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# Mechanistic Study of the Synthesis of CdSe Nanocrystals: Release of Selenium

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Supporting Information

**ABSTRACT:** We outline a reaction pathway for the cleavage of the P═Se bond in trialkylphosphine selenide during the synthesis of CdSe nanocrystals. The reaction between cadmium carboxylate and trimethylphosphine selenide in the presence of an alcohol produces alkoxytrimethylphosphonium (**2**). Control experiments and density functional theory calculations suggested that the cleavage of the P═Se bond is initiated by nucleophilic attack of carboxylate on a $Cd^{2+}$-activated phosphine selenide to produce an acyloxytrialkylphosphonium intermediate (**1**), which is converted to **2** in the presence of an alcohol.

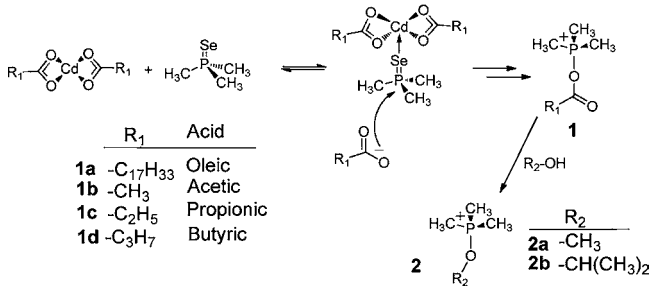
Semiconductor nanocrystals have made a great impact in numerous applications, including lasers,[1−3] photovoltaic cells,[4,5] biomarkers,[6,7] and light-emitting diodes.[8−10] The synthesis of group II−VI nanocrystals from trialkylphosphine chalcogenides ($R_3P$═E; E = S, Se, Te) and metal salts has been used for almost 20 years.[11] Over the years, a large number of recipes have been developed, and a good control over size and shape has been achieved.[12−14] More recently, a number of studies have aimed at understanding the chemical mechanism of nanocrystal formation[15−21] and in particular the mechanism by which the monomers are generated.[22−25] These studies have been motivated by the need for better control of the nanocrystals synthesis and potentially will allow new synthesis recipes developed by rational design.

Among the two precursors, the trialkylphosphine chalcogenide ($R_3P$═E) is special in that the chalcogen atom is covalently bound to the phosphorus atom. The P═E bond must be cleaved to "release" the chalcogen atom for nanocrystal growth. Previous studies have suggested that this bond cleavage is initiated by nucleophilic attack of carboxylate on the phosphine chalcogenide.[15,23,24] However, the details of this important P═E bond cleavage are largely unknown.

Herein we report a mechanistic study of the synthesis of CdSe nanocrystals from cadmium carboxylate and trimethylphosphine selenide. We identified acyloxytrialkylphosphonium (**1**) as a key intermediate following cleavage of the P═Se bond. A kinetics study suggested that the rate-limiting step of the CdSe nanocrystal synthesis is or precedes the P═Se bond cleavage. Density functional theory (DFT) calculations indicated that the P═Se bond is cleaved in two steps: nucleophilic attack by carboxylate on a $Cd^{2+}$-activated phosphine selenide followed by proton transfer from carboxylic acid to the selenium atom.

The previously proposed nucleophilic attack of carboxylate on $Cd^{2+}$-activated phosphine selenide should produce **1** upon cleavage of the P−Se linkage (Scheme 1). Compound **1** has been suggested as the key reactive intermediate in many other synthetically important reactions, including the Mitsunobu reaction,[26−29] the synthesis of amides[30] and thioesters,[31] and a number of peptide coupling reactions.[32,33] Its structural characterization, however, has not been well described in the literature because of its instability, which has made its isolation impossible.[28,29,34]

