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From Sulfur−Amine Solutions to Metal Sulfide Nanocrystals: Peering into the Oleylamine−Sulfur Black Box

Jordan W. Thomson,[†] Kaz Nagashima,[‡] Peter M. Macdonald,[†,‡] and Geoffrey A. Ozin*[,†]

[†]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

[‡]Department of Chemical and Physical Sciences, University of Toronto Mississauga, 3359 Mississauga Road North, Mississauga, Ontario L5L 1C6, Canada

Supporting Information

ABSTRACT: In this Article, we present our findings on the formation of metal sulfide nanocrystals from sulfur−alkylamine solutions. By pulsed field gradient diffusion NMR along with the standard toolbox of 1D and 2D NMR, we determined that sulfur−amine solutions used as a sulfur precursor exist as alkylammonium polysulfides at low temperatures. Upon heating to temperatures used in nanocrystal synthesis, the polysulfide ions react with excess amine to generate H_2S, which combines with the metal precursor to form metal sulfide. Four different reaction pathways were found, each of which produced H_2S and the byproducts identified in this Article. Thioamides were identified as an intermediate and were shown to exhibit much more rapid kinetics than sulfur−alkylamine solutions at low temperatures in the synthesis of metal sulfide nanocrystals.

INTRODUCTION

Semiconductor nanocrystals, also known as quantum dots, show great promise in applications ranging from sensing and imaging to photovoltaics and optoelectronics.[1] While good control over monodispersity has been achieved for many technologically relevant compositions, very little is still understood about the mechanism of precursor reaction and the formation of reactive species. For instance, the synthesis of II−VI and IV−VI nanocrystals from trioctylphosphine selenide (TOPSe), a reaction that has been used for 20 years, was only very recently and unexpectedly shown to require dialkylphosphine impurities present in very small amounts in commercial trioctylphosphine.[2,3] Understanding the different molecular species responsible for the formation of nanocrystals is crucial to controlling size and shape, size distributions, yields, properties, and ultimately utility in functional devices.

While phosphine-based syntheses are commonly used for the formation of metal selenides and tellurides, the precursor of choice for metal sulfides is sulfur powder dispersed in long chain primary alkylamines, most typically oleylamine.[4] This precursor is both cheaper and less environmentally hazardous as compared to phosphine-based precursors and is tolerant of air and moisture. Its popularity as a precursor has led to many interesting and novel structures and materials.[4] However, its chemistry has been little studied in comparison to phosphine-based precursors. The purpose of this work is to uncover the nature of the sulfur−oleylamine precursor and how it reacts at temperatures typically used for nanocrystal syntheses.

Previous work on sulfur−amine solutions has suffered from the inability to isolate pure compounds from reaction mixtures.[5−7] Attempts to crystallize components typically resulted in deposition of oil, which decomposed upon distillation attempts.[8] Notable exceptions include ethylenediamine and benzylamine, for which crystalline products were obtained and characterized by NMR in the case of benzylamine.[8,9] For simple aliphatic amines where the solvent is also a reactant, spectroscopy must be performed on reaction mixtures, making characterization very difficult.

Two similar proposed steps in the "solubilization" of sulfur and liquid amines are found in the literature. Note that sulfur exists as S_8 rings at its standard state.[10] In reaction 1 shown in Scheme 1, proposed by Davis and Nakshbendi,[6] direct nucleophilic attack by nitrogen on S_8 occurs causing ring-opening, thereby forming an open chain alkylammonium *N*-polythioamine salt with an N−S bond. The second, proposed by Levi[11] and shown in reaction 2, results in the formation of hydrogen sulfide and an *N*,*N*′-polythiobisamine with two N−S bonds. Levi[11] claimed the isolation of the tetraalkylpolythiodiamine from secondary amines and sulfur, but characterized the products only with elemental analysis. Hodgson et al.[7] have ascribed the ESR spectrum of sulfur and primary/secondary amines to the homolytic scission of S−S bonds in *N*,*N*′-polythiobisamines.

