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KINETICS AND MECHANISM OF THERMAL DECOMPOSITION OF CADMIUM(II) COMPLEXES WITH SUBSTITUTED THIOUREAS

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From the thermal decomposition curves of cadmium(II) complexes with substituted thioureas (methyl-, dimethyl-, ethyl-, diethyl-, butyl-, dibutyl-, phenyl-, diphenyl-, acetyl- and benzoylphenylthiourea), the kinetic parameters of the thermal decompositions of these complexes were determined and a decomposition mechanism was suggested. The following thermal stability sequence is given for the Cd(II) complexes: complexes with alkylthioureas < complexes with phenylthioureas < complexes with acylthioureas.

Systematic studies on chemical and physical changes brought about by heating in chemical compounds provide information on the mechanisms and steps of their decomposition, and permit determination of the kinetic parameters of the reactions [1–3].

The metal compounds of thioureas comprise an extensive series of sulfur-bonded complexes. Thermal decomposition studies here have been concerned with a few nickel(II) thiourea compounds [4], and acetylthiourea complexes of molybdenum [5] and Cd(II) [6]. The thermal decompositions of methylthiourea and dimethylthiourea complexes of several transition metals, and of cadmium complexes containing various thioureas, have been studied by thermogravimetry in air and in vacuum. In vacuum, the dimethylthiourea complexes decomposed to a mixture of metal chloride and sulfide. The organic products included dimethylthiourea, methyl isothiocyanate, HCl and polymerized material. In air, intermediates were formed in which part of the organic ligand was retained, followed by complete decomposition to inorganic salts at higher temperatures. While the overall pattern of decomposition was generally similar to that of thiourea itself, coordination

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clearly has an important influence of the thermal stability. The objectives of our study were to consider the decompositions of some substituted thiourea complexes, both to determine kinetic parameters and to explore stability relationships.

Experimental

Thermogravimetry was performed with a Paulik–Paulik derivatograph (MOM Budapest), on 50 mg samples. Air runs were in a static atmosphere. α-Al_2O_3 was the reference material. The samples were heated up to 1073 K at a heating rate of 10 deg/min. Compounds (Table 1) were prepared by methods described in the literature [6–8] and were analysed by standard methods for metal and chloride, with good agreement with the calculated values. When required, sulfur was determined as $BaSO_4$. IR spectra were taken on a Specord 71 spectrometer, using KBr pellets for solid samples.

Results and discussion

Crystalline complexes of Cd(II) were prepared with substituted thioureas, and all of the thioureas and their complexes were subjected to thermal decomposition. The results are given in Figs 1 and 2 and Table 2.

Except for EtTU, BuTU and AcTU, the thioureas themselves decompose in a single step. The gaseous products of decomposition of the thioureas were not

Table 1 Complexes of Cd(II) with thiourea

No.	Composition	Ligand	Color	M.p., K
1	$Cd(MeTU)_4(ClO_4)_2$	N-methylthiourea	colorless	383
2	$Cd(EtTU)_4(ClO_4)_2$	N-ethylthiourea	colorless	370
3	$Cd(BuTU)_4(ClO_4)_2$	N-butylthiourea	colorless	376
4	$Cd(DMeTU)_4(ClO_4)_2$	N-N′-dimethylthiourea	colorless	330
5	$Cd(DEtTU)_4(ClO_4)_2$	N-N′-diethylthiourea	colorless	365
6	$Cd(DBuTU)_4(ClO_4)_2$	N-N′-dibutylthiourea	colorless	331
7	$Cd(PhTU)_4(ClO_4)_2$	N-phenylthiourea	colorless	408
8	$Cd(DPhTU)_4(ClO_4)_2$	N-N′-diphenylthiourea	colorless	418
9	$Cd(BPhTU)_3(ClO_4)_2$	N-benzoyl-N′-phenylthiourea	white	440
10	$Cd(AcTU)_3(ClO_4)_2$	N-acetylthiourea	white	430

