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Mechanistic Insights into the Role of Alkylamine in the Synthesis of CdSe Nanocrystals

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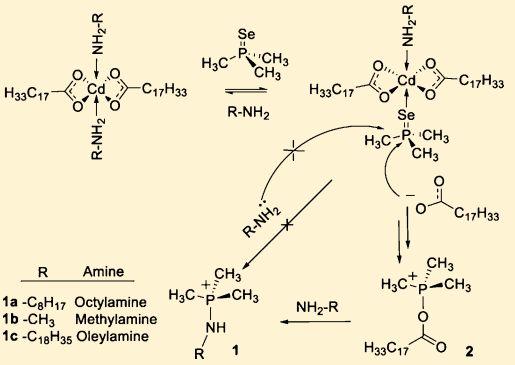
Supporting Information

ABSTRACT: This paper reports a detailed mechanistic study of the effect of alkylamine on the synthesis of CdSe nanocrystals. Alkylamines are one of the most important additives for the synthesis of colloidal semiconductor nanocrystals. However, their effect on the monomer production as well as nanocrystal nucleation and growth are not well understood, as indicted by inconsistent and contradictory conclusions in the literature. We found that alkylamines slow down the reaction between cadmium oleate and trialkyl phosphine selenide by binding to cadmium and preventing the activation of trialkyl phosphine selenide. A linear correlation was observed between the observed reaction rate constant and the ^{31}P NMR chemical shift or $^{1}J_{P-Se}$ of phosphine selenide. In the presence of alkylamine, an alkylaminophosphonium intermediate was observed. Mechanistic study suggests that the cleavage of P═Se bond is through nucleophilic attack by carboxylate instead of alkylamine. Interestingly, although alkylamines decrease the rate of monomer production, it increases the rate of CdSe nanocrystal growth. Although seemingly contradictory, this is due to a drastic decrease in the nanocrystal nucleation events in the presence of alkylamines. As a result, each nucleus is fed with more monomers and grows faster in the presence of alkylamine than in its absence.



INTRODUCTION

Primary alkylamines are one of the most important additives for the synthesis of group II−VI and group IV−VI nanocrystals.[1−6] Adding alkylamine to a nanocrystal synthesis was shown to significantly impact the nucleation and growth of nanocrystals. These effects were generally attributed to the chemical interaction of alkylamines with the molecular precursors and the nanocrystal surface.[7,8] However, there is considerable controversy and even contradiction in the mechanistic interpretation of these observations. While some studies claim that amine "activates" precursors and/or increases the rate of nanocrystal growth, others demonstrated exactly the opposite effect, claiming that amine decreases the activity of precursors and/or the growth rate of nanocrystals.[3,5−7,9−11]

The early use of amine in semiconductor nanocrystal synthesis was in part motived by its ability to produce highly monodispersed nanocrystals and improve their optical properties. For example, Guyot-Sionne group reported that hexadecylamine is an effective ligand for synthesizing ZnSe nanocrystals.[3] Talapin et al. and others reported that alkylamines can significantly improve the fluorescence quantum yield of semiconductor nanocrystals, decrease their size distribution, and increase the "focusing" phase of the synthesis.[6,12−14] These unique effects of alkylamine significantly improve the quality and reproducibility of nanocrystal synthesis. In fact, alkylamine is one of the most important ligands for the synthesis of metal and semiconductor nanocrystals.[15−23]

These reports triggered a numbers of in-depth studies aimed at understanding the role of alkylamine in the nucleation and growth of colloidal semiconductor nanocrystals. However, these studies claimed very different effect of alkylamine on nanocrystal growth, and some of their conclusions are even contradictory to each other. In particular, some studies claimed that alkylamine is an "activating" agent and enhances nanocrystal growth, while others asserted the opposite. Foos et al. reported that the main effect of amine is to slow the growth rate of nanocrystals and narrow its size distribution.[11] Jose et al. reported that hexadecylamine extended the nucleation phase of the synthesis.[10] Li et al.[4] and Pradhan et al.[9] suggested that alkylamine activates precursors of ZnSe, ZnS, and CdSe nanocrystals; they also showed that the overall effect of alkylamine on the nanocrystal growth is temperature-dependent. At low temperature, amine slows down the growth, while at high temperature, it enhances growth. Similarly, Sun et al. reported that dodecylamine increases the rate of consumption of phosphine selenide precursor as well as the rate of CdSe nanocrystal growth.[5] In contrast, Guo et al. suggested that alkylamines decrease its reactivity instead.[24]

One of the possible reasons that contributed to the inconsistencies in the literature is the lack of clear mechanistic understanding of the reaction and the role of alkylamine. Herein we reported a detailed study of the effect of alkylamines

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on the synthesis of CdSe nanocrystals using cadmium carboxylate and phosphine selenide as the precursors. Unlike previous work, the present study focuses on understanding how alkylamines affect the mechanism of the P═Se bond cleavage and other molecular processes that are relevant to the production of monomer as well as the nucleation and growth of CdSe nanocrystals. Through a set of ^{1}H, ^{31}P, and ^{113}Cd NMR experiments, we show that alkylamines bind to cadmium carboxylate and by doing so inhibit the binding of phosphine selenide to cadmium. Mechanistic study suggests that alkylamines do not directly attack phosphine selenide to cleave the P═Se bond and produce monomer. The overall effect of adding alkylamines to the nanocrystal synthesis is to slow down the production of monomer. Interestingly, the slower production of monomer in the presence of alkylamines resulted in a drastic decrease in the concentration of nuclei. As a result, the rate of nanocrystal growth actually increased because each nucleus is fed with more monomer.