While reaction 2 directly forms H_2S, Davis and Naskshbendi[6] propose H_2S formation from the reaction of sulfur with the methylene protons α to nitrogen, which forms a thioamide (reaction 3). In both papers, H_2S is proposed to react with S_8 to form alkylammonium polysulfides as shown in reaction 4. Alkylammonium polysulfides have been isolated in the case of ethylenediamine and benzylamine and have been proposed to produce solution conductivity in other amines.[6,8,9]

In this Article, we will study the reaction between sulfur and alkylamine by performing NMR experiments directly on the

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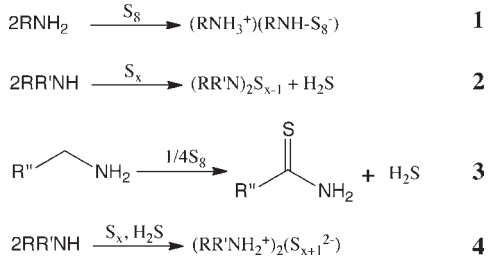
Scheme 1. Proposed Reactions of Sulfur with Amine from the Literature



reaction mixtures and without the addition of deuterated solvents. The use of pulsed field gradient (PFG) NMR allows us to study diffusion behavior,[12] and the extension, diffusion ordered spectroscopy (DOSY), correlates the diffusion coefficient with the chemical shift.[13,14] By investigating the translational diffusion behavior, we can indirectly probe the nature of the sulfur species. The standard toolbox of 1D and 2D NMR experiments, along with diffusion data, can then establish what byproducts are formed during a nanocrystal reaction and determine the active species in the formation of metal sulfide nanocrystals.

The results of our study show that, at low temperatures, sulfur−alkylamine solutions employed as a sulfur precursor exist mainly as alkylammonium polysulfides. Upon heating to nanocrystal growth temperatures, the polysulfide ions react with excess alkylamine to liberate H_2S, which under appropriate conditions combines with the metal precursor to form metal sulfide nanocrystals. The byproducts formed in the initial reaction react further, forming H_2S. We believe this work will lead to a better understanding of metal sulfide nanocrystal reactions and should allow for improvements in control over nanocrystal size, shape, and yields.

EXPERIMENTAL SECTION

Materials. Sulfur (Aldrich, reagent grade) and octylamine (Aldrich, 99%) were used as received without further purification.

Reaction of Sulfur and Octylamine. Sulfur−octylamine solutions were prepared by pipetting 1.50 mL of octylamine into a 20 mL scintillation vial (low temperature solution) or round-bottom flask (high temperature solution). Sulfur powder was then added to the vial (flask) to prepare solutions with sulfur-to-octylamine (S:OA) ratios ranging from 0.01 to 0.5. Specifically, in the preparation of the 0.5 S:OA low temperature precursor solution, 145.3 mg of sulfur powder was added to 1.50 mL of octylamine in a scintillation vial. The mixture was sonicated for 10 min and heated at 80 °C for 10 min. This procedure was repeated three times until a clear red solution was formed. The sample was then directly pipetted into a 5 mm NMR tube for analysis. For the samples heated at 130 °C, an identical mixture of sulfur and octylamine was prepared and purged with N_2 at room temperature while stirring for 10 min in a flask fitted with a condenser. The flask was then immersed in an oil bath at 130 °C for 2 h. The solution was cooled to room temperature under N_2 before being pipetted directly into a 5 mm NMR tube for analysis. Neat octylamine was subjected to the same procedure as a control and shown to remain unchanged.

NMR Spectroscopy. All NMR spectra were recorded on a Varian Unity 500 MHz NMR spectrometer using a Varian 5 mm switchable broadband liquids probe. The NMR samples were not diluted with deuterium solvent to preserve the original condition. Deuterium field lock was turned off during the whole measurement, and the static field was shimmed using a ^{1}H NMR gradient shimming macro. Caution was taken to minimize the radiation damping from the strong samples.[15] All spectra were recorded at a sample temperature of 25 °C. PFG diffusion measurements were conducted using a stimulated-echo sequence.[16] Slice-selection with sinc pulse and gradient[17] was used to excite the sample nuclei only in the central region of the RF coil to mitigate radiation damping and to compensate the inhomogenieity of the field gradient. Two methods of ^{1}H−^{13}C correlation 2D NMR experiments, gradient-selected heteronuclear single quantum coherence (gHSQC)[18] and heteronuclear multiple bond coherence (gHMBC),[19] were conducted, using default pulse sequences and parameters of the spectrometer.

