SULFUR-CONTAINING ORGANIC MOLECULES THAT HAVE BEEN COMPLEXED WITH METALS

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ABSTRACT

The synthesis of COCs and APCs by the coupling of carbon dioxide with epoxides is a promising new environmentally friendly option. The goal of this study is to explain the most important findings in a brief manner while providing a broad overview of metal complexes with sulfur-containing ligands as homogeneous catalytic systems able to efficiently drive this transition. Also highlighted is sulfur's pivotal function as the hemilabile ligand and the impact it has on the catalytic activity. Using the capacity of sulfur-containing compounds to delay the photoreduction kinetics of gold ions to gold nanoparticles, this study offers a new, equipment-free, general technique for the identification of sulfur-containing compounds. The approach entails measuring the time between adding the target analyte and the appearance of a red colour in the tested sample, which is indicative of the creation of gold nanoparticles, and comparing the two times. The method may be implemented with few and straightforward measures, since it calls for only two solutions (a buffer and a gold solution), a UV or visible light source, and a timer. The method has been used to determine compounds like dithiocarbamate and organophosphorous pesticides, biothiols, pharmaceutically active compounds, and sulfides in various samples like natural waters and wastewater, biological fluids, and prescription drugs because it reacts to a wide range of sulfur-containing compounds. strong sensitivity (quantitation limits at the low M levels), strong recoveries (from 93 to 109%), and decent repeatability (from 4.8 to 9.8%) are some of the analytical figures of merit of the technique. The approach is simple enough for a user with no special training to implement, flexible enough to be used for both quantitative and semiquantitative analysis outside of a laboratory setting, and inexpensive.

KEYWORDS: homogeneous catalysis; sulfur; carbon dioxide; epoxides; cyclic carbonates; polycarbonates

INTRODUCTION

Homogeneous catalysis is a rapidly growing field of chemistry because the course of a particular reaction may be precisely tuned via the logical design of the catalyst architecture. In fact, the processes driving the activity and selectivity are well known, allowing for a significant increase in overall performance, in comparison to heterogeneous catalysis. Using soluble transition-metal complexes in catalysis, in particular, has provided hitherto unimaginable opportunities for fine-tuning product characteristics by careful manipulation of the auxiliary ligand's electronic and steric properties. Ingenious stereoselective processes spanning all classes of chemical synthesis (oxidations, cross-coupling reactions, polymerizations, etc.) have been developed thanks to this one basic idea. In a similar vein, the need for more environmentally friendly chemical processes has boosted the usage of renewable feedstocks during the past two decades.

Due to the potential to complete, via the use of renewable energy, an anthropogenic carbon cycle avoiding net production of greenhouse gases, carbon dioxide utilization (CDU) has emerged as a key instrument for the transition to a carbon-neutral society. In addition, as compared to other C1 feedstocks (such as phosgene and carbon monoxide), CO2 clearly demonstrates benefits in terms of toxicity, flammability, and the potential of storage, which makes the implementation of industrial processes based on this molecule highly feasible. Because of their versatility and simple synthetic pathway beginning with the equivalent CO2, cyclic organic carbonates (COCs) and aliphatic polycarbonates (APCs) have garnered a lot of interest. Many factors, including the type of the substrate, the reaction conditions, and the catalytic system, determine whether or not the cyclic or polymeric product is formed during the coupling of CO2 with an epoxide. However, most active systems rely on the combination of a metal complex activated by a suitable nucleophile, generally provided as an ammonium or phosphonium salt, despite efforts to build effective metal-free catalysts. The fundamental steps of the reaction process are shown in Metal-epoxide coordination, ring-opening of the activated epoxide by nucleophilic assault, and carbon dioxide (CO2) insertion. Path A leads to the synthesis of the COC by an intramolecular ring-closing reaction, while Path B leads to the formation of the APC via the alternating insertion of epoxide and CO2. Since a third pathway (route C) allows for two successive epoxide insertions, the resultant polymer frequently features polyether links as well.

