circ\prime}$ considerably. Therefore, a series of calibration titrations with variable acetonitrile concentrations was carried out. The relationship between acetonitrile concentration and $E^{\circ\prime}$ was linear and used to correct the data from titrations with high acetonitrile concentrations. The data files from the gold(I) titrations contained 91 points. Most were taken in the region where the slope of the curve began to rise (see Fig. 4). Depending on the onset of obvious irreversible decomposition, later points were excluded from calculations, but 60 points per curve were left at least. The data were subjected to analysis by the SUPERQUAD program,[9] which does a least-squares fit of a selected model to the experimental curve by adjusting the equilibrium constants.

Results and Discussion

In order to study its decomposition, solutions of Au^I in acetonitrile were mixed with aqueous electrolyte solutions of ionic strength $I = 0.1$ mol dm⁻³ and of variable pH. The temperature was kept at 25 °C with a water-bath thermostat. When decomposition was incomplete after 10 h the solution was boiled the next day for 1 h, which was sufficient to remove the gold(I) completely from the solution. The reaction time for completion ranged from more than 1 d below pH 2 to some minutes in alkaline solutions of pH 12. Unfortunately, it was impossible to follow the rate by a physical technique, because of the heterogeneous mixture of products. In all cases a black precipitate was formed. The acidic, neutral and weakly alkaline solutions were colourless after the reaction; the strongly alkaline ones were slightly yellow. According to the product analysis, the theoretical ratio of 2:1 of Au^0:Au^{III} was never reached, the gold(III) fraction being only a few percent of the total amount of gold (Table 1). It was then tested whether pro-

Table 1 Average decomposition-product distribution of Au^I in aqueous solution

	mol %	
Initial pH	Au^0	Au^{III}
2	99.4	0.6
7	98.3	1.7
12	98.1	1.9

tons were released during the decomposition. An unbuffered solution of $I = 0.1$ mol dm⁻³ was brought to pH ≈ 9, thus [OH⁻] was around 10^{-5} mol dm⁻³, measured with a glass electrode. Gold(I) in acetonitrile was injected with stirring so that its concentration became 5×10^{-4} mol dm⁻³, and the pH was observed. The pH quickly dropped to 4, indicating release of H⁺ by the reaction.

The above findings imply that disproportionation does not take place; instead the Au⁺ is simply reduced. The possible reducing agents in this case were acetonitrile, trifluoromethanesulfonate and water. Dry acetonitrile, however, is one of the few solvents in which Au⁺ is stable for weeks, together with perchlorate, tetrafluoroborate, trifluoromethanesulfonate or hexafluorophosphate. This type of solution is slowly decomposed only upon the uptake of moisture. The stability of Au^I in acetonitrile is not caused by exceptional donor properties of this solvent, because the corresponding complexes are only moderately stable in water.[4] More likely, it is impossible for Au^I to oxidize acetonitrile. Acetonitrile is one of the solvents in electrochemistry with the broadest working range, which means that the activation energies for both oxidation and reduction are very high. In such an environment Au^I has no possibility to get an electron. This leaves water as the reducing agent. Together with the observation that the decomposition is much more rapid in alkaline solution, one can postulate the reactions (1) and (2).

$$Au^+ + H_2O \rightleftharpoons Au(OH) + H^+ \qquad (1)$$

$$Au(OH) \longrightarrow Au + OH^\bullet \qquad (2)$$
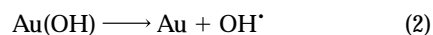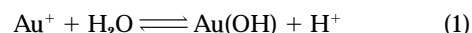
There is evidence from the voltammetric measurements of the gold(I) concentration that a hydroxo compound is formed with increasing pH. The onset potential of the gold(I) reduction was found to be variable with the pH at constant acetonitrile concentration (Fig. 1). It shifted towards more negative values when the pH was increased, which means stabilization of Au^I by hydroxide against reduction by the electrode. Concurrently, Au^I is reduced faster in solution. The above scheme explains why the formation of Au^0 is preferred. The fate of the supposed hydroxyl radical can be described by the known reactions (3) and (4). Recombination of OH$^\bullet$ seems probable in the solutions