NMR Assignment of Products. Octanethioamide: ^{1}H NMR (500 MHz) $R_1C\mathbf{H_2}C(S)NH_2$ 3.60 ppm (t); ^{13}C NMR (125 MHz) $R_1CH_2\mathbf{C}(S)NH_2$ 204 ppm, $R_1\mathbf{C}H_2C(S)NH_2$ 45.6 ppm. Octanamide: ^{1}H NMR (500 MHz) $R_1C\mathbf{H_2}C(O)NH_2$ 3.69 ppm (t); ^{13}C NMR (125 MHz) $R_1CH_2\mathbf{C}(O)NH_2$ 186 ppm, $R_1\mathbf{C}H_2C(O)NH_2$ 47.0 ppm. *N*′-Octyloctanamidine: ^{1}H NMR (500 MHz) $R_1C\mathbf{H_2}N'$ 3.15 ppm (t); ^{13}C NMR (125 MHz) $RN'{=}\mathbf{C}R_1(NH_2)$ 149.6, $R_1\mathbf{C}H_2N'$ 44.5 ppm. *N*′-Octyl-2-thioketooctanamidine: ^{1}H NMR (500 MHz) $R_2C\mathbf{H_2}C(S)$ 5.08 ppm (t), $R_1C\mathbf{H_2}N'$ 3.45 ppm (t); ^{13}C NMR (125 MHz) $R_2CH_2\mathbf{C}(S)$ 190 ppm, $R_2CH_2C(S)\mathbf{C}{=}N'R(NH_2)$ 160 ppm, $R_2\mathbf{C}H_2C(S)$ 75.5 ppm, R_1CH_2N' 51.9 ppm. Note: Characterization of resonances other than those shown was not possible due to signal overlap. All spectra were internally referenced to the CH_3 reference value of 0.887 ppm for the ^{1}H NMR and 14.10 ppm for the ^{13}C NMR.

RESULTS AND DISCUSSION

To understand which reaction pathway(s) occur in the synthesis of metal sulfide nanocrystals, we first studied a model sulfur-in-amine solution typically injected into the metal precursor. This solution is generally formed with sonication and mild heating (<80 °C) before being injected into the hot metal precursor solution/slurry. To minimize variables, most especially in diffusion measurements, we chose octylamine, which is commercially available at 99% purity and is a liquid at room temperature, making it a good model for technical grade oleylamine (70% pure).

Figure 1 (left) shows a stack plot of the ^{1}H NMR spectra of octylamine with increasing concentrations of S. As mentioned previously, the NMR sample contains only octylamine and sulfur. The sulfur-to-octylamine molar ratio of 0.5 (thereafter referred to as 0.5 S:OA ratio) is the same as a typical composition used in the nanocrystal synthesis using oleylamine and was close to the solubility limit of sulfur in octylamine at room temperature. The majority of chemical shifts remain largely unchanged as the sulfur concentration increases from 0 to 0.5 S:OA ratio. The N−H protons, however, show a large drift from 1.17 ppm in neat octylamine to 3.39 ppm in the most concentrated solution. When the chemical shift is plotted against S:OA ratio, a linear relationship is observed, as shown in Figure 1 (right). This trend suggests an increase in the degree of amine protonation. In both the ^{1}H and the ^{13}C NMR spectra, only one major species is observed. Minor components can be observed at approximately 50 ppm in the ^{13}C NMR spectrum (Figure S1 in the Supporting Information).

Figure 2 shows the diffusion coefficient of octylamine as a function of S:OA ratio. The two diffusion coefficients, as determined by the methyl and the amine resonances, almost overlapped. This indicates that the N−H protons diffuse associating with the backbone, although they are expected to be more or less labile and actually do not show a clear splitting due to scalar coupling. A linear decrease is observed as sulfur concentration increases, in an analogous fashion to the chemical shift.

