Thermal Decomposition of Cadmium Thiourea Coordination Compounds

V. N. Semenov and A. V. Naumov

Voronezh State University, Voronezh, Russia

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Abstract — Thermal decomposition of cadmium thiourea coordination compounds was considered. Cadmium sulfide is the final product for all the compounds, whereas the composition of other products of the thermolysis substantially depends on the nature of the acido ligand or the outer-sphere anion. Thermal stability parameters of the coordination compounds under study and effective activation energies of their thermolysis were determined, and a mechanism of the thermolysis was proposed.

Alongside with conventional physical procedures for production of semiconductor films of cadmium sulfide by vacuum and cathode spraying, chemical procedures find increasing application. One of them is the method of spraying of solutions of thiourea coordination compounds onto a heated support [1]. An important stage of this procedure is the thermal decomposition of the thiourea complex with CdS formation.

Previous studies of reactions of cadmium chloride and acetate with thiourea and of the mechanism of thermolysis of the resulting coordination compounds showed [2, 3] that the latter process is rather complicated and that, apart from cadmium sulfide, various solid and gaseous products can be formed, depending on temperature. It is necessary to point out that different authors differently explain the nature of the elementary act of the process and that no data on the mechanisms of thermal decomposition of other cadmium thiourea complexes are available. The thermal decomposition is considered to be due to mere thermal excitation of C-S bonds [4], but at the same time the belief was stated that the excitation of this bond results from fluctuation of a negative charge localized on the complex during cleavage of hydrogen bonds in the crystal of the coordination compound on its melting [5].

The aim of this work was to study features of thermal decomposition of a number of coordination compounds formed by cadmium salts with thiourea (thio) and effect of the chemical nature of the anions (F^- , CI^- , Br^- , I^- , SO_4^{2-} , NO_3^- , and CH_3COO^-) on the process. The knowledge of these features will make it possible not only to select optimal regimes of sulfide

deposition, but also to control the amount of active admixtures in CdS semiconductor films.

The derivatograms of almost all the coordination compounds under study (Figs. 1 and 2) show similar endo- and exo- effects associated with melting and decomposition of the complexes and also with transformations of their decomposition products. The similar shapes of the derivatograms for the halide complexes under study and [Cd(thio)₂Cl₂] [3] suggest that the thermolyses products are also similar. These are gaseous H₂S, NH₂CN, and NH₃, and also intermediate solid ammonium and guanidine thiocyanates and the more thermally stable melam and melem.

The thermal stability of cadmium thiourea complexes depends on the nature of the acid residue and on the composition of the inner sphere. Comparison of the decomposition onset point of the complexes (see table) allows us to arrange them in the following order by increasing thermal stability:

$$\label{eq:chi} \begin{split} & [Cd(thio)_2(CH_3COO)_2], \ [Cd(thio)_4](NO_3)_2, \ [Cd(thio)_4]F_2, \\ & [Cd(thio)_2I_2], \ [Cd(thio)_2Br_2], \ [Cd(thio)_2SO_4], \\ & [Cd(thio)_2Cl_2], \ [Cd(thio)_4]SO_4. \end{split}$$

Examination of the derivatograms of thiourea complexes of cadmium halides (Fig. 1) shows that the chloride [3] and bromide complexes are closest to each other in the decomposition pattern. The complicated nature of thermal transformations of the fluoride complex in the range 500–600 K is connected with the effect of the outer-sphere fluorine. The tendency of fluorine to form strong hydrogen bonds $F\cdots$ H–NH with thiourea amino groups (as indicated by a long-wave shift of the v_{NH} absorption band at 3100 cm⁻¹ [6]) and also the presence of the F⁻ ion in



Fig. 1. Derivatograms of halide coordination compounds: (a) $[Cd(thio)_4]F_2$, (b) $[Cd(thio)_2Br_2]$, and (c) $[Cd(thio)_2I_2]$.



Fig. 2. Derivatograms of coordination compounds with oxygen-containing anions: (a) $[Cd(thio)_4](NO_3)_2$, (b) $[Cd(thio)_2SO_4]$, and (c) $[Cd(thio)_4]SO_4$.

the outer sphere of the complex favor hydrogen fluoride formation on decomposition. Hydrogen halides are also liberated on thermolysis of others halide-containing complexes, but the process involving $[Cd(thio)_4]F_2$ is qualitatively distinguished from the above cases, first, by that here the F^- ion is not bound directly to the cadmium ion and, second, by a peculiar chemical behavior of HF. The latter can add to decomposition products by their multiple bonds to give new compounds, which are not formed by decomposition of thiourea and other coordination compounds. The resulting fluorocarbons are not oxidized by air oxygen and are low-volatile. Actually, an IR spectral study of solid decomposition residues shows that the greatest amount of admixtures remains upon decomposition of the fluoride complex. The purest

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cadmium sulfide is obtained from the complex $[Cd(thio)_2Cl_2]$.