$$2\, OH^\bullet \longrightarrow H_2O_2 \qquad (3)$$

$$2\, H_2O_2 \longrightarrow 2\, H_2O + O_2 \qquad (4)$$
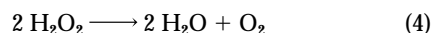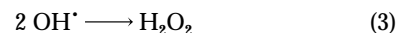
that were used in the experiments, because, at first glance, there were no substrates for it to react with. We tried to trap H_2O_2 by its reaction with Ti^{IV},[8] however this was never achieved. The H_2O_2 was then thought to undergo rapid disproportionation (4) by heterogeneous catalysis on the gold metal powder formed in reaction (2). Surprisingly, the detection of oxygen evolution in argon-saturated solutions using a micro Clark cell also failed. It was noticed that the UV absorption in these solutions between 200 and 230 nm was increased after gold(I) decomposition. A control experiment was performed by preparing a water–acetonitrile–H_2O_2 mixture, recording its UV spectrum before and after exposure to the radiation of a mercury-arc lamp (50
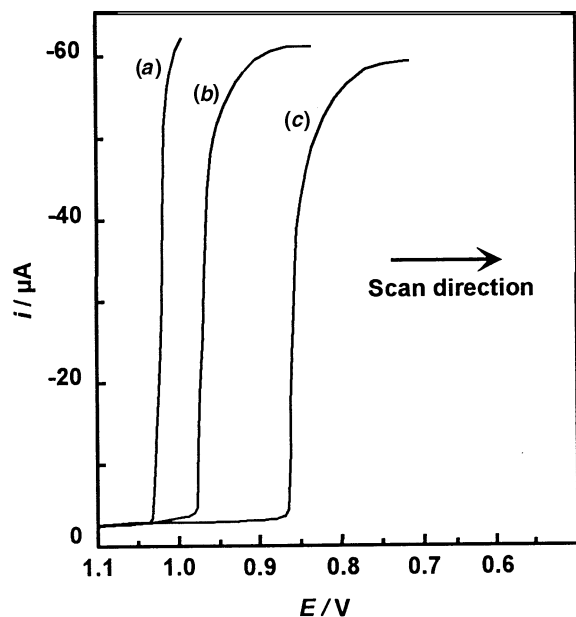
Fig. 1 Reductive scans (250 μV s⁻¹) at a 7.1 mm² rotating gold-disc electrode (3000 min⁻¹) in aqueous solutions containing 2.5×10^{-3} mol dm⁻³ AuO_3SCF_3, 0.46 mol dm⁻³ acetonitrile and 0.025 mol dm⁻³ $NaClO_4$. Reference electrode: Ag–AgCl in 0.01 mol dm⁻³ KCl. pH 2(*a*), 4(*b*) and 7(*c*)
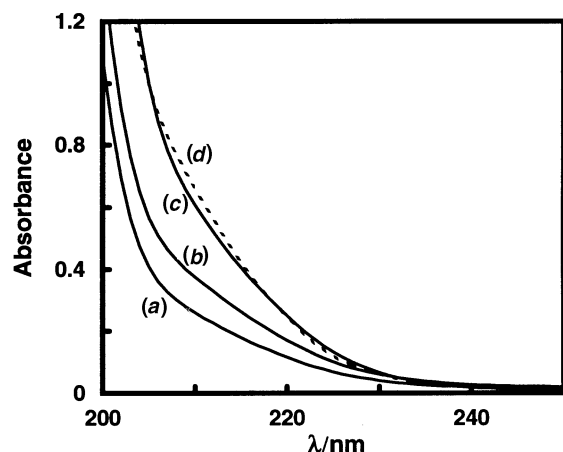
Fig. 2 The UV spectra of water–acetonitrile mixtures: similar effect of Au^I and photolysis of H_2O_2. (*a*) 0.46 mol dm⁻³ acetonitrile in water, (*b*) mixture (*a*) with 10^{-3} mol dm⁻³ H_2O_2, (*c*) mixture (*b*) after 15 min of photolysis with a 50 W mercury lamp, (*d*) mixture (*a*) with 10^{-3} mol dm⁻³ AuO_3SCF_3 after removal of solid Au