**Scheme 1. Cleavage of the P═Se bond**




We prepared compound **1a** by reacting a substoichiometric amount of oleic acid or cadmium oleate with hexamethyloxodiphosphonium triflate in $CDCl_3$.[35] While compound **1a** was too reactive to be isolated in pure form, its structure could be unambiguously identified through solution-phase NMR spectroscopy and high-resolution mass spectrometry. The $^{31}P\{^1H\}$ NMR spectrum of **1a** gave a singlet at 98.8 ppm;[28] its $^{13}C\{^1H\}$ NMR spectrum showed a doublet at 169.5 ppm for the carbonyl carbon with the expected P−C coupling constant ($^2J_{P-C}$ = 10 Hz). The $^1H$ NMR spectrum showed, among the signals expected for the oleyl fragment and the $P(CH_3)_3$ fragment, a resonance for the $\alpha$-$CH_2$ group adjacent to the carbonyl that was ∼0.3 ppm downfield relative to that of oleic acid; this $CH_2$ peak also showed a cross-peak with the phosphorus signal (98.8 ppm) in the $^1H-^{31}P$ heteronuclear multiple bond correlation (HMBC) spectrum. High-resolution spectrometry of the crude reaction mixture showed an $[M + H]^+$ peak at $m/z$ 507.2474 (calcd 507.2521). To the best of our knowledge, this is the most complete characterization of an acyloxyphosphonium species reported to date [see the Supporting Information (SI)].

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Upon its addition to a mixture of $Cd(OA)_2$ (OA = oleate) and trimethylphosphine selenide, compound **1a** was immediately consumed, and trimethylphosphine oxide and oleic acid anhydride were produced (see the SI).[23] The rapid conversion of **1a** in this reaction mixture suggests that if this compound is formed as an intermediate during the synthesis of CdSe nanocrystals, its direct observation would be difficult. Indeed, the reaction mixture of $Cd(OA)_2$ and trimethylphosphine selenide only showed $^{31}P$ NMR signals from trimethylphosphine selenide and trimethylphosphine oxide; no other $^{31}P$ peak was observed. Similar observations were also made when triphenylphosphine selenide or methyldiphenylphosphine selenide was used as the selenium precursor for nanocrystal synthesis (see the SI).

Failing to observe this key intermediate directly, we then sought indirect ways to detect its formation during the synthesis of CdSe nanocrystals. The strong electrophilicity of **1a** suggests that it may be trapped by reaction with a suitable nucleophile. We found that the reaction between **1a** and an alkyl alcohol resulted in the immediate and quantitative transformation of **1a** to alkoxytrimethylphosphonium (**2**), which is considerably more stable than **1a** (see the SI). This result suggests that trapping of **1** in the synthesis of CdSe nanocrystals may be achieved by addition of alcohol to the reaction mixture.[36]

We investigated the effect of alcohol on the synthesis of CdSe nanocrystals. In the presence of ROH [R = $-CH_3$, $-CH(CH_3)_2$], we observed a new $^{31}P$ NMR signal at 99.9 ppm (R = $-CH_3$) or 93.0 ppm [R = $-CH(CH_3)_2$] from the crude reaction mixture (Figure 1). Detailed analysis showed that this

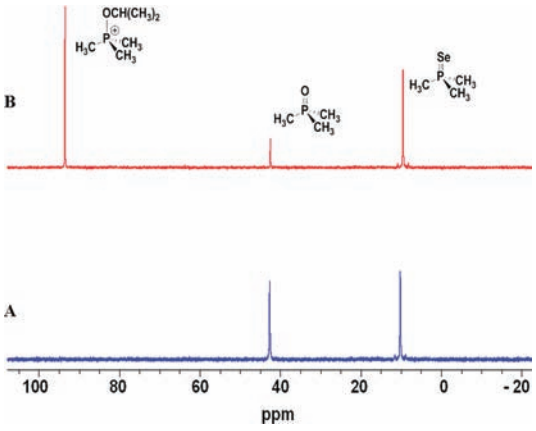



**Figure 1.** $^{31}P\{^1H\}$ spectrum of the reaction between $Cd(OA)_2$ and $Me_3P{=}Se$ (A) without and (B) with added 2-propanol.