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SILVER COMPLEXES OF SPECIFIC ENVIRONMENTAL MERCAPTANS

Since mercaptans readily form silver complexes, you can probably find a reference to the silver derivative of any mercaptan you can think of in the literature. The startling issue is how little we know about many of these chemicals, especially environmental mercaptans. To our knowledge, no one has ever characterized silver complexes of N-acetyl cysteine or 3-mercaptopyruvic acid, and until recently, no crystalline forms of any of the other known complexes had ever been produced. provides a brief overview of the known characteristics of silver thiolates derived from ambient mercaptans and a list of sources addressing these compounds. The ligand's extra functionality, such as amino acids, carboxylic acids, or neutral substances, informs the table's categorization. The presence of hydrophilic groups in all of the ligands, with the exception of mercaptomethane, when the sulfur is coupled to silver is the most striking aspect of all of the mercaptans listed in from an ecological perspective. This results in a notable solubility in water; however, this solubility is pH sensitive due to the fact that amine and carboxyl groups may or may not be charged, therefore we can only assume that most of these silver complexes will be dissolved at the micromole level at pH values slightly above or below 7. The complexes appear to be significantly aggregated even at very modest concentrations. D-penicillaminato-silver proton NMR spectra, for instance, displayed wide signals, indications of aggregation, even at 50 mM concentration (pH 7), which were identical to those seen at higher doses. The many classes of chemicals are now discussed briefly.

ENVIRONMENTAL FATE OF SILVER

Ultimately, Ag(I) in silver thiolates will create Ag2S when exposed to a sulfur-rich environment. The organic fragment could be oxidatively degraded (likely via radical processes with dioxygen), leaving Ag2S as the most stable residual species, or it could be released as the mercaptan upon reaction of the silver thiolate aggregate with hydrosulfide ion. Figure 6 presents a potential framework for the environmental cycling of Ag(I). For the sake of clarity, the plan is arbitrarily split between inorganic and organic routes, however in reality, these routes will be intertwined. The plan is also not comprehensive. It's meant to get people thinking and serve as a roadmap for further research. Take the kinetics of Ag(I) transfer as an example. How do factors like particle size, particle density, and particle composition influence the rate? Is it possible to study this in simplified model systems to learn more about the underlying environmental mechanism?

Can Ag(I) exist in a metastable complexed form with slow enough exchange kinetics to be physiologically active? How could sorbtion on colloids alter the rates at which different silver thiolates interact with cells or organisms? Many biological investigations have hinted at solutions to these concerns, but it is still a major future objective to collect precise kinetic and biochemical route data for the vast majority of species. We have Ag2S(s) as Ag(I)'s final destination in our scheme. But does this have to be the case? Under what circumstances is Ag(I) remobilized from Ag2S(s)? How dangerous, if any, will these Ag(I) concentrations be? Such concerns call for in-depth research. Organic Ag(I) thiolates, according to laboratory findings, slowly breakdown over time, especially in the presence of light, and yield Ag2S(s). There are no available accounts detailing what happened to the organic component, although it was likely destroyed by oxidation. Through the use of powerful oxidants, we have demonstrated that the sulfur atom may be transformed into a sulfonate, where the silver ion is coupled to an oxygen and is hence considerably more kinetically labile. Do oxidative enzymes have the potential to do the same thing? Evolution may have determined that any remobilization of Ag(I) is so insignificant that Ag2S(s) or a silver metallothionein complex may be disregarded. However, it is prudent to verify nature's judgement.

OBJECT

1. The research an increasingly environmentally friendly option is coupling carbon dioxide with epoxides.
2. The research Sulfur's impact on catalytic activity as a key hemilabile ligand