W) for 15 min in a quartz cuvette in order to split H_2O_2 into OH˙ radicals. In the UV spectrum measured after exposure a similar change of absorbance was observed as for the gold(I) decomposition (Fig. 2). The OH˙ radical seems to be capable of attacking acetonitrile, while Au^+ itself is not. In a set of experiments, 0.5 cm³ of 0.01 mol dm⁻³ Au^+ solution in acetonitrile was added to 20 cm³ perchloric acid solution of pH 1. Then the acetonitrile was removed by vacuum evaporation at 5–25 °C. No decomposition was detectable during this process. The solution was saturated with argon and sealed in an air-tight flask together with the Clark cell. A suitable quantity of argon-saturated 0.1 mol dm⁻³ KOH solution to establish a final pH around 12 after mixing was injected through a rubber septum into the acidic solution. A black precipitate of gold powder was formed immediately, and a couple of seconds later the Clark cell indicated the evolution of molecular oxygen. This implies that the acetonitrile indeed must have trapped the OH˙ radicals in the experiments before. Indirect evidence for the formation of peroxide is the fact that, in decomposition products from alkaline solutions, some Au^{III} was recovered. At a pH greater
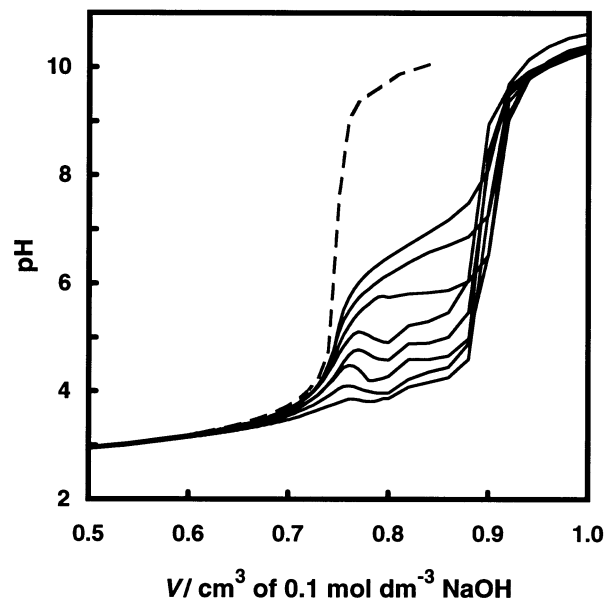
**Fig. 3** Titrations of 1.7×10^{-2} mol AuO_3SCF_3 in solutions of variable acetonitrile content and excess of trifluoromethanesulfonic acid with 0.1 mol dm⁻³ sodium hydroxide; gold(I) total concentration between 6.0×10^{-4} and 7.8×10^{-4} mol dm⁻³. Solid curves from top to bottom: 4.39, 1.73, 0.91, 0.42, 0.29, 0.19, 0.09 and 0.05 mol dm⁻³ acetonitrile. Dashed curve: acid excess only

than 10 the reaction is so fast that even in the presence of acetonitrile some peroxide may be formed. This peroxide then can oxidize unreacted Au^+ in a single step to Au^{III} while it is reduced to hydroxide. The assumption of a gold(II) intermediate is thus not necessary, since peroxide is a suitable two-electron acceptor. The hypothesis also explains why 33.3% Au^{III} is never obtained, because it is impossible that all the H_2O_2 formed reacts with Au^+ instead of undergoing disproportionation. A satisfactory explanation is also given for the acceleration in alkaline solution. Since it is a reasonable assumption that step (2) is irreversible and fast, the rate depends on the formation of Au(OH), which depends on the position of equilibrium (1).

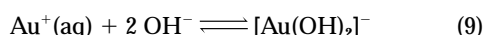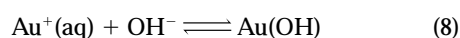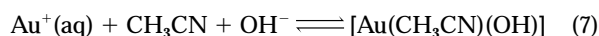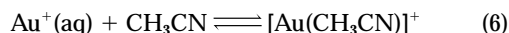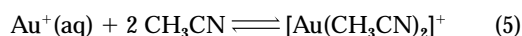Based on these preliminary investigations, base-titration experiments were carried out in acetonitrile–water mixtures which were acidified with trifluoromethanesulfonic acid. The alkalimetric method was chosen over direct potentiometry with a gold electrode because other workers reported slow settling of the Au^+–Au equilibrium.[3–5] The glass electrode, however, approaches the final reading closely within a couple of seconds. All the curves were smooth during the initial neutralization of the acid excess. When the pH began to rise as the acid excess was consumed an irregular behaviour set in depending on the acetonitrile concentration (Fig. 3). With high acetonitrile concentrations the curve continued rising smoothly and monotonously towards higher pH, showing a distinct buffering region. With lower acetonitrile concentrations, the pH began to drop back after a certain total amount of NaOH was added. This event indicated the beginning of irreversible formation of free protons together with decomposition of the buffering compounds. When more NaOH was added the pH shortly rose and dropped back again. The pH decrease was accompanied by the evolution of a dark turbidity in the solution, which finally resulted in a dark gold precipitate. The end of the range to be used for the evaluation of equilibrium constants was determined by the NaOH dosage at which the pH no longer increased steadily.