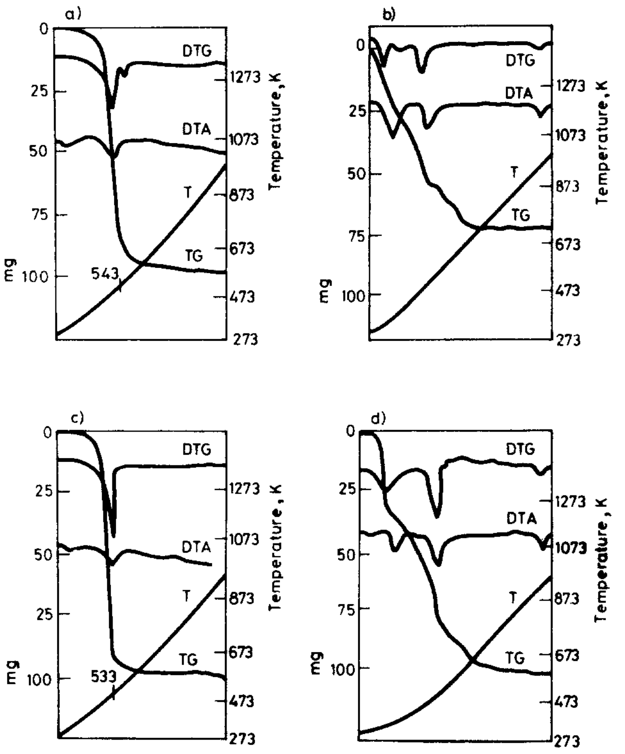

Fig. 1 Thermal decomposition curves of DMeTU (a), DBuTU (c) and of complexes $Cd(DMeTU)_4(ClO_4)_2$ (b) and $Cd(DBuTU)_4(ClO_4)_2$ (d)

derivatives, and their characteristics

Analysis of chemical composition												
calculated, %							found, %					
Cd	C	H	N	S	O	Cl	Cd	C	H	N	S	O
16.69	14.31	3.57	16.69	19.07	19.08	10.58	16.55	14.20	3.50	16.70	19.00	19.10
15.41	19.80	4.41	15.41	17.60	17.60	9.49	15.50	19.70	4.45	15.31	17.60	17.70
13.34	28.61	5.72	13.34	15.25	15.25	8.46	13.30	28.70	5.69	13.40	15.20	15.27
15.41	19.81	4.41	15.41	17.60	17.60	9.49	15.37	19.52	4.34	15.38	17.51	17.45
12.88	27.62	5.52	12.89	14.72	14.72	8.17	13.08	27.60	5.47	12.90	14.68	14.70
10.54	40.64	7.53	10.53	12.04	12.04	6.68	10.60	40.70	7.60	10.52	12.10	12.06
12.19	36.56	3.48	12.18	13.93	13.93	7.73	12.05	37.01	3.32	12.15	13.85	13.79
9.16	51.02	3.92	9.16	10.47	10.47	5.81	9.10	51.11	3.85	9.10	10.50	10.48
10.37	46.71	3.34	7.78	8.90	16.31	6.58	10.20	46.80	3.20	7.70	8.89	16.40
16.84	27.07	2.71	12.63	14.43	26.46	10.68	16.93	27.10	2.75	12.81	14.53	27.00

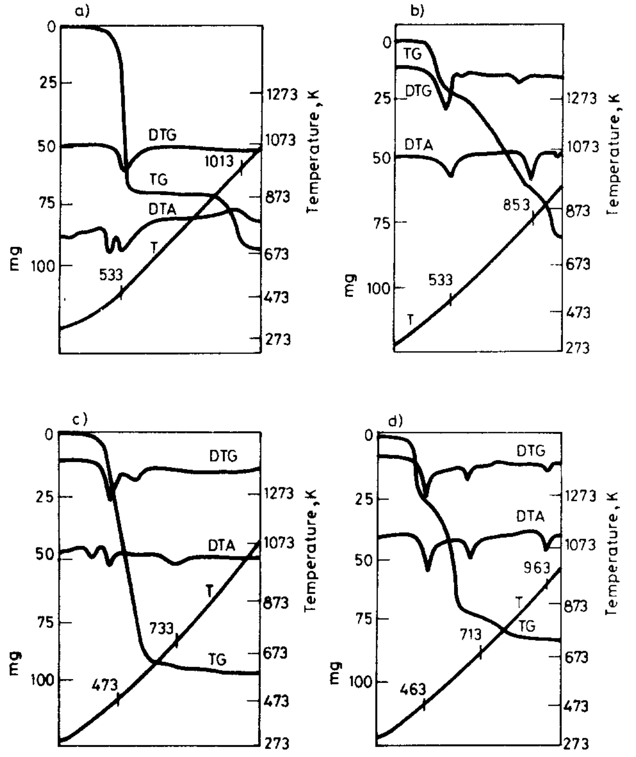

Fig. 2 Thermal decomposition curves of AcTU (a) and BPhTU (c) and of $Cd(AcTU)_3(ClO_4)_2$ (b) and $Cd(BPhTU)_3(ClO_4)_2$ (d)

