Time Resolved Chemisorption of I^- and SH^- on Colloidal Silver Particles (A Stopped-Flow Study)

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An aqueous silver sol (mean particle size: 6 nm) is mixed with KI and NaSH solution, and the changes in optical absorption and light scattering are recorded. When iodide adsorbs on the silver particles, the 225-nm band of I⁻ disappears concurrently with the decreasing of the silver plasmon absorption band. In the same time range, the intensity of light scattering slightly decreases, which is explained as a detachment of the colloidal particles from the polyphosphate stabilizer. At a later stage, the silver plasmon band is red-shifted and the light scattering finally increases again, which is understood in terms of loose cluster formation of the particles. The adsorption of H₂S leads to damping and a simultaneous blue shift of the plasmon absorption band. The adsorption of H₂S is faster than that of SH⁻, as there is no Coulomb repulsion between the adsorbant and the negatively charged metal particles.

Introduction

The adsorption of nucleophilic anions, such as I⁻, and SH⁻, on colloidal silver particles in aqueous solution is accompanied by strong optical changes. The surface plasmon absorption band of the silver particles, which generally is positioned close to 380 nm, is damped and its maximum is shifted to shorter or longer wavelengths, depending on the nature of the adsorbed species and its concentration.¹ The adsorption of nucleophilic reagents also leads to an increase in the reactivity of the silver particles toward electron acceptors, such as oxygen and nitrobenzene.²

In the present study, time resolved measurements are carried out using the stopped-flow method. The silver sol is mixed with a solution of the above additives, and the changes in the absorption and scattering of the mixed solution are recorded as a function of time. In some cases, the intensity of the silver plasmon absorption decreases in two steps, the first step being ascribed to changes in the electronic properties of the silver particles by the adsorbed substances, and the second one being attributed to the electronic changes resulting from the clustering of the particles. Time resolved measurements give therefore more detailed information than the simple mixing experiments carried out previously, which allow one to observe only the overall effect (i.e. the sum of the two steps). In all of the experiments, rather dilute solutions were used, i.e. with a silver concentration between 50 and 125 μ M and additive concentrations ranging from some micromoles to about 100 micromol/ L.

Experimental Section

Preparation of the Solutions. The silver sol was prepared by γ -irradiating 400 mL of a solution of 250 μ M AgClO₄, 0.1 M propanol-2, and 200 μ M sodium polyphosphate for 1.5 h with the γ -rays of a ⁶⁰Co-source. The dose rate was 1 × 10⁵ rad/h. After the irradiation, all of the silver ions were reduced. The solution was deaerated by flushing with argon prior to the irradiation. The glass vessel had a side arm equipped with a septum. Samples of 5 mL each from this stock solution were transferred into the syringe of the stopped-flow apparatus. An excess pressure of argon was maintained over the stock solution.

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Solutions of the additives were also deaerated by flushing with argon. The NaSH solution was prepared by deaerating a 100 μ M NaOH solution and adding an equimolar amount of gaseous H₂S.

Stopped-Flow Equipment. The apparatus was a stopped-flow spectrofluorimeter DX 17MV from Applied Photophysics Ltd. The silver sol was mixed with the solution of the additive in the volume ratio 1:1. Thus, the overall concentration of the colloidal silver was $125 \,\mu$ M. A problem arose concerning the penetration of small amounts of air into the flow system, as the silver colloid is sensitive to oxygen. The following measures were taken to make sure that the solutions did not come into contact with air to a disturbing extent. The thermostat bath was flushed continuously with argon. Additional seals were used for the syringes. When not in use, the syringes and the sample flow circuit were filled with a deaerated 10^{-2} M sodium dithionite solution as recommended by the manufacturer.

In the absorption measurements, a 1-cm optical cuvette was used. In order to obtain time resolved spectra, kinetic traces were recorded at every 5 nm. The two monochromators in series for the incident light had a band pass of 2 nm. In the scattered light measurements, the light was detected rectangular to the incident light beam using a 2-mm cuvette. The traces of several shots were averaged. The scattering signals were very weak; in some experiments, silver solutions of higher concentration (up to $500 \,\mu$ M) were used where the signals were stronger.

The resolution of the stopped-flow apparatus was 1.5 ms.