This type of titration was carried out in solutions with variable acetonitrile and constant gold(I) concentrations and with variable gold(I) but constant acetonitrile concentrations. The equilibrium constants were determined using the program SUPERQUAD.[9] The quality of the fit can be judged by the
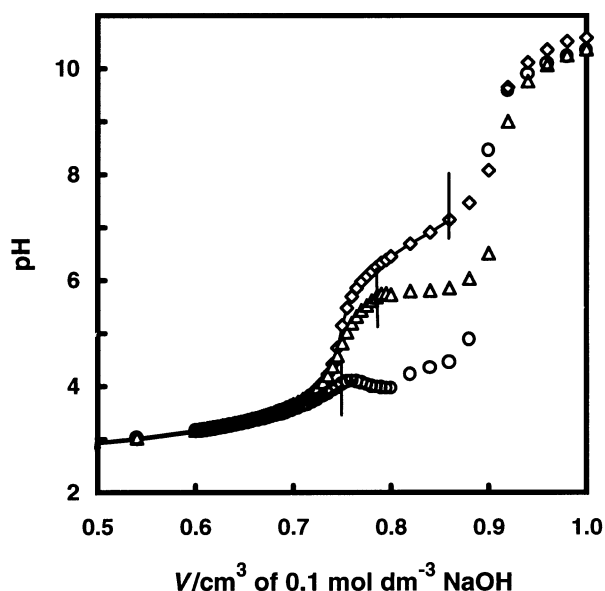
Fig. 4 The SUPERQUAD fits with a model including $[Au(CH_3CN)_2]^+$, $[Au(CH_3CN)(OH)]$, $Au(OH)$ and Au^+ to three curves from Fig. 3; 1.7×10^{-2} mol AuO_3SCF_3 with 4.39, 0.19 and 0.09 mol dm^{-3} acetonitrile (from top to bottom). Total gold(I) concentration between 6.0×10^{-4} and 7.8×10^{-4} mol dm^{-3}. Symbols, experimental data. Vertical bars, end of fitted ranges

residual vector resulting from the difference between the experimental and the calculated titration curve. To obtain the set of equilibria with significant contributions the following strategy was applied: for each titration a set of all plausible equilibria was applied. Then, the model was reduced by omitting one by one equilibria which were thought to be less important for the specific titration conditions with subsequent recalculation. Finally, a control calculation was performed by starting over and omitting the more probable species. The initial model for all calculations was formulated assuming the equilibria (5)–(9). Formation constants for reactions (5) and (6)

$$Au^+(aq) + 2\ CH_3CN \rightleftharpoons [Au(CH_3CN)_2]^+ \qquad (5)$$

$$Au^+(aq) + CH_3CN \rightleftharpoons [Au(CH_3CN)]^+ \qquad (6)$$

$$Au^+(aq) + CH_3CN + OH^- \rightleftharpoons [Au(CH_3CN)(OH)] \qquad (7)$$

$$Au^+(aq) + OH^- \rightleftharpoons Au(OH) \qquad (8)$$

$$Au^+(aq) + 2\ OH^- \rightleftharpoons [Au(OH)_2]^- \qquad (9)$$

were available from potentiometry with gold electrodes.[4] Values of $\log K_1 = 1.44$ and $\log \beta_2 = 1.77$ respectively were found. They were fed to SUPERQUAD as starting parameters, but left variable for optimization. For the titrations in solutions with high acetonitrile concentrations, equilibria (5) and (7) were necessary to describe the titration curve. In solutions with low acetonitrile concentrations equilibrium (8) had to be added to the model to obtain a good fit. In this case a substantial concentration of $Au^+(aq)$ was obtained in the calculation. Interestingly, models containing equilibria (6) and (9) always led to strong deviations of the calculated curve from the experimental one, so these reactions do not seem to contribute significantly to the system. Examples of fits to three curves in Fig. 3 are shown in Fig. 4.