RESULTS AND DISCUSSION

Our model system is the synthesis of CdSe nanocrystals using cadmium oleate ($Cd(OA)_2$) and trialkyl phosphine selenide ($SePR_3$, R = methyl and octyl) as the precursors. For the convenience of characterization, our mechanistic and kinetics studies were conducted at a relatively low temperature (<110 °C) using trimethylphosphine selenide ($SePMe_3$) as the Se precursor. However, we also carried out high temperature experiments using trioctylphosphine selenide (TOPSe) as the Se precursor to verify that the conclusions we made also apply to real nanocrystal synthesis.

Effect of Alkylamines on the Binding of Phosphine Selenide to $Cd(OA)_2$. Previous studies have shown that the binding of phosphine selenide to Cd^{2+} precedes the cleavage of P═Se bond and production of monomer.[1,2,25−29] Given that alkylamines are good ligands for Cd^{2+}, it is reasonable to believe that alkylamines will compete with phosphine selenide for cadmium carboxylate.

We have used multinuclear NMR to study the interaction between Se═PR_3 and $Cd(OA)_2$ in solution. Our results indicated that alkylamines indeed inhibit binding of Se═PR_3 to Cd^{2+}. After the addition of 1 equiv of $Cd(OA)_2$ to a solution of TOPSe in $CDCl_3$, a downfield shift of the ^{31}P NMR resonance along with a reduction of the P−Se coupling constant ($^{1}J_{P-Se}$) was observed (Figure 1A); the line width of the ^{31}P resonance also became considerably broader. Both observations suggest a dynamic exchange between Cd-coordinated and uncoordinated TOPSe. Additions of octylamine to this mixture progressively shifted the ^{31}P resonance of TOPSe upfield, along with an increase of $^{1}J_{P-Se}$, approaching values similar to the ones obtained for free TOPSe. Similar change of ^{77}Se chemical shift was also observed and can be found in Figure S1 of the Supporting Information (SI). These observations indicate that octylamine coordinates to Cd^{2+}, thus preventing the coordination of TOPSe. Further evidence of amine binding to Cd^{2+} arises from ^{113}Cd NMR data. As shown in Figure 1B, a $Cd(OA)_2$ solution gave a broad peak, consistent with its polymeric nature.[30] Addition of 1 equiv of TOPSe caused additional peak broadening that makes the peak unobservable. However, as increasing amount of octylamine was added to the mixture, the ^{113}Cd resonance sharpened and was shifted downfield. This result is consistent with coordination of octylamine to Cd^{2+} because it is well established that alkylamines break $Cd(OA)_2$ polymer into small complexes[30]

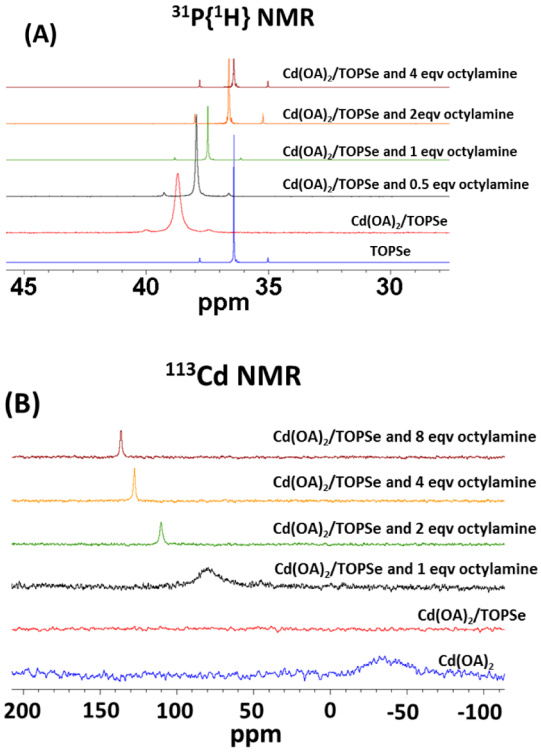

Figure 1. (A) From bottom to top, $^{31}P\{^{1}H\}$ NMR spectra in $CDCl_3$ at 300 K of free TOPSe and after additions of 1 equiv of $Cd(OA)_2$ and 0.5, 1, 2, and 4 equiv of octylamine. (B) From bottom to top, ^{113}Cd NMR spectra in $CDCl_3$ at 300 K of pure $Cd(OA)_2$ and 1:1 mixtures of $Cd(OA)_2$ and TOPSe in the presence of 0, 1, 2, 4, and 8 equiv of octylamine.

and that nitrogen ligands produce a marked deshielding of Cadmium nucleus.[31,32]

A surprising result was that the presence of oleic acid does not prevent the coordination of alkylamine to Cd^{2+}. In the presence of excess oleic acid, one would expect that protonation of alkylamine prevents its coordination to Cd^{2+}. However, when 1 equiv of octylamine was added to a mixture of $Cd(OA)_2$ (1 equiv), $SePMe_3$ (1 equiv), and oleic acid (2 equiv), we observed a significant (3.5 ppm) upfield shift of the ^{31}P peak of $SePMe_3$ (Figure S2 (SI)). Similarly, the ^{113}Cd spectrum of a mixture of $Cd(OA)_2$:oleic acid (1:2) also showed noticeable downfield shift upon addition of 1 and 2 equiv of octylamine (Figure S3, Table S1 (SI)). These observations suggest that octylamine preferentially binds to Cd^{2+} even in the presence of excess amount of carboxylic acid.