Results

Influence of Air. Despite the above measures, the penetration of a very small amount of air into the reacting system could not be avoided. In the time range of our measurements, the amount is too small to cause any noticeable effect. Two experiments were carried out to detect the penetrating oxygen. First, a 30 μ M solution of the cation radical of methyl viologen, which has a deep blue color and is sensitive toward oxygen, was mixed with deaerated water. The solution of the radical was prepared by γ -irradiating a 100 μ M methyl viologen solution, which also contained 0.1 M propanol-2. Figure 1 shows the 600-nm absorbance of the radical cation as a function of time. It can be seen that a decrease is not noticeable in the millisecond to second range, in which most of the experiments

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Figure 1. Mixing of a solution of the radical cation of methyl viologen with deaerated water. Normalized 600-nm absorbance of the radical cation as a function of time.



Figure 2. Mixing of colloidal solutions of silver with deaerated water. Normalized absorbance at 380 nm as a function of time.



Figure 3. Absorption spectrum of the silver solution at various times after mixing with the KI solution. Silver concentration: $125 \,\mu$ M. Iodide concentration: $16 \,\mu$ M.

with the colloidal solutions were performed. In fact, only 0.5% of the methyl viologen radical had been consumed after 100 s. In the second experiment, silver solutions of various concentrations were mixed with deaerated water, and the change in the 380-nm absorption was recorded. Figure 2 shows the results. It can be seen that practically no change occurred for the 125 and 50 μ M concentrations. In the case of the 10 μ M silver concentration, a 4% decrease in the 1–10-s range was observed.

Time Resolved Absorption Spectra. In the experiment of Figure 3, the silver sol was mixed with a KI solution to produce an iodide concentration of $16 \,\mu$ M in the mixed solution. The absorption spectrum at various times after mixing is shown. One can see that the plasmon band, which in the beginning is peaking at 380 nm, decreases and becomes broader. The maximum shifts toward longer wavelengths at longer times to reach a final value at about 1 s. Note that an isobestic point exists at 410 nm. In the experiment of Figure 4, a much higher concentration of iodide was used. The decrease in the absorption occurs faster. In the beginning, the 410-nm isobestic point still shows up. However, at the longer times, there appears a much more drastic red shift of the band maximum than in Figure 3. It is concluded from these observations that the absorption changes occur in two steps and have to be explained by two different processes.



Figure 4. Absorption spectrum of the silver sol at various times. Iodide concentration: $60 \ \mu M$. Silver concentration: $125 \ \mu M$.



Figure 5. Absorbance (full line) and wavelength (dashed) of the band maximum as functions of time. Upper diagrams: Addition of $25 \,\mu M$ iodide. Lower diagrams: Addition of $60 \,\mu M$ iodide. Silver concentration: $125 \,\mu M$.

That two steps in the damping of the plasmon band are involved can also be seen from the data in Figure 5. The absorption and wavelength of the maximum of the plasmon band are plotted here versus the time on two time scales. Samples of 25 and 60 μ M iodide had been added to the silver sol. It can be seen that there is practically no or very little change in the position of the absorption maximum when the intensity decreases at short times. The shift in wavelength mainly occurs after the absorption has decreased.

To follow directly the adsorption of iodide, the changes in the intensity of the 225-nm absorption band of the free ion were also studied. The band is present immediately after mixing. It decreases in the same time interval in which the plasmon band of silver decreases. Unfortunately, the signals at this wavelength were so weak that they could not be used for a detailed kinetic analysis.

Figure 6 shows how the absorption spectrum of the silver sol changes when it is mixed with 40 μ M NaSH. One observes damping again and a slight blue shift of the maximum. The wavelength of the maximum and the decrease in absorbance are shown in Figure 7 as functions of time. Note that, contrary to the iodide adsorption in Figure 5, the two changes occur in the same time interval.

The absorption changes can be reversed by loading the silver particles with excess electrons.¹ Figure 8 shows the results of a typical experiment. A sample of 20 μ M KI was added to the silver sol, and the spectra before and after addition were recorded in a conventional spectrophotometer. The solution, which also contained 0.1 M propanol-2, was then exposed to γ -rays for 15



Figure 6. Absorption spectrum of the silver solution at various times after mixing with the NaSH solution. Silver concentration: $125 \,\mu$ M. SH⁻ concentration: $40 \,\mu$ M.