The results imply that $[Au(CH_3CN)_2]^+$ must be the predominant species at an acetonitrile excess in acidic solution. Upon increasing pH it is hydrolysed to $[Au(CH_3CN)(OH)]$ and $Au(OH)$. One could also speculate about the formation of hydroxo-bridged polynuclear species, but including such equilibria in the model did not improve the residual vector of the fit.

Table 2 Results from the gold(I)–acetonitrile titrations in water

Species	$\log \beta$ (2σ error)
$[Au(CH_3CN)_2]^+$	3.1 ± 0.2
$[Au(CH_3CN)(OH)]$	10.7 ± 0.3
$Au(OH)$	10.2 ± 0.4

Their existence is not ruled out therefore, but it is impossible to determine their composition by the methods used in this work. Thus, the best treatment is to consider all completely hydrolysed species as 'Au(OH)'.

The ion $[Au(CH_3CN)]^+$ is probably formed only at acetonitrile concentrations close to that of gold(I); $[Au(OH)_2]^-$ is also not present, but this is easily understood. The titrations at low acetonitrile concentrations could never be followed to pH values so high that the formation of $[Au(OH)_2]^-$ would contribute enough to be detectable because of the decomposition. The absence of $[Au(OH)_2]^-$ and the fact that CH_3CN stablizes the solution against decay support the hypothesis that $Au(OH)$ and $[Au(CH_3CN)(OH)]$ are most probably the species to undergo subsequent redox decomposition.

Finally, a complete model including equilibria (5), (7) and (8) was set up using the constants obtained from the fits at the different conditions. This model was applied to fit all titration curves simultaneously, again by the SUPERQUAD program. The species distributions of the three titrations in Fig. 4 are shown in Fig. 5. It is remarkable that at an acetonitrile concentration of 0.09 mol dm^{-3} about 10% of the Au^I exist as $Au^+(aq)$. Our results suggest that this species really does exist at low pH. It can also be seen that above pH 3.5 the hydrolysed species are formed in significant concentrations.

Whereas $\log K_1^{CH_3CN}$ could not be determined for the above reasons, $\log \beta_2^{CH_3CN}$ was found to be 3.1 ± 0.2 (Table 2), one order of magnitude higher than the $\log \beta_2^{CH_3CN} = 1.77$ found by other workers.[4] The probability of the higher value being correct is increased by the interpretation of the voltammetric measurements that served to detect the presence of gold(I) species in the decomposition experiments. As mentioned above, it was noticed that the reduction onset potential in the negative potential sweep varied with pH (Fig. 1). The stability constants found for the hydroxo species (Table 2) indicate that they exist only in minor concentrations below pH 3, so it can be assumed that the Au^+–Au signal measured at pH 2 was influenced mainly by acetonitrile. It was also shown that the reduction onset potentials measured at different sweep rates approached a positive limit upon slowing down the rate. This limit can be considered as a rough approximation to the equilibrium potential. Using this value ($+1.36$ V *vs.* normal hydrogen electrode, NHE) at acetonitrile excess (0.46 mol dm^{-3}), and taking E° (Au^+–Au) $= 1.7$ V,[3,4] $\log \beta_2^{CH_3CN}$ can be estimated upon substitution of the equilibrium expression, $\beta_2^{CH_3CN} = [Au(CH_3CN)_2^+]/[Au^+][CH_3CN]^2$, into the Nernst equation $E = E^\circ$ (Au^+–Au) $+ (RT/F)\ln[Au^+]$ which yields equation (10) with

$$E = E^\circ(Au^+\text{–}Au) + \frac{RT}{F} \times \ln \frac{[Au(CH_3CN)_2^+]}{\beta_2^{CH_3CN}[CH_3CN]^2} \qquad (10)$$

$[Au(CH_3CN)_2^+]$ being equal to the total Au^I concentration and $[CH_3CN]$ being equal to the total acetonitrile concentration. A value of $\log \beta_2^{CH_3CN} = 2.9$ is obtained in good agreement with the result of the alkalimetric titrations.