Mechanism of P═Se Bond Cleavage in the Presence of Alkylamine: Formation of Alkylaminophosphonium Species. In the absence of alkylamine, the reaction between $Cd(OA)_2$ and $SePMe_3$ produced only one new resonance peak for the phosphine oxide product when monitored by ^{31}P NMR. In contrast, when the reaction was carried out in the presence of a primary alkylamine (octylamine, oleylamine, or methylamine), an additional ^{31}P resonance was observed at around 48 ppm (Figure 2A). This new species was unstable in the reaction mixture and had a transitory existence, decomposing eventually to phosphine oxide (see below). It was thermally and air sensitive, being only observable at low temperatures (typically <90 °C) and under inert atmosphere. Notably, this new peak was only observed when a primary amine was used (e.g., oleylamine, octylamine, and methylamine) and not observed in

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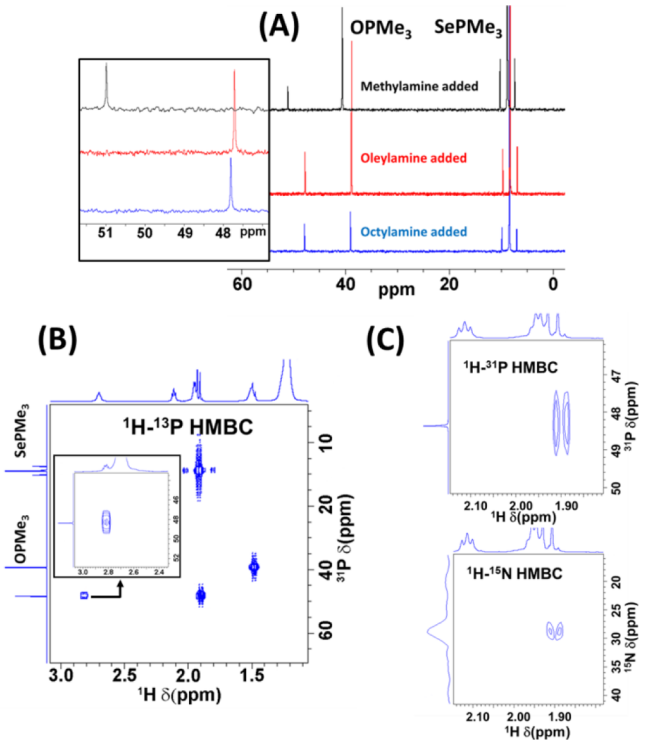
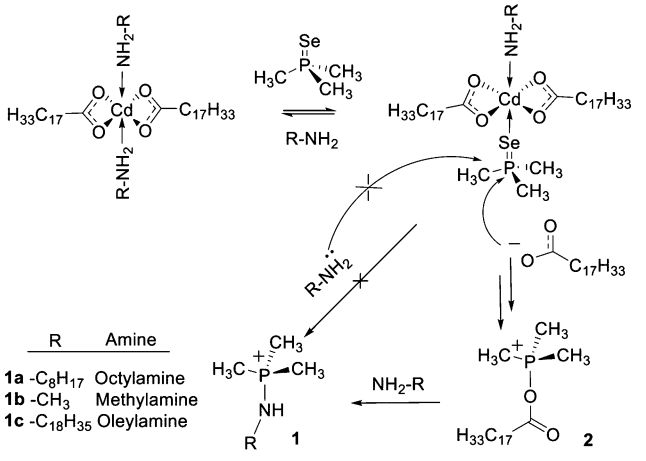


Figure 2. (A) $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$) of the reaction between $Cd(OA)_2$ (1 equiv), oleic acid (2 equiv), and $SePMe_3$ (1 equiv) at 315 K in the presence of methylamine (black), oleylamine (red), and octylamine (blue) showing the formation of a new compound at 51−48 pm, which does not contain selenium satellite (inset). (B) $^{31}P-^{1}H$ HMBC spectrum of the reaction in the presence of octylamine showing the presence of the octylaminophosphonium compound at 48 ppm and (C) $^{31}P-^{1}H$ HMBC and $^{1}H-^{15}N$ HMBC spectra evidencing the presence of the fragment $(CH_3)_3P-N$ of the alkylaminophosphonium compound.

the presence of a secondary amine (e.g., piperidine or dioctylamine) nor tertiary amine (e.g., *N*,*N*-diisopropylethylamine).

This new phosphorus species was identified as alkylaminophosphonium **1** through a set of solution NMR experiments (Scheme 1). First of all, the absence of Se satellites of this 48 ppm peak indicates the absence of P−Se linkage in this

Scheme 1. Mechanism of P═Se Cleavage in the Presence of an Alkylamine



intermediate (Figure 2A inset). The $^{31}P-^{1}H$ heteronuclear multiple-bond correlation spectroscopy (HMBC) spectrum (Figure 2B) showed a crosspeak correlating the phosphorus peak at 48 ppm with a doublet ($^{2}J_{P-H}$ = 14 Hz) at 1.90 ppm in the ^{1}H spectrum. This ^{1}H doublet partially overlapped with the $SePMe_3$ doublet at 1.92 ppm, suggesting itself to be a $-P(CH_3)_3$ fragment as well. An additional and weaker second cross peak was also observed between the ^{31}P resonance at 48 ppm and a multiplet at 2.82 ppm in the ^{1}H dimension, which was ∼0.1 ppm downfield relative to the resonance of *α*-hydrogens of octylamine (Figure 2B inset). This second cross peak is consistent with a coupling between phosphorus and vicinal protons on an octylamino fragment ($-NHCH_2-C_7H_{15}$). An additional support of this assignment is the fact that if methylamine was used in place of octylamine, a doublet ($^{3}J_{P-H}$ = 14 Hz) was observed instead of a mutliplet, consistent with having a $-PNHCH_3$ fragment (Figure S4 (SI)). Finally, $^{1}H-^{15}N$ HMBC experiment (Figure 2C) indicates that the doublet at 1.90 ppm, which arises from for the $-PMe_3$ fragment, also correlates with a ^{15}N resonance at 28.8 ppm, confirming the presence of a $(CH_3)_3-P-NH-CH_2-$ linkage.