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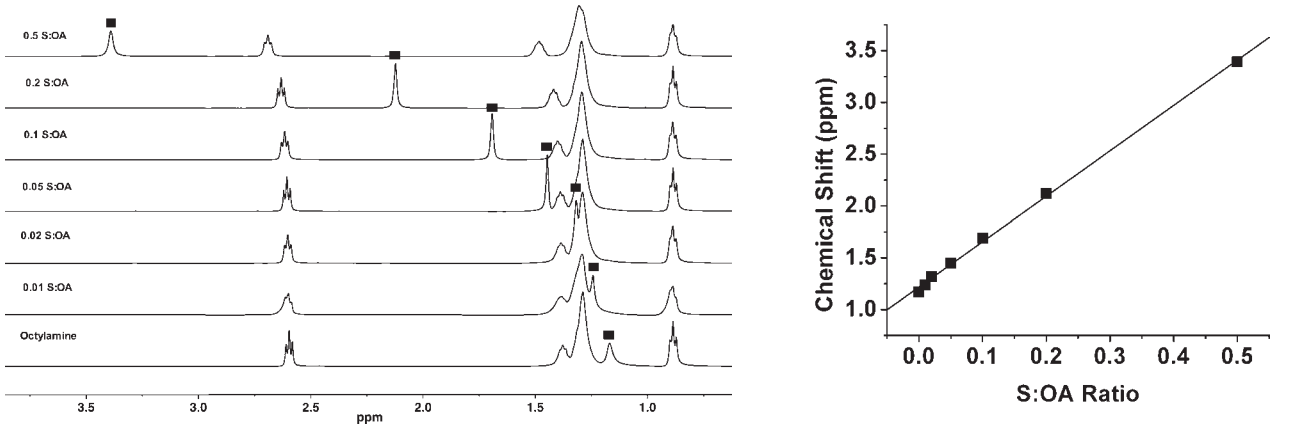

Figure 1. (Left) A stack plot of the ^{1}H NMR spectra of octylamine with an increasing concentration of sulfur (S:OA ratio) from bottom to top. The black rectangles denote the N−H resonance. (Right) ^{1}H NMR chemical shift of the N−H resonance of octylamine (and octylammonium polysulfides) plotted against S:OA ratio.

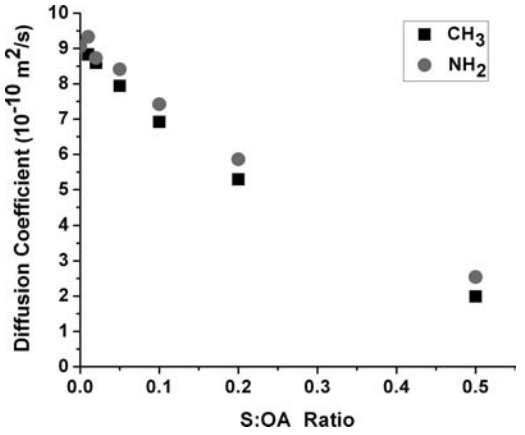

Figure 2. Diffusion coefficients of octylamine, as determined by the methyl and the amine resonances, as a function of S:OA ratio.

The PFG NMR intensity profiles (Figure S2 in the Supporting Information) for each concentration of sulfur decayed single-exponentially and identically for both the methyl and the N−H resonances. The 0.5 S:OA sample showed a small degree of multiexponentiality, probably due to the increase of slowly diffusing components with increases in sulfur contents.

These results are most consistent with the large majority of sulfur existing as octylammonium polysulfides. The apparent diffusion coefficient decreases as the amount of alkylammonium polysulfide increases. Observed in this case is an average diffusion coefficient as the molecular exchange between octylammonium and octylamine molecules is expected to be very rapid due to very low activation energy of ammonium ion formation. The same reasoning explains the apparent existence of only one species in the ^{1}H and ^{13}C NMR spectra, as well as the increase in the degree of amine protonation caused by an increasing fraction of alkylammonium ions (cf., Figure 1).

N-Polythioamines/*N*,*N*′-polythiobisamines, if present, would exchange much more slowly with unprotonated octylamine as the N−S bonds would need to be broken and re-formed, which likely would have a significant energy barrier. If appreciable quantities of *N*-polythioamines/*N*,*N*′-polythiobisamines were present, we would expect to see multiple components in the form of curvature in the PFG NMR intensity profiles and additional resonances in the ^{1}H and ^{13}C NMR spectra. While the N−H protons in *N*-polythioamines/*N*,*N*′-polythiobisamines are chemically and magnetically inequivalent, they would likely be labile and exchange rapidly with protons supplied by octylamine, octylammonium molecules, and others, leading to the observation of one average resonance.

Although the majority of sulfur exists in the form of octylammonium polysulfides, the question of where the hydrogen sulfide came from is still unclear. At the low temperatures used in the formation of the unheated solution, it is clear from the ^{13}C NMR that thioamide formation as in reaction 3 does not occur to an appreciable extent. It appears that only a small amount of *N*,*N*′-polythiobisamine is formed, which produces enough H_2S to form octylammonium polysulfides. The small degree of curvature in the PFG NMR intensity profiles may be due to the presence of this species.