RESEARCH METHODOLOGY

Here, we provide a unique nanotechnology-based approach that, for the first time, takes use of the kinetics of the photochemical reduction of gold ions to gold nanoparticles in sensing applications. The technique relies on employing a basic clock and the naked eye as detectors to record the time lag in the photoinduced production of gold nanoparticles in the presence of sulfur-containing chemicals. The photoreduction kinetics of gold ions were found to be slowed by a broad variety of organic and inorganic compounds containing various sulfur moieties, including thiols, thioesters, disulfides, thiophosphates, metal-sulfur linkages, and inorganic sulfur. We applied this idea to the analysis of sulfur-containing chemicals and showed its usefulness in a number of sensing applications without the need for any special equipment.
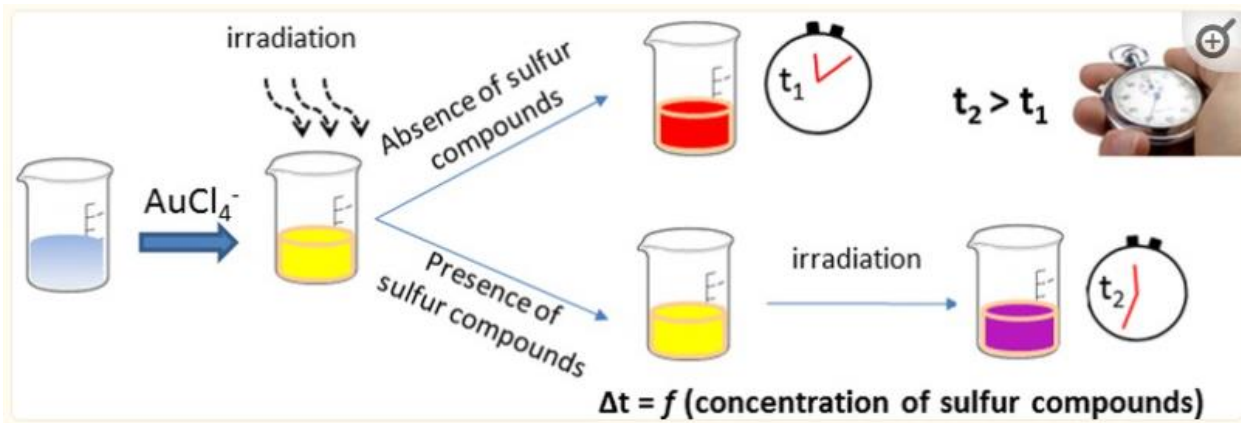
Figure 1 Graphical Representation of The General Experimental Procedure for The Time-Based Assay of Sulfur-Containing Compounds.

DATA ANALYSIS

When compared to chemical reduction (bottom-up) methods, those that involve the formation and controlled synthesis of gold nanoparticles from aqueous gold solutions under the influence of light have several advantages. For one, (b) irradiation diffuses throughout the entire mass of the solution, so reduction occurs uniformly under controlled reaction r. UV irradiation is most commonly used because it corresponds to the absorption band of $Au3+$ (about 323 nm), while other light sources (including UV, sunshine, laser, -irradiation) have been used.

Studies have shown that when UV light is shone on $AuCl4-$, the excited $Au3+$ is immediately reduced to the more stable $Au2+$, which then quickly disproportionate to generate $Au+$ and $Au3+$. After then, $Au+$ either disproportionate slowly into $Au0$ and $Au2+$ or absorbs another photon and photo reduces to $Au0$. Possibly catalyzing the disproportionation further is the formation of gold nuclei and AuNPs from $Au0$ gold atoms. The presence of an additive is essential to all of these processes because it speeds up or triggers the synthesis of AuNPs in a variety of chemical ways. Many other substances have been tried as sensitizers for the photochemical reduction of gold ions to AuNPs, including surfactants, polymers, ethylene glycol, citrate, etc.