Figure 7. Decrease in the absorbance (full line) and wavelength of the band maximum (dashed) as functions of time. Addition of $40 \,\mu M$ SH⁻.



Figure 8. Absorption spectrum of a silver sol before and after the addition of KI and after 15 min electron storage by free radicals (which were produced by γ -irradiation).

min. As is well-known from radiation chemistry, reducing organic radicals, $(CH_3)_2COH$, are generated under these conditions.³ The radicals transfer electrons to the particles, one particle being able to accept and store electrons from many radicals. It can be seen that the silver plasmon band recovers to a large extent. At the same time, the 225-nm charge-transfer-to-solvent band of free iodide appears. Obviously, iodide is desorbed as excess electrons are present on the particles.

Time Resolved Scattering. The measurements were made by recording the changes in the intensity of scattered light at 275 nm, a wavelength where the silver sol does not strongly absorb. Figure 9 shows the temporal changes in both the absorption and scattering at this wavelength. The absorption increases slightly upon the adsorption of iodide and then decreases a little at longer times. The scattering intensity decreases in the time interval in which the absorption increases. The analysis of the curves showed that the decrease in scattering is slower by a factor of 2 than the increase in absorption. In Figure 10, upper part, the decrease in scattering intensity is compared to the change in wavelength of the plasmon absorption



Figure 9. Absorption and scattering at 275 nm as functions of time. The sol contained 500 μ M silver and 100 μ M KI (concentrations after mixing). The scattering intensity is given as a voltage signal at the photomultiplier.



Figure 10. Wavelength (upper part) and intensity (lower part) of the plasmon band and intensity of scattering as functions of time: 500 μ M silver, 100 μ M KI.



Figure 11. Scattering at longer times: 500 μ M silver, 300 μ M KI.

band of the silver particles. One can see that the decrease in scattering occurs rather early, i.e. when the wavelength is not yet shifted. In the lower part of Figure 10, the changes in scattering intensity and the intensity of the 380 nm plasmon absorption are compared. One can see that the changes occur in the same time range. The analysis of the curves revealed that the scattering change was a little slower than the absorption change. To make sure that the observed changes in the scattering intensity are due to the interaction of the iodide with the silver particles, blank experiments were carried out, in which the silver sol was simply mixed with water. No decrease in the scattering intensity was recorded.

In the experiments of Figures 9 and 10, the decrease in scattering intensity was finished after a few tenths of a second. However, at much longer times, the scattering intensity increased again. This effect was especially strong when iodide had been added in rather high concentration (Figure 11). It is concluded that the chemisorption of iodide causes changes in the size and/



Figure 12. Absorbance in the maximum of the plasmon band as a function of time. Addition of 50 μ M H₂S at different pHs.

or size distribution of the silver particles. It should be emphasized that the solutions were non-opalescent before as well after the addition of I^- as viewed by the naked eye.

A decrease in scattering intensity was also observed when SH^- ions were adsorbed. In this case, the decrease in scattering occurred as fast as the decrease in the intensity of the plasmon band. At longer times, the scattering intensity also increased again.

The scattering of light of the solutions described in Figure 8 was also investigated, using a commercial fluorimeter. It was found that the storage of excess electrons on the silver particles which were covered by adsorbed iodide was accompanied by a slight decrease in light scattering.

pH-Dependence of the Rate. In the experiment of Figure 12, the decrease in the absorption of a silver sol is shown, which was mixed with an H_2S solution at different pH's. It can be seen that the adsorption is much faster in acidic solution where H_2S is present in the undissociated form. In fact, the reaction is so fast under these conditions that part of it occurs already during the dead time of the apparatus. In the case of iodide absorption, the rate was found to be independent of the pH of the solution.