In an attempt to better understand the precursor reactivity at temperatures employed in nanocrystal synthesis, we heated the precursor solution containing octylammonium polysulfides (0.5 S:OA ratio) for 2 h at 130 °C. Figure 3 (left) shows the ^{13}C NMR spectrum after heating, which clearly indicates the formation of new species substantially deshielded as compared to the octylamine−octylammonium resonances. The ^{1}H NMR spectrum, Figure 3 (right), also shows a series of new resonances. The new products still represent a very small percentage of the overall solution (∼1% by resonance integration as compared to octylamine α-CH_2 resonance), and the solution still contains a large amount of unreacted octylamine and octylammonium polysulfides. As a control, neat octylamine was heated to 130 °C under N_2 gas for 2 h and did not show any new resonances in the ^{13}C and ^{1}H NMR spectra. The significant downfield drift of the N−H proton resonance, from 3.39 ppm before heating to 3.83 ppm after heating, is attributable to the production of H_2S. The presence of H_2S could be confirmed by placing PbO-coated paper in the headspace of the flask, which immediately turned black due to the formation of PbS.

^{1}H−^{13}C correlation 2D NMR experiments, gHSQC[18] and gHMBC,[19] were conducted to determine the structural connectivity of the new products in the mixture. The spectra are shown in the Supporting Information (Figures S3 and S4). Very high signal strength is recorded for octylamine/octylammonium polysulfide; however, connectivity could still be observed for the weaker resonances.

Figure 4 shows the DOSY plot for the heated sulfur−octylamine solution. DOSY[13] is perfectly suited for resolving

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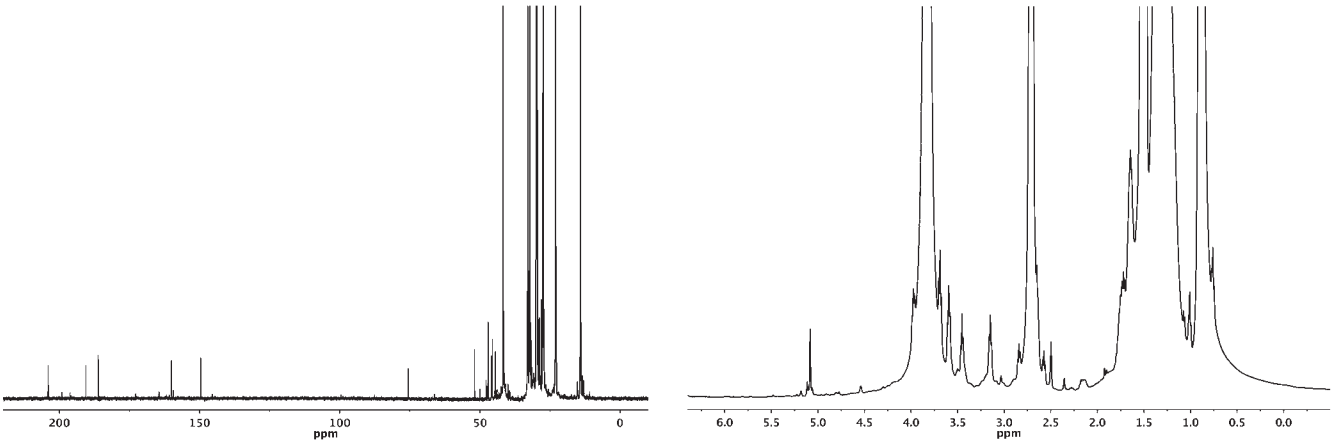


Figure 3. (Left) ^{13}C NMR spectrum and (right) ^{1}H NMR spectrum for the 0.5 S:OA solution heated at 130 °C for 2 h. Note: The strong resonances were cut off at the top for clarity.

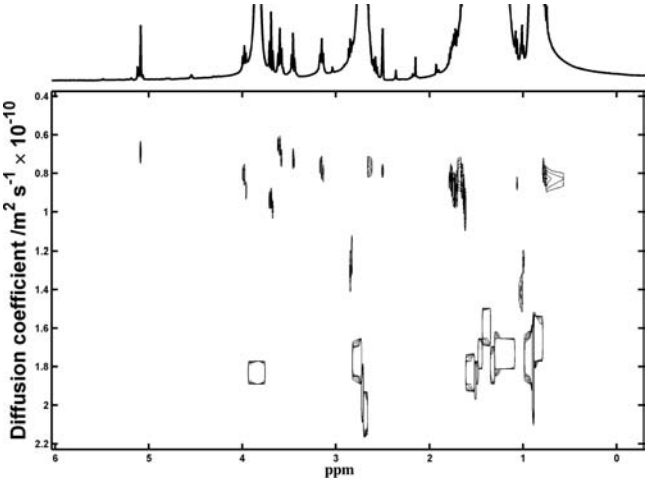


Figure 4. ^{1}H DOSY plot for the 0.5 S:OA sample heated at 130 °C for 2 h. The software designed by Nilsson[14] was used for the processing with single-exponential fitting.