All this data strongly support the formation of **1** when the synthesis of CdSe nanocrystal is carried out in the presence of a primary amine (Scheme 1). The final confirmation of our structural assignment came from the addition of authentic samples to the crude reaction mixture. We prepared $[(CH_3)_3PNHR]^+$ (R = octyl and methyl) by reacting the corresponding amine with hexamethyloxodiphosphonium triflate[27] in chloroform (see the Supporting Information for experimental details and Figures S5−S9). Such additions resulted in an increase of the expected resonances in the ^{1}H and $^{31}P\{^{1}H\}$ spectra; no additional ^{31}P peak was observed (Figures S10 and S11 (SI)).

Additional experiments suggest that the formation of **1** is through the formation of a more reactive acyloxyphosphonium **2**, which is then trapped in the presence of excess of alkylamine yielding **1**. Previous studies showed that the nucleophilic attack of carboxylate to an Cd^{2+}-activated $SePR_3$ produces an unstable **2**, which could react with an alcohol to produce alkoxyphosphonium compound.[27] We believe that a similar reaction occurred here between **2** and alkylamines to produce **1**. Although we cannot completely rule out the possibility that a small amount of **1** is formed by direct attack of alkylamine on $SePR_3$, several pieces of evidence suggest that this pathway is unlikely. First of all, $SePR_3$ (*R* = methyl and octyl) was stable in octylamine (solution or neat) even at high temperatures (T > 245 °C) (Figures S12−S14 (SI)). Second, the concentration of **1** showed an initial increase and peaked at low conversion of $SePR_3$ (Figure S15 (SI)). Finally, the kinetics of the decay of $SePR_3$ in the reaction with $Cd(OA)_2$ were found to be slower when alkylamines were present (see below), suggesting that alkylamines do not open an additional reaction channel for the cleavage of P═Se bond.

Effect of Alkylamines on the Kinetics of Monomer Production. As we discussed above, the major effect of alkylamines is to inhibit binding of $SePR_3$ to $Cd(OA)_2$. This binding process is known to activate $SePR_3$ for P═Se cleavage and eventually lead to the production of monomer for the nucleation and growth of CdSe nanocrystals.[1,2,25,27−29,33] Therefore, the addition of alkylamines should result in a decrease in the reaction kinetics.

Indeed, we found that alkylamines slow down the rate of P═Se cleavage. We prepared a stock solution by mixing equimolar

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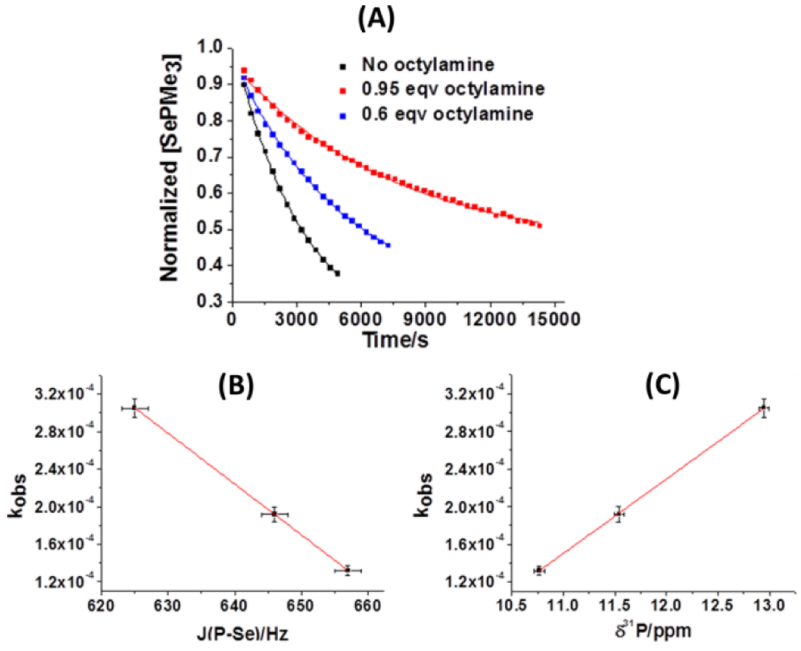

Figure 3. (A) Reaction kinetics and single exponential fits to the disappearance of $SePMe_3$ in the reaction with $Cd(OA)_2$ at 315 K ($CDCl_3$) with 0, 0.6, and 0.95 equiv of octylamine. Linear correlation between the observed rate constant and $^1J_{P-Se}$ (B) or ^{31}P δ of the $SePMe_3$ (C).