Table 2 Stages of thermal decomposition of TU derivatives and their complexes with Cd(II)

No.	Compound	Temperature range, K	Mass loss, %		DTA peak temperature, K
			found	calculated	
1	2	3	4	5	6
1	MeTU	453– 673	97.1	100	473 endo
2	$Cd(MeTU)_4(ClO_4)_2$	423– 523	28	26.8	463
		623– 723	54	53.6	653 endo
		923–1023	81	80.9	973
3	EtTU	438– 546	74	—	546 endo
		546– 813	97	100	673
4	$Cd(EtTU)_4(ClO_4)$	373– 473	30	29	393
		563– 673	60	58	593 endo
		873–1073	84	82	1003

Table 2 cont.

1	2	3	4	5	6
5	DEtTU	432– 573	98	100	521 endo
6	Cd(DEtTU)$_4$(ClO$_4$)$_2$	373– 573	28	31	403
		563– 673	63	62	573 endo
		873–1073	86	85	973
7	DMeTU	393– 623	99	100	543 endo
8	Cd(DMeTU)$_4$(ClO$_4$)$_2$	373– 473	30.5	29	393
		473– 623	60.0	58	563 endo
		963–1013	80	82	983
9	BuTU	423– 513	75		513 endo
		643– 773	98	100	723
10	Cd(BuTU)$_4$(ClO$_4$)$_2$	373– 523	32	31.5	413
		673– 873	64	63.0	773 endo
		923–1003	86	84.7	973
11	DBuTU	433– 613	98	100	533 endo
12	Cd(DBuTU)$_4$(ClO$_4$)$_2$	373– 473	34	35	383
		473– 573	71	70	543 endo
		953–1003	90	98	973
13	PhTU	363– 563			473 endo
		873– 963	100	100	823 exo
14	Cd(PhTU)$_4$(ClO$_4$)$_2$	473– 573	33.5	33	473
		573– 933	67	66.2	803 endo
		933–1003	86.5	86.0	973
15	DPhTU	433– 543	100	100	463 endo
16	Cd(DPhTU)$_4$(ClO$_4$)$_2$	423– 553	37	37	473
		653– 773	75	73	713 endo
		873–1033	90	89	1003
17	BPhTU	453– 513	90		473 endo
		663– 803	98	100	733
18	Cd(BPhTU)$_3$(ClO$_4$)$_2$	373– 523	24	23.7	463
		673– 823	72	71.1	713 endo
		923–1003	89	88.1	963
19	AcTU	473– 653	70		533 endo
		673–1033	90	100	1013 exo
20	Cd(AcTU)$_3$(ClO$_4$)$_2$	473– 673	20	18	533
		673– 873	55	52	853 endo
		873–1053	80	82	1003

investigated. Only IR spectra were taken of the vapor condensate materials in the intermediate stages. The IR spectra showed strong bands (at 2174–2041, 945–925 and 700–650 cm^{-1}), exactly matching those of isothiocyanates. In the cases of DMeTU, DEtTU and DPhTU, other bands (at 2105–2096 cm^{-1}) were obtained, which are attributable to $N=C=N$ stretching vibrations characteristic of carbodiimides. Carbodiimides have previously been found in the decomposition products of substituted thioureas [9]. On the basis of the IR spectra, it can be concluded that the decompositions of the parent thioureas result in the formation of alkyl or aryl isothiocyanates and carbodiimides.

The cadmium complexes with thioureas show definite stepwise decomposition behavior. The first step of decomposition of $CdL_4(ClO_4)_2$ occurs through the total loss of two ligand molecules, while from $CdL_3(ClO_4)_2$ one ligand molecule is lost. This was supported by analysis of the intermediates from the decomposition of the complexes. The intermediates were prepared in larger quantity for characterization. Several 50 mg samples were decomposed up to a temperature of about 480 K. An average weight loss of from 28% to 37% was obtained for complexes of formula $CdL_4(ClO_4)_2$, and of 20% to 24% for $CdL_3(ClO_4)_2$. Analytical results are given in Table 3. The atomic ratios firmly suggested the presence of one or two ligand molecules in the products after the first stage of decomposition of $CdL_3(ClO_4)_2$ or $CdL_4(ClO_4)_2$.