In this study, we found that sulfur-containing compounds not only slowed the photoreduction kinetics of AuNPs creation but also affected the photochemical synthesis and development of AuNPs. Kinetics of photochemical production of AuNPs under UV light irradiation, as shown by UV-vis absorbance spectra (inset graphs) in the absence and presence of cysteine as a model sulfur-containing substance. The procedure is shown on film (at actual speed but shortened from 1:43 to 3.06 minutes) in an aqueous solution containing 50.0 M of cysteine under natural light. No AuNPs were generated during longer irradiation periods, i.e., >30 min under 40 W of irradiation at 254 nm, indicating that citrate was required to sensitize and expedite the photoreduction of gold to AuNPs. The photoreduction of citrate to acetone-1,3-dicarboxylate and free electrons, which reduce $Aum+$ (m = 1, 2, 3) to $Au0$, or the direct excitation of the citrate-$Au3+$ complex, which reduces $Au3+$ through electron-transfer mechanisms, could make AuNPs more photosensitive.
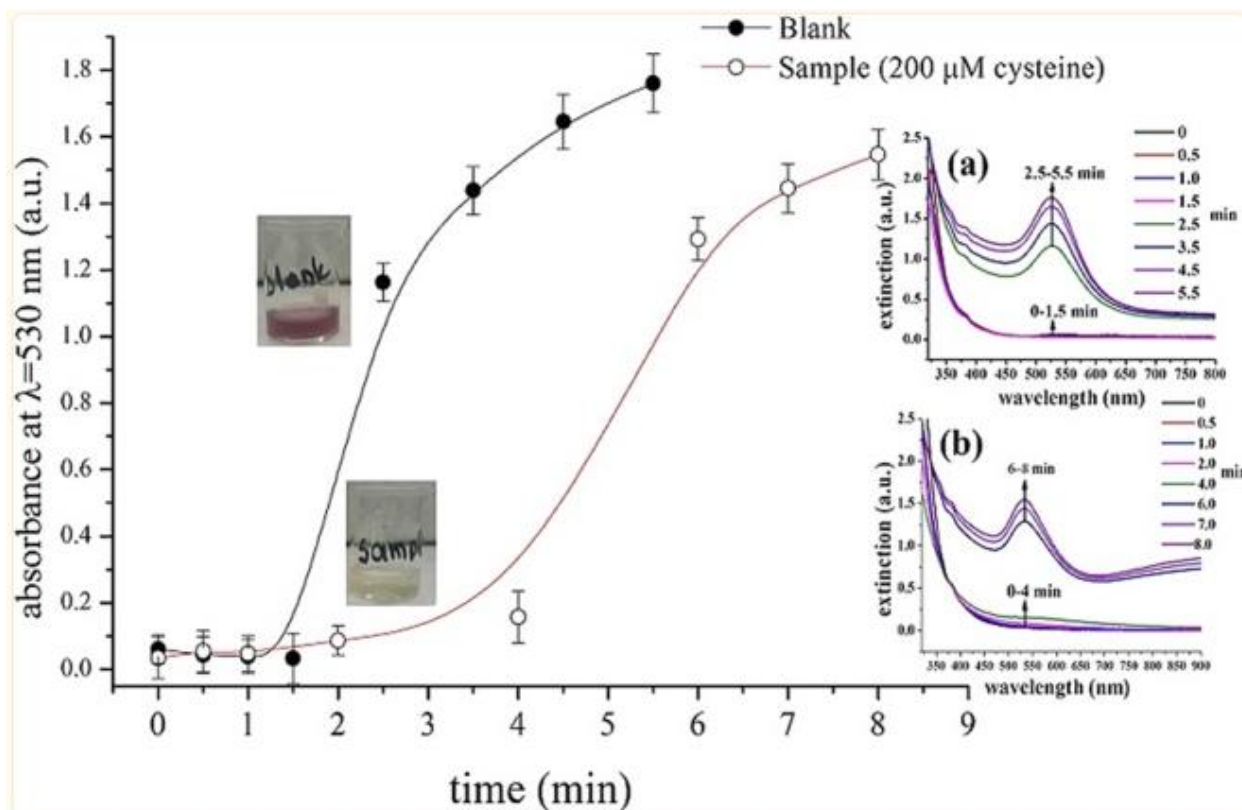
Figure 2 Kinetics Of Aunps Photochemical Formation In The Absence And Presence Of 200.0 Mm Cysteine. Inset Graphs Show The Respective UV–Vis Spectra At Different Time Intervals (A) UV–Vis Spectra Of Aunps Formation In The Absence Of Cysteine And (B) UV–Vis Spectra In The Presence Of 200.0 Mm Cysteine. Experimental Conditions: Ph 4 (Citrate Citric Acid Buffer, 8.0 Mm), Λ = 254 Nm, And 40 W.

OPTIMIZATION OF GOLD PHOTOREDUCTION

The production and development of AuNPs by photochemistry in gold chloride solutions is a kinetic event that persists after irradiation has been turned off. The creation and development of AuNPs may continue for many hours after the irradiation is turned off, depending on the experimental circumstances (intensity of UV irradiation, concentration of gold ions, presence of additives, etc.). Our time-based assay is unaffected by this occurrence since the analytical signal is the duration of time needed for a colored solution to arise; once this occurs, the synthesis of AuNPs is no longer being tracked. However, we employed solution absorbance to acquire (absorbance) values at a constant time in order to adjust the assay's experimental conditions. Therefore, the first factor examined was incubation time (after the cessation of UV irradiation). After exposing the solutions to UV light (254 nm, 40 W) for 1.5 minutes and incubating them in the dark at room temperature for varying amounts of time, we evaluated the absorbance of the blank and sample solutions at 525 nm.