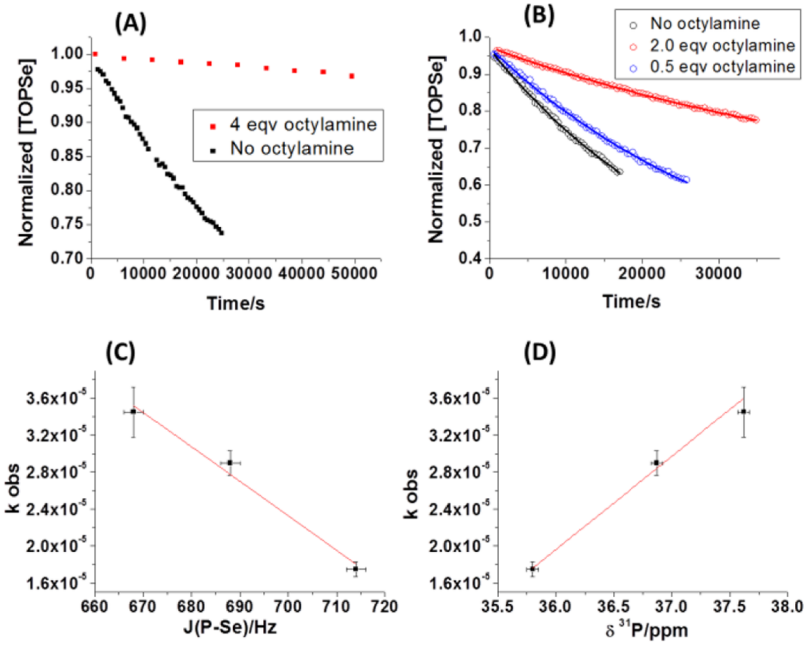

Figure 4. (A) Reaction kinetics at 353 K (toluene-d_8) for a 1:2:1 mixture of $Cd(OA)_2$, oleic acid, and TOPSe in the presence of 0 and 4 equiv of octylamine. (B) Reaction kinetics at 373 K for a 1:1 mixture of $Cd(OA)_2$, and TOPSe in the presence of 0, 0.5, and 2 equiv of octylamine. (C) Linear correlation between the observed rate constant and $^1J_{P-Se}$ or (D) ^{31}P δ of TOPSe.

amounts of $Cd(OA)_2$ and $SePMe_3$ in $CDCl_3$ and studied the conversion of $SePMe_3$ to $OPMe_3$ in the presence of different amounts of octylamine. Figure 3A shows the disappearance of $SePMe_3$ without the addition of octylamine and in the presence of 0.6 and 0.95 equiv of octylamine, as quantified by ^1H NMR. The decay of $SePMe_3$ could be fit with a single exponential decay, and the observed rate constant (k_{obs}) was extracted from the fit. As we expected, the addition of 0.6 equiv of octylamine clearly slowed down the $SePMe_3$ decay, which was even slower in the presence of 0.95 equiv of octylamine. No rate increase was observed when up to 8 equiv of octylamine was added. These observations are consistent with the picture that alkylamine coordinates to Cd^{2+} and prevents activation and cleavage of P═Se bond in phosphine selenide. In addition, the slower reaction rate in the presence of alkylamine argues against direct nucleophilic attack by alkylamine to break P═Se bond.

We found that both the ^{31}P NMR chemical shift (δ) and the $^1J_{P-Se}$ of phosphine selenide are good indicators to evaluate the degree of activation of phosphine selenide and the rate of P═Se cleavage. As illustrated in Figure 3B,C, when the observed rate constant for P═Se cleavage (k_{obs}) is plotted against $^1J_{P-Se}$ or ^{31}P δ of $SePMe_3$, a linear correlation is obtained (R^2 = 1.00

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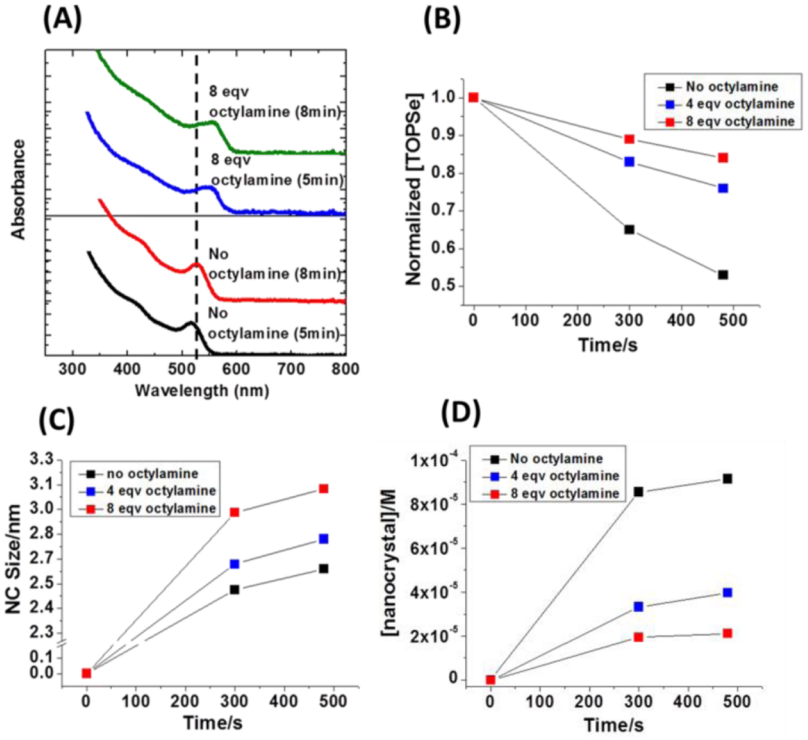

Figure 5. (A) Representative UV−vis spectra obtained at different time reactions for the synthesis of CdSe nanocrystals in the absence and presence of 8 equiv of octylamine. (B) Decay of TOPSe as determined by ^{31}P NMR for the reactions with 0, 4, and 8 equiv of octylamine. (C) Temporal evolution of the CdSe nanocrystal size and (D) nanocrystal concentration in the presence of 0, 4, and 8 equiv of octylamine.

and R^2 = 0.9998, respectively). A higher reactivity is linked to a higher δ (more downfield signal) or a smaller $^1J_{P-Se}$. This observation should not come as a surprise because interaction between $Cd(OA)_2$ and $SePR_3$ should lead to a decrease of electron density on P atom and weakening of P═Se bond. It is known that coupling constant can be a good measure of bond strength.[34]

Very similar effects on the decay kinetics of $SePMe_3$ were observed when different types of amines (octyalmine, oleylmine, methylmine, piperidene, dioctylmine, and aniline) were added as well as in the presence of oleic acid. In all these cases the addition of amine slowed down the reaction kinetics, and linear correlations between k_{obs} and ^{31}P δ or $^1J_{P-Se}$ of $SePMe_3$ were found (Figure S16−S27 (SI)). These results again highlight the importance of $SePR_3$ activation by coordination to Cd^{2+} and the possibility of tuning the kinetics of monomer production by controlling such interactions.