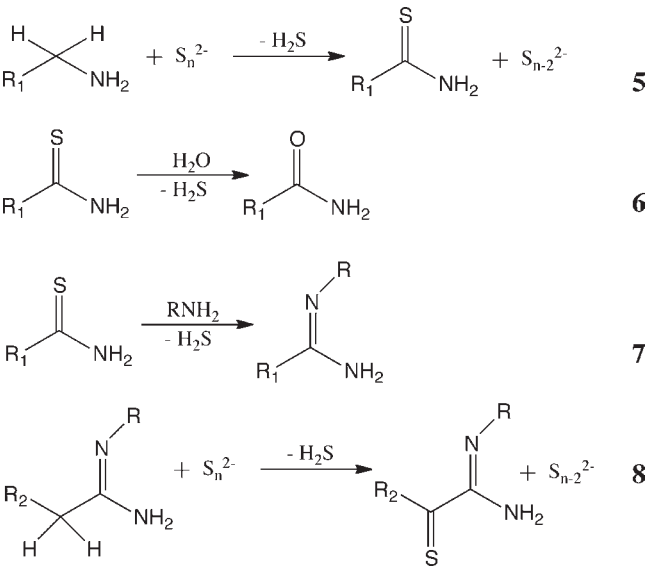
the overlapping resonances observed in complex mixtures like this sample. It is clear that there are two distinct diffusion coefficient ranges. The most intense and fastest diffusing species (bottom of DOSY plot) corresponds to octylamine/octylammonium polysulfide. The second extreme is the slow diffusing species (top of DOSY plot), which corresponds to the new species produced after heating.

On the basis of the data presented, we can deduce that there are four new species produced at 130 °C. Scheme 2 shows the new products and the possible reaction pathways.

If the unheated sulfur−octylamine solution contains mostly octylamine and octylammonium polysulfides, and if products 5−8 were not present in significant concentrations before heating, it follows that the polysulfide ions represent the reactive sulfur precursor. Open chain polysulfide ions have previously shown greater reactivity than S_8 rings.[20]

Reaction 5 shows the formation of octanethioamide, which is the same as reaction 3 proposed by Davis and Nakshbendi.[6] At 130 °C, it is possible that a radical polysulfide ion could be the reactant, as the open chain S−S bonds are fairly weak and radicals have been detected in sulfur−amine solutions at room temperature.[7] In the presence of trace water, the thioamide will be hydrolyzed, releasing hydrogen sulfide as in reaction 6.

Scheme 2. Reaction Pathways in Sulfur−Octylamine Solution at 130 °C and New Product Identities (R = C_8H_{17}, R_1 = C_7H_{15}, R_2 = C_6H_{13})



Both octanamide and octanethioamide are characterized by a distinct quaternary ^{13}C NMR resonance at 186 and 204 ppm, respectively, slightly downfield from aliphatic amides/thioamides. The diffusion coefficient as determined from the DOSY plot is about one-half of that of octylamine. It is plausible that in octylamine, which is relatively nonpolar, these species form hydrogen-bonded dimers because the N−H protons are good H-bond donors and the O/S atoms are good H-bond acceptors. The downfield shift of both the α and the β carbon atoms relative to typical aliphatic (thio)amides is also consistent with this.

Excess octylamine molecules are expected to attack octanethioamide in a fashion similar to water. Reaction 7 shows the formation of *N*′-octyloctanamidine. As in reactions 5 and 6, the formation of the amidine releases H_2S. This reaction has been shown to occur at low temperatures in the presence of Lewis acid.[21] The observation of a quaternary carbon at 150 ppm in the ^{13}C NMR is consistent with this assignment. The DOSY plot shows the roughly one-half slower diffusion than octylamine. This is expected, as the amidine is essentially a dimer of two octylamine molecules.