Special attention should be paid to $[Cd(thio)_2I_2]$. Two endo-effects without weight change (393 and 413 K) are detected in the DTA curve. This fact can be connected with isomerization of iodide complexes. According to [6], the neutral complex $[Cd(thio)_2I_2]$ is formed in the synthesis of iodide thiourea complexes, and, as a result of the greater stability of the complex ion $[CdI_4]^{2-}$ in solution [7], the bis-complex $[Cd(thio)_4][CdI_4]$ is also formed. Owing to the strong *trans*-effect of thiourea [8], the bis-complex is thermally transformed to the neutral complex: $[Cd(thio)_4] \cdot [CdI_4] \rightarrow 2[Cd(thio)_2I_2]$.

It should be noted that the melting points (453 K) in all the derivatograms of the halide complexes, given in Fig. 1 coincide with the melting point of thiourea, whereas in the case of a mixed chloride complex [3] the melting peaks of the complex (483 K) and thiourea are detected separately. This fact can be explained by expulsion of one thiourea molecule into the outer sphere as a result of thermal decomposition of the complex. This is confirmed by the observation in the IR spectra of molten complex $[Cd(thio)_2I_2]$ of the v_{CS} , v_{CN} , and δ_{HNH} bands of uncoordinated thio-urea at 634, 732, 1086, and 1472 cm⁻¹ [6]. The detachment and expulsion of one thiourea molecule from the inner sphere of the complex $[Cd(thio)_2I_2]$ are connected with mutual influence of the ligands, primarily steric. The immediate environment of the cadmium atoms in the [Cd(thio)₂Hlg₂] complexes has $C_{2\nu}$ symmetry. By the immediate environment we mean a system of atoms directly bound with the complexforming ion, i.e., $Cd(S)_2(Hlg)_2$. The arrangement of iodine atoms, having a considerable covalent radius, in the tops of the distorted tetrahedron is sterically hindered, and this is the reason for the expulsion of one thiourea molecule upon thermal excitation of the complex. We could detect the intermediate compound $[Cd(thio)I_2]$ with reduced coordination number by IR spectroscopy: It shows v_{CS} , v_{CS} , and v_{CN} bands at 612, 708, 1093 cm⁻¹, respectively.

Thus, the liberation of cadmium sulfide from thiourea complexes with CI^- and I^- ligands can be considered as a process involving an intermediate with reduced coordination number. Offering this scheme for the two above complexes, we do not exclude that it works with other thiourea coordination compounds. However, we have yet found any experimental evidence for this assumption, apparently because of a low stability of the intermediates.

From thermogravimetric curves we could estimate the apparent activation energies (E_a) of the decomposiTemperature parameters and activation energies of thermal decomposition of cadmium thiourea coordination compounds

	Temperature, K			
Compound	onset of weight loss	melting (endo- effect)	decom- position (exo- effect)	E _a , kJ/mol
$[Cd(thio)_4]F_2$	433	453	473	231.0
$[Cd(thio)_2Cl_2]$	483	483	523	190.7
$[Cd(thio)_2Br_2]$	463	453	498	251.0
$[Cd(thio)_2I_2]$	443	453	483	194.6
$[Cd(thio)_2(CH_3COO)_2]$	423	433	443	679.0
$[Cd(thio)_4](NO_3)_2$	433	408	443	806.6
$[Cd(thio)_2SO_4]$	473	473	498	813.3
[Cd(thio) ₄]SO ₄	488	493	513	845.2

tion. According to [8], the C–S bond energy in thiourea is 100.5 kJ/mol. Coordination of thiourea decreased this energy, and, consequently, the E_a for the thermal decomposition should be lower. However, we obtained high activation energies (see table) indicative of a complicated character of the process and of the influence of a number of additional solid-phase interactions on its energy. Mixed complexes with inner-sphere Cl⁻ and I⁻ ligands decompose via intermediate formation and thus with lower E_a . The complex [Cd(thio)₂Cl₂] has a strong intramolecular hydrogen bond Cl···H–NH, and thus the corresponding E_a is the lowest.

Examining thermolysis of the complexes with oxygen-containing acido ligands (Fig. 2) one can note that with the nitrate complex conditions are created for oxidation of organic products at fairly low temperatures. This complex decomposes with explosion, and the presence of such a strong oxidant as $NO_3^$ which evolves oxygen at the decomposition point of the complex [9], provides not only removal of organic products, but also oxidation of CdS to sulfate. The IR spectra at temperatures above 443 K show bands at 405, 602, 624, and 1100 cm⁻¹ due to sulfate absorption. The exo-effects at 443 and 483 K and the endoeffects at 493 and 513 K are attributable to formation of oxidation products which are removed as gases according to the DTG curve. It is necessary to note that such organic admixtures as guanidine thiocyanate, melam, and melem were not found in the solid residue. Thus, taking account of the resutls of analysis of gaseous products, we can propose the following general scheme of thermal decomposition of the complex $[Cd(thio)_4](NO_3)_2$.