The observed reduction of the kinetics of P═Se cleavage in the presence of alkylamines can be extended to conditions typically found in the synthesis of CdSe nanocrystals (also see discussion in the next section). Shown in Figure 4 is the effect of octylamine on the kinetics of TOPSe decay under different conditions: in the presence of 1 equiv of $Cd(OA)_2$ in toluene at 353 K with 2 equiv of oleic acid (Figure 4A) and at 373 K without addition of oleic acid (Figure 4B). In both cases, we observed that the addition of octylamine resulted in a decrease of the reaction rate. The degree of deactivation can be predicted by the values of ^{31}P δ and $^1J_{P-Se}$ of TOPSe (Figure 4C,D).

Impact of Alkylamines on the Nucleation and Growth of CdSe Nanocrystals. We have studied the impact of adding alkylamines to the nucleation and growth of CdSe nanocrystals. A synthesis of CdSe nanocrystals using a mixture of 1:1:2 of TOPSe, $Cd(OA)_2$, and oleic acid was conducted at 200 °C in 1-octadecene. The effect of adding 0, 4, and 8 equiv of octylamine was studied by UV−vis (Figure 5A) and ^{31}P NMR (Figure 5B) spectroscopy. We note that our reaction conditions were not optimized for producing monodispersed nanocrystals.

We observed that the rate of P═Se cleavage was slowed down by adding octylamine, consistent with our observations made in the low temperature experiments. This can be seen from Figure 5B, which shows the decay of TOPSe measured by ^{31}P NMR in the presence of 0, 4, and 8 equiv of octylamine at 200 °C. The effect of octylamine in decreasing the kinetics is clear, as we observed for different conditions and types of amines at lower temperatures shown above. A good correlation was also found between the [TOPSe] measured by quantitative ^{31}P NMR and the [CdSe] determined from the absorbance at 350 nm by UV−vis (Table S2 (SI)),[35] confirming that monomer production limits the overall nanocrystal growth.[27−29]

However, in contrast to this decrease of precursor reactivity, the presence of octylamine actually increased the particle size and growth rate of CdSe nanocrystals. Figure 5A,C shows that the nanocrystal size, as determined from their absorption spectra,[36] showed a consistent increase with increasing amount of octylamine. These results clearly demonstrate that larger CdSe nanocrystals were obtained in the presence of octylamine despite the fact that it "deactivates" cadmium oleate.

The increase of nanocrystal growth rate with increasing concentration of alkylamine may appear counterintuitive at the first glance. Indeed, it was often argued that a high concentration of ligand should decrease growth rate because of ligand binding to nanocrystals. We find that this seemingly contradictory result was due to a drastic decrease of nanocrystal concentration in the presence of octylamine. As shown in

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Figure 5D and Table S2 (SI), compared to the case of not adding octylamine, the rate of monomer production (i.e., rate of P═Se cleavage, as determined from ^{31}P NMR data at 5 min) was decreased by a factor of ∼2.1 and ∼3.2, when 4 and 8 equiv of octylamine were added, respectively. In contrast, the corresponding decreases in the concentration of nanocrystals are a factor of ∼2.6 and ∼4.4. Thus, a 2.1 (3.2) fold decrease in the rate of monomer production resulted in a 2.6 (4.4) fold decrease in the concentration of nuclei. As a result, adding amine will actually increase of amount of monomer available to each nucleus even though the overall rate of monomer production is slower. We note that this interpretation is consistent with the idea that the nanocrystal growth is limited by monomer supply instead of chemical reactions on the nanocrystal surface. A detailed study on the dependence of growth kinetics on the concentration of amine may offer additional insight.

It is worth noting that the dependence of nucleation yield on monomer production rate we observed here is quite different from that reported for the synthesis of CdSe nanocrystals using phosphonic acid as surfactant at a much higher temperature (315 °C).[29] In that case, the CdSe nanocrystal concentration is a sublinear function of monomer production. In contrast, our observation indicated that nucleation yield is superlinear with respect to monomer production rate (i.e., doubling the rate of monomer production resulted in more than doubling of the nucleation yield). Currently, it is not known if the different behaviors are due to the different precursor, temperature, or both. Work is underway to understand the detailed effect of alkylamine on the nanocrystal nucleation process.

CONCLUSIONS

We showed that the addition of alkylamines reduces the reactivity of cadmium carboxylate and trialkyl phosphine selenide because of the binding of alkylamines to Cd^{2+}. The reactivity of phosphine selenide can be evaluated by ^{31}P NMR spectroscopy. Linear correlations between the observed rate constant (k_{obs}) and the $^{1}J_{P-Se}$ or the ^{31}P NMR chemical shift (δ) of phosphine selenide were found. In the presence of a primary alkylamine, compound **1** was formed during the synthesis of CdSe nanocrystals. Control experiments and kinetics data suggest that **1** is produced by the reaction between alkylamine and a previously identified reactive intermediate **2**. No evidence suggests the cleavage of P═Se bond by direct attack of alkylamine on phosphine selenide.

We showed that the rate of nanocrystal growth is faster in the presence of amine although the rate of monomer production is slower. Our experimental observation echoes previous studies reporting similar enhancement effect of alkylamine on the growth kinetics of nanocrystals. However, our explanation of this result is quite different.[4,5,9] Previously, the large nanocrystal size and faster growth rate in the presence of alkylamine were rationalized on the basis of the assumption that alkylamines are *activation* reagents when zinc or cadmium carboxylates were used as the precursors. Our results, however, show that alkylamines actually *deactivate* precursors by coordinating to Cd^{2+} and preventing activation of phosphine selenide. The observed increase in the nanocrystal size and growth rate arises from the fact that precursor conversion determines the rate of nanocrystal nucleation and growth. A decrease in the reaction rate could produce an even more drastic decrease in nanocrystal concentration, and as a result, in the presence of alkylamines, each nanocrystal is fed with more monomer and grows faster.