Based on the kinetic curves, we found that irradiating the samples for 1.5 minutes did not significantly raise the absorbance values of either the sample or the blank solutions, but irradiating them for longer resulted in a sudden increase in the absorbance of the blank. Light, which can cause photoreduction of AuCl4, was also avoided by keeping the samples in the dark.– The results show that after 5 minutes of incubation at room temperature (25 °C), the net analytical signal (i.e., absorbance intensity of the sample minus absorbance

intensity of the blank solution) increases initially, but sharply drops with time. Since AuNPs form more quickly in the blank sample during the first 4 min of incubation, and more slowly in the presence of cysteine, the difference in the net absorbance value peaks at 5 min and then decreases over the remaining incubation time. Similar studies conducted at 4 °C slowed the reaction rate and caused the absorbance signal to peak after 12 minutes of incubation. According to these results, the rate of gold photoreduction also depends on ambient temperature. In light of these results, all absorbance readings were taken under the same conditions: 1.5 minutes of exposure to UV radiation (40 W, 254 nm), followed by 5 minutes of incubation at room temperature in a darkened environment, away from any external light.
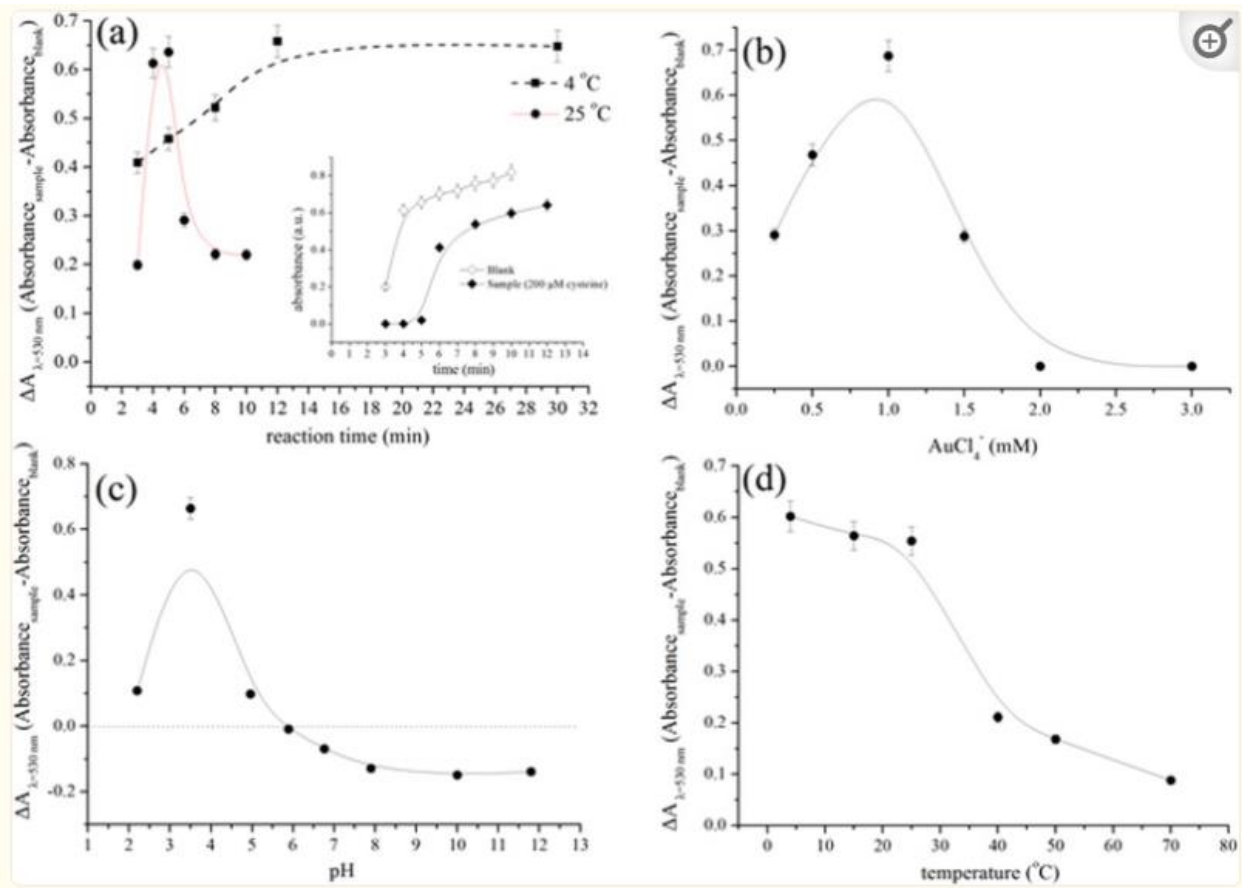