Discussion

An estimate may first be made for the rate of the fastest reactions of the colloidal silver particles. If no electrostatic forces existed between the colloidal particles and the reacting anions, such as I^- and SH^- , and if the reaction occurred at every encounter, the Smoluchowski rate constant $(M^{-1} s^{-1})$ would be equal to

$$k = 2 \times 10^{-3} \pi D N_{\rm A} d \tag{1}$$

where D is the diffusion coefficient of the anion, d the diameter of the silver particles, and N_A the Avogadro number. The time of reaction would approximately be equal to

$$\tau = n/kc \tag{2}$$

where *n* is the atom number of the colloidal particles and *c* the overall silver concentration. For spherical particles of silver, the relation $n = 30.7d^3$ (*d* expressed in nanometers) can readily be derived assuming that the density of silver is the same as in the bulk material. Using the mean diameter of d = 6 nm of the present sol and a diffusion coefficient of $D = 10^{-5}$ cm² s⁻¹ of the reacting anions, one obtains a reaction time of 1.7 ms for $c = 125 \,\mu$ M. This is just about the dead time of the stopped-flow apparatus. The observed reaction times were always much longer, i.e. of the order of 0.01 or 0.1 s, with the exception of the reaction of H₂S in acidic solution, which took place already during the mixing (Figure 12). The slow reaction times of the anions are explained by the repulsion due to a negative overall

charge of the silver particles. It should be remembered that they are stabilized by a negatively charged polymer. In the reaction of H_2S with the silver particles no Coulomb barrier is expected.

We also consider the fastest rate that can be expected for the reaction between the silver particles themselves. In the case of a *fast coagulation*, i.e. in the absence of a repulsive potential between the particles, the reaction would take place at every encounter. Applying again the Smoluchowski equation, a bimolecular rate constant of

$$k = 8 \times 10^{-3} \pi D N_{\rm A} d \tag{3}$$

is obtained, where $D = RT/3\pi\eta d$ now is the diffusion coefficient $(\eta = \text{viscosity of the solvent})$ and d the diameter of the colloidal particles. For d = 6 nm and $c = 125 \ \mu\text{M}$, one calculates a reaction time of 8 ms from these equations. Reactions between the colloidal particles can therefore readily be time-resolved in the stopped flow apparatus.

As has previously been pointed out,¹ the chemisorption of a nucleophilic anion should be accompanied by an increase in the free electron density of the silver particle, and this, in turn, should cause a blue shift of the plasmon absorption band (besides the decrease in intensity of the band). A blue shift is indeed observed in the adsorption of SH⁻. It occurs simultaneously with the decrease in the intensity of the plasmon band. On the other hand, the adsorption of iodide leads to a decrease in intensity without a blue shift and is then followed by a red shift at longer times. However, also in the case of SH⁻ adsorption, a red shift is observed at a higher concentration of sulfide.¹

The decrease in light scattering upon the adsorption of I⁻ and SH⁻ is tentatively explained by the detachment of the colloidal particles from the polymer stabilizer, as they are repelled electrostatically from the polyanion. This detachment seems to be rather fast in the case of SH⁻ adsorption, the decrease in the intensity of the silver absorption band and the decrease in the intensity of scattered light occurring practically simultaneously, whereas the detachment is a little delayed in the case of I⁻ adsorption. Before the deposition of I⁻ or SH⁻, the silver particles are weakly bound to the phosphate groups of the polymer. The binding in all cases is attributed to the donation of electron density from the adsorbed anion into the silver particle. As has previously been pointed out, the adsorption of a stronger nucleophile leads to the desorption of a weaker one.¹ I^- and SH^- are stronger nucleophiles than phosphate.

Some time after the detachment from the polymeric stabilizer, the red shift of the absorption band takes place. This is attributed to cluster formation between the free particles in solution. The silver particles do not touch each other in the clusters but are sufficiently close together to influence the absorption of light by dipole-dipole interaction. It is known that this interaction leads to a red shift of the plasmon absorption band.⁴ The formation of larger clusters in the minute range is accompanied by increased light scattering of the solution.

When excess electrons are deposited on the particles, which carry adsorbed iodide, two effects occur. First, because of the increased negative charge of the particles, the clusters disintegrate by the Coulomb repulsion between their constituents, the result being less scattering. Second, adsorbed iodide is detached, the result being a recovery of the plasmon band.

A detailed analysis of the kinetic curves is difficult. It is not known whether and how the decrease in absorption per adsorbed I^- and the specific rate of adsorption depend on the degree of coverage of the surface by I^- . These difficulties are



Figure 13. Addition of iodide in various concentrations to a 50 μ M silver sol. Absorbance in the 385-nm maximum of the sol as a function of time.