new peak originated from the expected alkoxytrimethylphosphonium **2** (see the SI). For example, the $P-OCH_3$ fragment of **2a** gave a doublet at 3.89 ppm ($^3J_{P-H}$ = 12 Hz) in the $^1H$ NMR spectrum and a doublet at 55.8 ppm ($^2J_{P-C}$ = 8 Hz) in the $^{13}C\{^1H\}$ NMR spectrum; signals from the $-P(CH_3)_3$ portion were located at 2.17 ppm (doublet, $^2J_{P-H}$ =14 Hz) in the $^1H$ spectrum and 11.39 ppm (doublet, $^1J_{P-C}$ = 66 Hz) in the $^{13}C\{^1H\}$ spectrum. These 1D NMR assignments were confirmed by $^1H-^{13}C$ heteronuclear multiple quantum coherence (HMQC) and $^1H-^{31}P$ HMBC experiments. The final confirmation of our structural assignment came from the addition of authentic samples of **2a** to the crude reaction mixture. Such additions resulted in an increase of the expected peaks in the $^{31}P\{^1H\}$ spectrum; no additional peak was observed (see the SI).

The conversion of **1** to **2** was quantitative within several minutes of addition of alcohol. However, the formation of **2** during the CdSe nanocrystal synthesis was apparently limited by the much slower decay of phosphine selenide, which is known to occur at the same rate as the formation of CdSe nanocrystals. In addition, the addition of alcohol did not significantly change the decay rate of phosphine selenide (see the SI). These facts indicate that the rate-limiting step of the CdSe nanocrystal synthesis must be or precede the complete cleavage of the P−Se linkage.

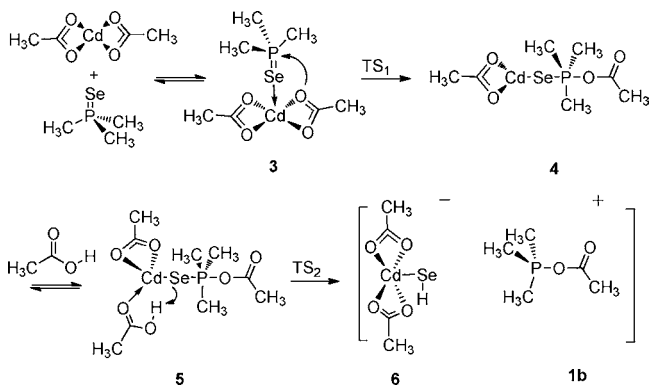
We found that compound **2** was also formed when an alcohol was added to the synthesis of CdS or CdTe nanocrystals using trimethylphosphine sulfide or telluride as the precursor, respectively (see the SI). These results suggest that a common mechanism is responsible for the release of the chalcogen atom from trialkylphosphine chalcogenide precursors.

The reaction between $Cd(OA)_2$ and a secondary phosphine selenide showed a very different behavior. The crude reaction mixture of diphenylphosphine selenide and $Cd(OA)_2$ gave a $^{31}P$ NMR peak at 98.6 ppm. We assigned this peak to oleyloxydiphenylphosphine on the basis of $^1H-^{13}C$ and $^1H-^{31}P$ HMBC experiments (see the SI). In this case, however, we also observed $^{31}P$ peaks at 77.2 and −15.0 ppm that were tentatively assigned to oleyloxydiphenylphosphine selenide and tetraphenyldiphosphine, respectively.[22,37] Diphenylphosphine selenide was consumed within 30 min at room temperature with very little formation of diphenylphosphine oxide. Similar observations were recently reported by Krauss et al.[22] and Owen et al.[37] for nanocrystal syntheses using the same selenium precursor. We believe that a different mechanism is responsible for the cleavage of the P=Se bond in secondary phosphine selenides.

We modeled the P=Se bond-cleavage process during the reaction between $Cd(OAc)_2$ and $Me_3P{=}Se$ using DFT/B3LYP calculations.[38−41] We used a triple-ζ-quality basis set for Cd, Se, and P and the 6-31+G* basis set for O, C, and H.[42−49] The electrostatic solvation energy was taken into account using a polarizable continuum model.[50] Our calculations showed that the formation of **1** is consistent with nucleophilic attack of carboxylate on phosphine selenide.