The formation constants for the hydroxo species are rather high for a typical soft metal centre. Two ligand properties, which may occur together, seem to be important for the formation of stable gold(I) complexes. As theoretically expected, softness, which is often accompanied by π-acceptor properties, leads to stable compounds. Additionally, basicity seems to play a role. The strongest ligand known for Au^I, cyanide, ideally
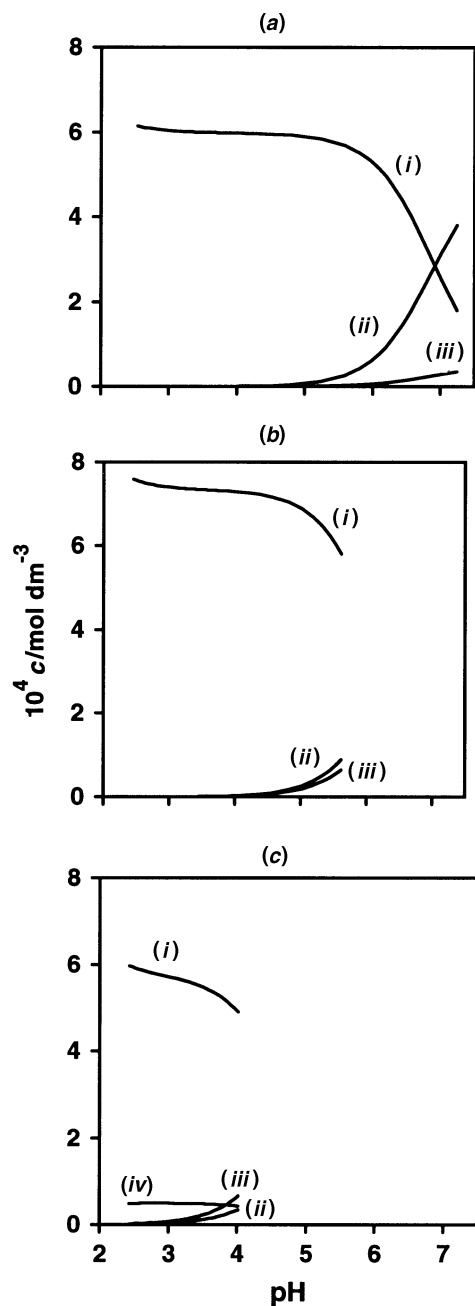
Fig. 5 Species distributions calculated from the SUPERQUAD fits in Fig. 4; AuO_3SCF_3 between 6.0×10^{-4} and 7.8×10^{-4} mol dm^{-3} with 4.39 (*a*), 0.19 (*b*) and 0.09 mol dm^{-3} (*c*) acetonitrile. Species are $[Au(CH_3CN)_2]^+$ (*i*), $[Au(CH_3CN)(OH)]$ (*ii*), $Au(OH)$ (*iii*) and Au^+ (*iv*)

combines moderate basicity, minor hardness and π-acceptor capability. The basic thiolates are more stable with Au^I than thiones, which are about equally soft. The more basic alkylphosphines bind more strongly to gold than arylphosphines,

although those are better π acceptors. Carboxylates and fluoride, which are both hard but weakly basic, are not known to form stable complexes with Au^I. Hydroxide, however, which is rather hard but strongly basic, is a good donor for Au^I.

It follows that Au^I has a distinct Lewis-acid property, which seems to be surprising for a univalent cation. However, if one takes in account the relativistic contraction of the 6s orbital of Au$^+$, which is the main acceptor orbital together with the 6p orbitals, the observed behaviour can be explained.[10–12] Mercury(II) is a similar example and forms hydroxo complexes of high stability,[1] but it must be compared cautiously because of its higher surface charge density. As the 6s orbital in such atoms is more contracted into the nucleus than expected by standard atomic orbital models, it is less shielded against the nucleus and therefore the donor electrons are subject to a stronger attractive force. It has been estimated by advanced quantum-mechanical calculations that the Au–NH$_3$ bond in $[Au(NH_3)_2]^+$ should be stronger than calculated by the standard Hartree–Fock method.[12] Like OH$^-$, NH$_3$ is basic and a strong σ donor and should behave in a similar way.

Since stability constants of Au^I have been determined mainly with soft donors until today, complex-formation studies of Au^I with strong hard bases besides OH$^-$ would be of interest. A preliminary voltammetric study in our laboratory has given hints that HPO$_4^{2-}$ may co-ordinate to Au^I.

Acknowledgements

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