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Finally, reaction 8 shows the formation of an α-thioketoamidine. While not having literature precedent as with the thioamide, it is not unexpected. N−H groups activate the α-methylene protons of octylamine to thioamide formation. This likely occurs due to the resonance stabilization of the relatively weak C═S bond by the nitrogen lone pair in the thioamide, making the resulting product stable. Similarly, the C═S bond can be stabilized through delocalization into the amidine group. For this reason, we expect similar reactivity of the amidine with polysulfide ions.

N′-Octyl-2-thioketooctanamidine is characterized by two quaternary ^{13}C NMR resonances at 160 and 190 ppm. The HMBC spectrum (Figure S4 in the Supporting Information) suggests that these carbons are adjacent. The 160 ppm resonance is attributed to the amidine carbon, while the 190 ppm resonance is likely due to the thioketo group. Two more ^{13}C resonances were characterized as adjacent to the thioketo and amidine carbons, respectively, and are listed in the Experimental Section. The DOSY plot shows a diffusion coefficient consistent with the dimeric nature of the α-thioketoamidine. Attempts to provide further evidence for the formation of this product through mass spectrometry of reaction mixtures is complicated by (i) ion suppression in electrospray ionization-mass spectrometry (ESI-MS), which is caused by the large concentration of octylamine and octylammonium molecules and (ii) reaction of polysulfide ions at high sampling temperatures (>300 °C) required in typical mass spectrometers. Separation with HPLC is complicated by the poor solubility of the products in the solvents typically required. While our NMR data indicate the formation of the α-thioketoamidine, more work may be needed to more confidently comfirm its presence.

Reactions 5−8 each produce H_2S, which likely exists as octylammonium hydrosulfide after partial neutralization with octylamine, consistent with the increased chemical shift of the N−H protons in the heated sample. We therefore postulate that the synthesis of metal sulfide nanocrystals proceeds by the reaction of in situ-produced octylammonium hydrosulfide with the metal precursor salt. The resulting product from this reaction is metal sulfide nanocrystals and the octylammonium salt (e.g., octylammonium chloride/citrate, etc.).

Our findings have important implications for the reaction kinetics in metal sulfide nanocrystal syntheses. We speculate that reaction 5 is the rate-limiting step, which results in characteristically slow reaction kinetics in nanocrystal reactions using sulfur and olelylamine, as compared to phosphine-based precursors or bis(trimethylsilyl)sulfide (BTS). In some cases, this may be essential for the formation of intricate structures such as ultrathin nanowires.[22] However, in others, it also may prevent the formation of very small nanocrystals, which typically require more reactive precursors to generate a large number of nuclei upon injection. Moreover, the byproducts, such as amidines, may be important not only as stabilizing ligands during the synthesis but also in aiding the formation of anisotropic structures.

While reaction 5 is likely rate limiting, reactions 6 and 7 are expected to proceed more rapidly at elevated temperatures. To test this hypothesis, we used commercially available thioacetamide dissolved in oleylamine as a sulfur precursor to react with $Pb(oleate)_2$. As compared to the synthesis of PbS nanocrystals from S in oleylamine, our reaction showed very rapid kinetics even at temperatures as low as 25 °C, which is as fast as BTS used by Hines and Scholes[23] to produce PbS nanocrystals. The ^{13}C NMR spectrum of the reaction between octylamine and thioacetamide showed a new resonance at 155 ppm, indicating the formation of an amidine (Figure S5). This reaction provides additional evidence for the occurrence of reaction **7**. Further investigation is underway to optimize this reaction.

CONCLUSION

We have shown that sulfur−amine solutions widely used as a "black box" precursor in metal sulfide nanocrystal synthesis exist as alkylammonium polysulfides at low temperature. Upon heating, H_2S is in situ produced, forming thioamides and other byproducts. The H_2S can then react with metal salts to form metal sulfide nanocrystals. Furthermore, we have shown that thioamides can be used as a sulfur precursor and have revealed its much more rapid kinetics as compared to sulfur in oleylamine. This work should lead to further optimization of metal sulfide nanocrystal syntheses using sulfur−amine solutions as well as a better understanding of their formation mechanisms.

ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra of sulfur−octylamine, PFG NMR intensity profiles, ^{1}H−^{13}C correlation 2D NMR spectra, and the thioacetamide−octylamine ^{13}C NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
gozin@chem.utoronto.ca

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