Figure 3 Optimization Of Gold Photoreduction In The Presence Of 50.0 Mm Cysteine As A Model Sulfur-Containing Compound And Citrate As Photosensitizer At Λ = 254 Nm (40 W). Effects Of (A) Reaction Time In The Dark (After UV Irradiation), (B) Aucl4– Concentration, (C) Solution Ph, And (D) Temperature On The Net Absorbance Signal Intensity (ΔA) Calculated As The Difference Between The Absorbance Signal Of The Sample And The Absorbance Signal Of The Blank At Λ = 530 Nm.

We investigated the effects of AuCl4- and citrate concentration, pH, temperature, and irradiation wavelength after reaction kinetics were optimized. Since the absorbance of the blank solution also increases dramatically at concentrations of AuCl4- up to 1.0 mM, the net absorbance signal also increases greatly (results not shown). Possibly because more energy is needed to photoreduce the huge concentration of gold ions, absorbance drops considerably with greater gold concentrations for both the sample and the blank solutions. So, 1 mM AuCl4- was utilized as a constant throughout all the tests.

It was discovered that the intensity of the light affected the concentration of citrate ions required to sensitize the photochemical reduction of gold ions. The longer the wavelength of the irradiating light, the less citrate was needed. Under the experimental conditions (40 W of light intensity at 254 nm, in the presence of 50.0 M of cysteine), the optimum citrate ion concentrations was 5.0 mM; at higher citrate concentrations, the net absorbance signal intensity decreased, possibly because citrate accelerated the photoreduction of gold ion solutions.

The best outcomes were observed at acidic pH values (pH 3.5) (when the pH is increased beyond the optimum (pH 3.5), the net absorbance signal intensity displays a behavior, which seems to be connected to the pKa of the dominating cysteine species. At pH 5, which is close to the isoelectric point of cysteine (i.e. 5.14), and the pKa of citric acid (i.e. 4.74), the signal drops to zero. Afterwards, the signal flips (the sample's absorbance signal strength is greater than the blank's) and steadily declines up to the value of pH 8.0, which matches with the acid dissociation constant of the sulfhydryl group (pKa2 = 8.18). When the pH is more than 8, the signal is reasonably stable. In the presence of charged species of cysteine and citrate, photoreduction of $AuCl_4^-$ ions is likely to be enhanced, most likely as a result of ligand-to-metal charge transfer reactions with the predominant gold species at these pH values (possibly $[AuCl(OH)_3]$ and $[Au(OH)_4]$). This is evidenced by the fact that the sample signal becomes higher than that of the blank at pH values above 5.

The photoreduction of $AuCl_4^-$ in the presence and absence of cysteine was likewise shown to be highly temperature dependent. The net analytical signal (A at = 530 nm) was lower when the samples were irradiated at temperatures above room temperature, indicating that the temperature sped up the reduction of $AuCl_4^-$ ions. We ascribed these findings to citrate, which is a powerful reducing agent of gold even at high temperatures. As a result, all the tests were conducted under ambient conditions.

We looked for the best UV (254, 312, and 365 nm) and visible light (i.e., artificial and room light) irradiation wavelengths. The photoreduction was shown to be possible at all wavelengths, including ambient light, however longer irradiation periods were needed with increasing wavelength (i.e. lower intensity). In the presence of 200.0 M cysteine and 40 W of UV irradiation at 254 nm, for instance, AuNPs formed after 6 hours at room temperature. It took more than 1 hour to get a detectable signal when the same experiment was carried out in ambient lighting conditions. In this section, we briefly recap the experimental setup and the parameters that were chosen as optimal.