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Fig. 3. Linearization of the TG curves for thermolysis of the coordination compounds (*I*) $[Cd(thio)_2Cl_2]$, (2) $[Cd(thio)_4]F_2$, (3) $[Cd(thio)_2I_2]$, (4) $[Cd(thio)_2Br_2]$, (5) $[Cd(thio)_4](NO_3)_2$, (6) $[Cd(thio)_2(CH_3COO)_2]$, (7) $[Cd(thio)_2SO_4]$, and (8) $[Cd(thio)_4]SO_4$.

$$\begin{split} & 8[\mathrm{Cd(thio)_4}](\mathrm{NO_3})_2 \longrightarrow 7 \ \mathrm{CdS} \ + \ \mathrm{CdSO_4} \ + \ 18\mathrm{NH_3} \\ & + \ 18\mathrm{HCNS} \ + \ 14\mathrm{H_2CN_2} \ + \ 16\mathrm{NO_2} \ + \ 2\mathrm{O_2} \ + \ 6\mathrm{H_2S} \ + \ 8\mathrm{H_2O}. \end{split}$$

Similar redox processes take place on thermolysis of $[Cd(thio)_2SO_4]$ and $[Cd(thio)_4]SO_4$ complexes, the main oxidants here being sulfate ions. However, the weaker oxidizing power of SO_4^{2-} ions compared with NO_3^- turns the process on a somewhat different pathway. This is evidenced by the observation of a number of exo- and endo-effects in the range 470– 660 K, different from the corresponding effects in the derivatograms of the nitrate complex. The low-temperature effect at 323 K at constant weight for the neutral complex $[Cd(thio)_2SO_4]$ can be assigned to a change in the dentacity of the SO_4^{2-} ligand.

The rather high decomposition point $[Cd(thio)_4]$. SO₄ is explained by the fact that the inner coordination sphere of $[Cd(thio)_4]^{2+}$ is saturated with thiourea. In $[Cd(thio)_4]F_4$ and $[Cd(thio)_4](NO_3)_2$, the thermal stability of such sphere is essentially reduced by the aggressive outer-sphere NO₃⁻ and F⁻ ions, while with such a soft oxidant as SO₄²⁻ this does not occur.

The complex $[Cd(thio)_2(CH_3COO)_2]$ thermolyzes similarly to $[Cd(thio)_2Cl_2]$. A difference consists in that here, apart from usual thermolysis products, ketene, acetone, and carbon dioxide are also formed [2] as a result of decomposition of the acetate ligand. The latter starts to decompose at 443 K, as judged from the disappearance of its characteristic bands from the IR spectrum. This fact seems to be responsible for the rather low thermal stability of the acetate complex.

The high apparent activation energies of the complexes with oxygen-containing ligands point to cleavage of the acido ligands and the outer-sphere anions and to their involvement in redox processes. The highest values of E_a for the sulfate and nitrate complexes are connected with the redox reactions that accompany the thermal decomposition.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in the range $400-4000 \text{ cm}^{-1}$ (Nujol mulls) in cells with KBr windows.

The coordination compounds were synthesized from aqueous solutions by the procedures [2, 6, 10–12] using the salts CdF_2 , $CdCl_2 \cdot 2.5H_2O$, $CdBr_2 \cdot 4H_2O$, CdI_2 , $Cd(CH_3COO)_2 \cdot 2H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, and $CdSO_4 \cdot 8/3H_2O$ of analytically pure grade and thiourea of ultrapure grade. The resulting compounds were identified by IR spectroscopy based on published data [6, 11, 12].

Identification of the CdS formed was carried out on a DRON-1 diffractometer with CuK_{α} radiation.

Thermal analysis of the coordination compounds was performed on a Paulik–Paulik–Erdey-3427 derivatograph. The heating rate was 10 deg/min for all the complexes apart from $[Cd(thio)_4](NO_3)_2$ which was heated at a rate of 2.5 deg/min. Weighed samples of ~40 mg were used.

The apparent activation energies E_a of thermolysis were calculated from the TG curves. It was therewith assumed that the process as a whole is described by the first-order kinetic equation $m = m_0 e^{-kt}$. Here *m* is the weight of the reactant, m_0 is its initial weight, and *k* is the rate constant. As the deviation *h* of the TG curve from zero line is proportional to the weight of consumed reactant $[(h_{\text{max}} - h)/h_{\text{max}} = m/m_0, \text{ where}$ h_{max} is the full deviation], we can deduce the following expression from Arrhenius's equation:

$$\ln \{\ln [h_{\max}/(h_{\max} - h)]^{1/t}\}$$

$$A = E/RT.$$

Here *A* is a constant. Linearization, according to this expression, of the TG curve in the F-1/T coordinates (where $F = \ln \{\ln [h_{\max}/(h_{\max} - h)]^{1/t}\}$ (Fig. 3) gives the required activation energy. This procedure for determination of the activation energy in nonisothermal conditions was offered by Zivcovic and Dobovisek [13].

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