Our findings shed new light on the complex chemistries associated with the nucleation and growth of nanocrystals. Although the role of alkylamine in the nanocrystal synthesis has been extensively discussed in terms of their binding to nanocrystal surface,[7,9] our work is the first to quantify its interaction with precursors. Our result also echoes recent work from Yu,[25,37−39] Krauss,[2,33] Owen,[29,40,41] Vela,[42] and Buhro[43−45] groups that have demonstrated strong dependence of nanocrystal nucleation and growth on the precursor structure and presence of impurities and dialkylphosphine additives.

EXPERIMENTAL SECTION

General Methods. All operations were performed under an atmosphere of dry nitrogen using Schlenk and vacuum techniques, or in a nitrogen filled glovebox. Selenium powder (≥99.5%, Aldrich), CdO (99.5%, Aldrich), trioctylphosphine (TOP, 97%, Aldrich), trimethylphosphine (99%, Strem), oleic acid (90 or 99%, Aldrich), octylamine (99%, Aldrich), methylamine (2.0 M in THF, Aldrich), and oleylamine (70%, Aldrich) were used as received. Trimethylphosphine selenide was prepared according to a previously reported method.[27]

NMR samples were prepared in $CDCl_3$ or toluene-d_8, which were previously degassed, dried with 4 Å molecular sieves, and stored in a glovebox. To prevent moisture from entering the samples, all the samples were prepared inside a glovebox flushed with N_2 and using J-Young NMR tubes. Solution NMR spectra were obtained on Bruker Avance III 400 MHz, Bruker Avance III 500 MHz, Bruker Avance III 600 MHz and Bruker Avance III 700 MHz spectrometers. Chemical shift values are given in ppm. ^{1}H and ^{13}C chemical shifts are referenced to TMS. ^{19}F chemical shifts are relative to $CFCl_3$. For ^{31}P spectra, 85% H_3PO_4 was used as external reference. ^{31}P NMR spectra were acquired either without proton decoupling or with inverse gated decoupling. Coupling constants (J) are given in Hz. The terms m, s, d, t, q, and br. represent multiplet, singlet, doublet, triplet, quadruplet, and broad, respectively. When reaction kinetics was measured, quantitative ^{31}P NMR spectra was collected using inverse gated proton decoupling with a flip angle of 30° and with at least 10 s of relaxation delay (d1) to allow full relaxation between scans. UV−vis spectra were collected on a GENESYS 10S UV−vis spectrophotometer with 1 nm resolution in a 1 cm path length quartz cell. Samples for mass analysis were prepared in CH_3CN. All mass spectra were collected on a Thermo Q-Exactive mass spectrometer equipped with electrospray ionization (ESI).

^{113}Cd and ^{1}H−^{15}N HMBC NMR Experiments. All ^{113}Cd NMR spectra were obtained on natural abundance samples and acquired without proton decoupling with a Bruker Avance III 500 MHz spectrometer operating at 111.00 MHz or a Bruker Avance III 600 MHz spectrometer operating at 133.35 MHz. The experiments were performed using a 9.5 microsecond 90° pulse and a recycle delay of 2.0 s. Chemical shifts were given in ppm and referenced to a 0.1 M solution of $Cd(ClO_4)_2$ in D_2O (0 ppm). Negative chemical shifts are upfield from the reference sample and indicate increased shielding. Chemical shift values can be referred to neat $Cd(CH_3)_2$, which is the Bruker default reference for ^{113}Cd, by subtracting 641.5 ppm from the reported values.

^{15}N HMBC NMR experiments were carried out using the standard pulse sequence from the Bruker library *hmbcgplpndqf*, correlation via heteronuclear zero and double quantum coherence optimized on long-range couplings with low-pass J-filter to suppress one-bond correlations (one-bond coupling constant, cnst2 = 100 Hz, and long-range coupling constant, cnst13 = 10 Hz). Typically 128 t1 increments, consisting of 64 (concentrated samples) or 220 (diluted) scans of 2048 sampled data points each were recorded with a 1.5 s relaxation delay. A sample of aniline in $CDCl_3$ exhibited the expected cross peak between ortho protons and a ^{15}N signal at 55.5 ppm, referred to liquid NH_3. This ^{15}N chemical shift agrees well with a value of 58 ppm previously reported for aniline.[46]

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Synthesis. TOPSe was prepared by a slightly modified literature procedure.[28] In a glovebox, selenium powder (1.105g, 0.014 mmol) was mixed with TOP (4.4 mL, 0.01 mmol) in a vial. The mixture was stirred for 48 h. After that, the supernatant was filtered with a syringe filter and stored in the glovebox at −35 °C, affording white crystals.

Cadmium oleate: CdO (1.036 g, 8.07 mmol) was added to 10.2 mL of oleic acid (32.2 mmol, 90% tech grade, Aldrich) in a 3-neck flask. The mixture was degassed at 100 °C and then heated at 190 °C until a colorless solution was observed. The solution was cooled to room temperature, and acetone was added to remove free oleic acid and precipitate $Cd(OA)_2$ as a white solid, which was filtered off and dried in vacuo overnight.

$Cd(OA)_2$ with 2 equiv of oleic acid ($Cd(OA)_2$·2H-OA) was prepared in a similar manner with the exception that the excess of oleic acid was not removed by precipitation with acetone. The solution solidified at room temperature yielding $Cd(OA)_2$·2H-OA as a waxy solid.