Scheme 2 shows the calculated reaction pathway.[51] It was found that $Me_3P{=}Se$ binds to $Cd(OAc)_2$ to give complex **3**

**Scheme 2. DFT-Calculated Reaction Pathway for P=Se Cleavage**





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[$\Delta H$ = −14.9 kcal mol$^{-1}$, $\Delta S$ = −37.0 cal mol$^{-1}$ K$^{-1}$; all calculated thermodynamic quantities are referenced to Cd(OAc)$_2$, $Me_3P$═Se, and HOAc]. The $Me_3P$═Se moiety in complex **3** can be attacked by an acetate of the same complex, going through a transition state featuring a six-membered ring ($TS_1$, $\Delta H^{\ddagger}$ = 24.0 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = −49.1 cal mol$^{-1}$ K$^{-1}$) to give intermediate **4** ($\Delta H$ = 15.7 kcal mol$^{-1}$, $\Delta S$ = −38.6 cal mol$^{-1}$ K$^{-1}$). The nucleophilic attack on the phosphorus atom converts the tetravalent phosphorus atom in complex **3** into a pentavalent one in **4**. Essentially, this reaction partially breaks the P═Se double bond into a P−Se single bond and forms the initial Cd−Se bond. Intermediate **4** binds an acetic acid to give **5** ($\Delta H$ = 6.7 kcal mol$^{-1}$, $\Delta S$ = −75.3 cal mol$^{-1}$ K$^{-1}$). The Se atom of **5** accepts the acid proton from the incoming acetic acid, going through a proton-transfer transition state ($TS_2$, $\Delta H^{\ddagger}$ = 11.3 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = −79.9 cal mol$^{-1}$ K$^{-1}$) to break the P−Se linkage completely, giving **1b** and **6.** We suggest that complex **6** may be considered as the precursor for the subsequent growth of CdSe clusters and nanocrystals.

Two transition states were identified before the complete P═Se bond cleavage: one for the nucleophilic attack of acetate on the phosphorus atom ($TS_1$, $\Delta H^{\ddagger}$ = 24.0 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = −49.1 cal mol$^{-1}$ K$^{-1}$) and the other for the proton transfer from carboxylic acid to the Se atom ($TS_2$, $\Delta H^{\ddagger}$ = 11.3 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = −79.9 cal mol$^{-1}$ K$^{-1}$). The calculated activation parameters of both transition states are in reasonable agreement with the experimental value ($\Delta H^{\ddagger}_{exptl}$ = 14.8 ± 0.7 kcal mol$^{-1}$, $\Delta S^{\ddagger}_{exptl}$ = −34.7 ± 1.9 cal mol$^{-1}$ K$^{-1}$).[23] More interestingly, the relative magnitudes of the two activation free energies are dependent on the temperature. Below ∼412 K, the activation free energy of the nucleophilic-attack transition state ($TS_1$) is higher; above ∼412 K, that of the proton-transfer transition state ($TS_2$) is higher. We note that this analysis should be considered qualitative and not quantitative: the DFT/B3LYP method we used here has an average deviation of 4−5 kcal mol$^{-1}$ (up to 19 kcal mol$^{-1}$) in enthalpy calculations[52] and tends to grossly overestimate the entropy penalty for solution-phase reactions.[53] Nevertheless, the calculation predicts that the activation parameters of the CdSe nanocrystal synthesis are temperature-dependent. In addition, one also expects a primary hydrogen kinetic isotope effect under conditions where the proton-transfer step is rate-limiting. Ongoing research in our lab is focused on validating these predictions.

In conclusion, we have proposed a detailed mechanism for the cleavage of the P═Se bond in trialkylphosphine selenide during the synthesis of CdSe nanocrystals. Our findings suggest that this bond cleavage is initiated by nucleophilic attack of carboxylate on a $Cd^{2+}$-activated phosphine selenide. This attack is followed by proton transfer from carboxylic acid to the Se atom to break the P−Se linkage completely, forming the initial Cd−Se bond. A signature of the P═Se bond cleavage is the formation of an acyloxytrialkylphosphonium ion, which could be trapped using an alkyl alcohol. Kinetic experiments showed that the rate-limiting step of the CdSe nanocrystal synthesis is or precedes the formation of this acyloxytrialkylphosphonium intermediate. We hope that these results will lead to a better understanding of the synthesis of group II−VI nanocrystals and the rational design of new synthetic methodologies.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Details of experimental procedures and DFT calculations and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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