Figure 14. Plot of the time, τ , required to produce a given absorption decrease, $-\Delta A$, versus the recipocal concentration of added iodide. Data from Figure 13.

avoided in the experiment of Figure 13 and the evaluation of the data in Figure 14. In Figure 13, the absorbance of a 50 μ M silver sol is shown as a function of time for various concentrations of added iodide. In Figure 14, the time, τ , required to decrease the silver absorption by a given amount, ΔA , is plotted versus the reciprocal I⁻ concentration. One is thus looking at the reciprocal rate required to bring about the same coverage using different iodide concentrations. At low values of $-\Delta A$, where the iodide consumption is small as compared to the amount of iodide added, a straight line is obtained, i.e. the rate is proportional to [I⁻] as expected. At higher $-\Delta A$ values, a deviation occurs at the lower iodide concentrations. At these concentrations, the consumption of iodide by adsorption is substantial; i.e., the reaction is no longer of pseudo-first order with respect to the iodide concentration.

Despite the above difficulties, which prevent one from deriving an exact kinetic law for the adsorption from the temporal decrease of the plasmon absorption band, one can at least try to fit the kinetic traces under simplified conditions. It seems reasonable to expect second order kinetics according to

$$-d[O]/dt = k[I^{-}]_{(t)}[O]_{(t)}$$
(4)

where [O] is the concentration of surface places at which iodide can be adsorbed. When $[O]_0$ iodide anions are adsorbed (full monolayer), the absorbance of the silver plasmon band decreases from A_0 to A_{∞} . Thus, the decrease per adsorbed iodide is

$$-dA/d[I^{-}] = (A_0 - A_{\infty})/[O]_0$$
(5)

assuming that it is not dependent on the number of anions already adsorbed. The assumption would be in accordance with the existence of an isobestic point in Figure 3. Similarly,

$$[\mathbf{O}]_{(t)} = (A_{(t)} - A_{\infty})[\mathbf{O}]_0 / (A_0 - A_{\infty})$$
(6)



Figure 15. Evaluation of data according to eq 8: O, experimental points; -, exponential curve fit. Inset: Absorption at 385 nm and in the maximum of the shifting plasmon band as functions of time.

One obtains from these equations

$$-dA/dt = k(A_{(t)} - A_{\infty})[I^{-}]_{(t)}$$
(7)

Regarding the pseudo-first order case where the initial iodide concentration is much larger than the concentration of surface places, one obtains after integration

$$A_{(t)} = A_{\infty} + (A_0 - A_{\infty}) \exp(-k[I^-]t)$$
(8)

In Figure 15, an experimental absorbance vs time curve was fitted by a single exponential function. The silver concentration was 50 μ M and and iodide concentration 40 μ M. From our earlier experience¹ it is known that the iodide consumption for full surface coverage is about 10 μ M under these conditions. Thus, the iodide concentration could be regarded as approximately constant. The absorbance decrease due to iodide adsorption and the following red shift in wavelength due to particle clustering are well separated under the conditions chosen. This can be seen from the inset in Figure 15, where the 380-nm absorbance as well as the maximum absorbance are plotted vs time. Up to about 1 s, the maximum lies at 380 nm, the wavelength before iodide addition; i.e., there is no significant cluster formation during this time. The curve fitting was therefore limited to this time interval. It was found that the curve could well be fitted using one exponential function. This appears surprising at first sight, as k in eq 8 must not necessarily be expected to be constant, the argument being that k should decrease with increasing time as the coverage of the surface proceeds, i.e. as the Coulomb repulsion between the colloidal particles carrying anions and the reacting I⁻ ions increases. A possible explanation lies in the above detachment of the colloidal particles from the polyanionic stabilizer as iodide anions are adsorbed; i.e., the repulsing charge on the particles by adsorbed polyanion is substituted by adsorbed iodide. We should, however, remember that our kinetic treatment is based on the assumption that the absorbance decrease per adsorbed iodide is constant and that we have not taken into account the particle size distribution of our colloid. The kinetic treatment presented is therefore only provisional.

References and Notes

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