In Situ Monitoring of CdSe Synthesis by NMR. In a typical reaction, $Cd(OA)_2$ (204 mg, 0.3 mmol) or $Cd(OA)_2$·2H-OA (372 mg, o.3 mmol) and $SePMe_3$ (47 mg, 0.3 mmol) were combined with 3 mL of the corresponding deuterated solvent ($CDCl_3$ or toluene-d_8) inside a glovebox, affording a stock solution with an approximate $Cd(OA)_2$ and $SePMe_3$ concentration of 0.1 M. For each kinetics run, 0.6 mL of the stock solution were added to a J-Young NMR tube and combined with the appropriate amount of the corresponding amine. The J-Young NMR tube was then inserted into a preheated NMR probe, and the reaction was monitored by ^{31}P NMR.

Identification of Compound 1. Alkylaminophosphonium species **1** were readily observed in the reaction between $Cd(OA)_2$ (1 equiv), $SePMe_3$ (1 equiv), and oleic acid (2 equiv) at 315 K. It was observed that its concentration decreases when the reaction was carried out at higher temperatures or in the absence of oleic acid to as low as 1% (normalized to the total amount of phosphorus species in solution, same below).

Typically, a stock solution was prepared by mixing $Cd(OA)_2$·2H-OA (372 mg, o.3 mmol) and $SePMe_3$ (47 mg, 0.3 mmol) in a glovebox with 3 mL of $CDCl_3$ or toluene-d_8. From this stock solution 0.6 mL were taken to a J-Young NMR tube and combined with the appropriate amount of amine; typically 2−4 equiv were optimal for the observation of alkylaminophosphonium. Increasing the amount of octylamine favors the formation of **1**; however, using more than 4 equiv resulted in the reaction proceeding too slowly to be followed at 315 K. $^{31}P\{^1H\}$ and $^{31}P-^1H$ HMBC spectra were collected following previously reported protocols.[27,47]

1a: Octylamine (4 equiv, 40 μL, 0.24 mmol) was added to 0.6 mL of $CDCl_3$ stock solution and the reaction monitored by $^{31}P\{^1H\}$ NMR at 315 K. Yield: ∼ 4% after 5 h (overall conversion of $SePMe_3$: 10%). ^1H NMR (600.71 MHz, $CDCl_3$, 300 K) δ = 2.82 [m, 2H, CH_2N] 1.90 [d(14), 9H, $(CH_3)_3P$], the rest of the resonances appeared overlapped in the spectrum of the reaction crude. $^{31}P\{^1H\}$ NMR (243.17 MHz, $CDCl_3$, 315 K): δ = 47.80 [s]. The peak shifted to δ = 48.36 at 3oo K.

1b: this compound was prepared in a procedure similar to that described above except 3.5 equiv of oleylamine (70%, 100 μL, 0.21 mmol) was used. Yield: 3.8% 11 h (overall conversion of $SePMe_3$: 17.5%). ^1H NMR (600.71 MHz, $CDCl_3$, 300K) δ = 2.83 [m, 2H, CH_2N] 1.93 [overlapped, 9H, $(CH_3)_3P$], the rest of the resonances appeared overlapped in the spectrum of the reaction crude. $^{31}P\{^1H\}$ NMR (243.17 MHz, $CDCl_3$, 315K) δ = 47.70 [s]. The peak shifted to δ = 48.90 at 300 K.

3c: this compound was prepared in a procedure similar to that described above except 4 equiv of CH_3NH_2 (120 μL of 2 M solution in THF, 2.2 equiv by ^1H NMR) were added. Yield: 1.5% after 2.5h (overall conversion of $SePMe_3$: 13%). ^1H NMR (600.71 MHz, $CDCl_3$, 300K.) δ = 2.52 [d(14.5), 3H, CH_3N] 1.82 [d(14.5), 9H, $(CH_3)_3P$], the rest of the resonances appeared overlapped in the spectrum of the reaction crude. $^{31}P\{^1H\}$NMR (243.17 MHz, $CDCl_3$, 315K) δ = 50.95 [s].

Reaction between Cadmium Oleate and TOPSe at 200 °C. In a glovebox, $Cd(OA)_2$·2H-OA (134 mg, 0.108 mmol) was dissolved in a vial in 4 mL of ODE. The solution was gently heated at 40 °C to ensure that all of the solid dissolved. This solution was then mixed with TOPSe (48.5 mg, 0.108 mmol) affording a stock solution ([Cd] = [Se] = 0.027 mM). Three J-Young NMR tubes were each loaded with 0.6 mL of the stock solution. Appropriate amount of octylamine (21.4 μL, 8 eqv, or 10.7 μL, 4 equiv) was added to two of the J-Young NMR tubes, while no octylamine was added in the remaining J-Young NMR. The three J-Young NMR tubes were taken out of the glovebox and placed into an oil bath at 200 °C. The initially colorless solutions changed from colorless to yellowish and later orange, evidencing formation of CdSe nanocrystals. After 5 min, the three NMR tubes were taken out of the oil bath and immediately studied by quantitative ^{31}P NMR. 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 by ^1H gradient shimming on the most intense resonance of the ^1H spectrum, using the TopShim algorithm incorporated in the Bruker TopSpin software. After that, 50 μL of the solution were taken from each NMR tube in the glovebox into a vial, diluted in 3 mL of hexane and studied by UV−vis spectroscopy. The three J-Young NMR tubes were reintroduced into the oil bath at 200 °C for an additional 3 min. After that they were again studied by ^{31}P NMR and UV−vis spectroscopy as previously described. Control experiments showed that removing 50 μL of reaction mixture from the NMR tube did not impact the conversion during the second heating.

■ ASSOCIATED CONTENT

Supporting Information

Detailed procedure for preparing authentic samples of **1**; Figures S1−S27; Tables S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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