CONCLUSION

Supporting metal ions in the interaction between carbon dioxide and epoxides with ligands containing sulfur has gained popularity in recent years. The inclusion of sulfur in the ligand backbone confers special features on the catalyst precursor, often increasing its activity, selectivity, and stability. Additionally, both cyclic carbonates and polycarbonates were produced with good activity and selectivity for a broad variety of substrates, indicating a great deal of room for growth. In particular, these ligands may be used with a wide range of metal centers, which improves catalytic performance and broadens the scope of the products that can be made. As a final goal, developing and synthesizing novel structural motifs with sulfur atoms in the ligand backbone is crucial for the potential development of other catalytic applications.

Most of the silver in aqueous Ag(I) is in a colloidal phase with a size of,0.45 mm and a molar mass of several kilobars. Therefore, the most significant part of aqueous Ag(I) is the colloidal phase, which is likely made up

of both organic and inorganic components. Understanding the behavior of Ag(I) in the very diluted condition in which it occurs in natural waters requires familiarity with the structure and chemistry of complexes of silver and sulfur, whether inorganic or organic. The strength of the silver-sulfur bond, which is greater than the binding of even chelating carboxylates by more than six orders of magnitude, is the most significant chemical fact to comprehend in silver chemistry. Therefore, trace amounts of inorganic sulfides or organic mercaptans in the environment must be considered. Some inorganic mineral structures and natural organic silver thiolates have a remarkable similarity: they are all solid state structures in which Ag(I) tends to create linear di-coordinate bonding with an S_2Ag_2S arrangement, resulting in the production of lengthy zigzag chains. Any mercapto group covalently attached on the surface, or at an accessible point in the interior of an organic, or inorganic colloid or particle, will operate as a site for reaction with Ag(I) due to the high formation constants for Ag(I) complexing with $S(II_2)$ or R_2S_2. Colloids and particles that contain HS_2 or H_2S will also serve as reaction sites, as will occluded mercaptans.

REFERENCES

1. Smith GJ, Flegal AR. 1993. Silver in San Francisco Bay estuarine waters. Estuaries 16:547–558.
2. San˜udo-Wilhelmy SA, Flegal AR. 1992. Anthropogenic silver in the southern California Bight: A new tracer of sewage in costal waters. Environ Sci Technol 26:2147–2151.
3. Shafer MM, Armstrong DE, Overdier JT, Walker MT. 1994. Partitioning and fate of silver in background streams and effluent-receiving streams. Argentum 2:99–104.
4. Rozan TF, Hunter KS, Benoit G. 1995. Silver in fresh water: Sources, transport and fate in Connecticut rivers. Argentum 3: 181–184.
5. Luoma SN. 1993. Bioavailability of silver to bivalves in estuaries. Argentum 1:67–68.
6. Crecelius EA. 1993. The concentration of silver in mussels and oysters from NOAA National Status and Trends mussel watch sites. Argentum 1:65–66.
7. Stumm W, Morgan JJ. 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, New York, NY, USA.
8. Martell AE, Smith RM. 1977. Critical Stability Constants: Other Organic Ligands. Plenum, New York, NY, USA.
9. Adams NWH, Kramer JR. 1998. Reactivity of silver(I) ion with thiol ligands in the presence of iron sulfide. Environ Toxicol Chem 17:625–629.
10. Kramer JR. 1996. Aqueous silver in the environment: Conceptual. Argentum 4:19–30.
11. Adams NWH, Kramer JR. 1999. Potentiometric determination of silver thiolate formation constants using a silver sulfide electrode. Aquat Geochem (in press).
12. Cloke PL. 1963. The geologic role of polysulfide—Part I. Distribution of ionic species in aqueous sodium polysufide solutions. Geochim Cosmochim Acta 27:1265–1298.
13. Cloke PL. 1963. The geologic role of polysulfide—Part II. Solubility of acanthite and covellite in sodium polysulfide solutions. Geochim Cosmochim Acta 27:1299–1319.
14. Giggenbach W. 1972. Optical spectra and equilibrium distribution of polysulfide ions in aqueous solution at 208. Inorg Chem 11:1201–1207.
15. Berthet B, Amirad JC, Amird-Triquet C, Martoja M, Jeantet AY. 1992. Bioaccumulation, toxicity, and physico-chemical speciation of silver in bivalve molluscs: Ecotoxicological and health consequences. Sci Total Environ 125:97–122.