Standard methods were used to analyse the products after the second and third stages of decomposition of the Cd complexes as well. In the products of the former we determined Cd, S and Cl. The latter materials consisted only of Cd and S.

In order to establish the gaseous products of decomposition, we condensed them by cooling and further investigated them by means of IR spectroscopy. The IR spectra showed bands matching those of isothiocyanates and carbodiimides. Similar results were obtained by Bailey and Tangredi [10]. The results permit the conclusion that the first stage of decomposition of the Cd(II) complexes occurs through the loss of one or two ligand molecules. Further heating leads to complete decomposition of the organic material and only CdS appears in the final residue. The following decomposition schemes are conceivable:

$$CdL_4(ClO_4)_2 \xrightarrow[-2\,L]{\text{stage I}} CdL_2(ClO_4)_2 \xrightarrow[-2\,L]{\text{stage II}} \begin{matrix} CdCl_2 \\ CdS \end{matrix} \xrightarrow{\text{stage III}} CdS$$

for L = MeTU, EtTU, BuTU, DMeTU, DEtTU, DBuTU, PhTU and DPhTU; and

$$CdL_3(ClO_4)_2 \xrightarrow[-L]{\text{stage I}} CdL_2(ClO_4)_2 \xrightarrow[-2\,L]{\text{stage II}} \begin{matrix} CdCl_2 \\ CdS \end{matrix} \xrightarrow{\text{stage III}} CdS$$

for L = AcTU and BPhTU.

Table 3 Analysis of the decomposition products of Cd(II) complexes with substituted thioureas

No.	Composition of undecomposed complex	Composition of decomposition product												
		Percentage							Atomic ratios (for 1 Cd)					
		Cd	C	H	N	S	Cl	O	C	H	N	S	Cl	O
1	$Cd(MeTU)_4(ClO_4)_2$	23.00	9.85	2.50	11.6	13.10	14.61	27.00	3.99	12.17	4.03	1.99	2.00	8.21
2	$Cd(EtTU)_4(ClO_4)_2$	21.70	13.75	3.01	10.70	12.30	13.61	24.70	5.91	15.54	3.94	1.98	2.00	7.98
3	$Cd(BuTU)_4(CiO_4)_2$	19.42	20.80	4.20	9.80	11.10	12.31	22.32	10.00	24.22	4.03	2.00	2.00	8.04
4	$Cd(DMeTU)_4(ClO_4)_2$	21.00	13.90	3.00	10.85	12.21	13.70	25.00	6.17	16.00	4.10	2.03	2.05	8.33
5	$Cd(DEtTU)_4(ClO_4)_2$	19.50	20.60	4.08	9.60	11.20	12.40	22.20	9.90	23.43	3.94	2.01	2.00	7.97
6	$Cd(DBuTU)_4(ClO_4)_2$	16.32	31.50	5.90	8.10	9.40	10.28	18.60	18.01	40.49	3.97	2.01	1.99	7.98
7	$Cd(PhTU)_4(ClO_4)_2$	18.25	27.40	2.62	9.20	10.42	11.50	20.90	14.01	16.07	4.03	200	2.00	8.01
8	$Cd(DPhTU)_4(ClO_4)_2$	14.65	40.70	3.18	7.32	8.30	9.21	16.80	25.93	24.31	4.00	1.98	1.98	8.02
9	$Cd(BPhTU)_3(ClO_4)_2$	13.60	40.91	2.89	6.90	7.80	8.65	19.40	28.07	23.80	4.06	2.00	2.00	9.99
10	$Cd(AcTU)_3(ClO_4)_2$	20.50	13.20	2.15	10.20	11.80	13.08	29.30	6.01	11.75	3.98	2.01	2.01	10.00

The estimated values of the activation energy (E_a), reaction order (n) and preexponential factor (A) are given in Table 4. The detailed calculation procedure and equations were reported previously [1, 3]. The results of thermogravimetric measurements on Cd(II) complexes with thioureas were used to determine the relationship between $\log dm/dt$ and $1/T$ (Fig. 3) or between $1/T \tan \alpha + \log dm/dt$ and $\log c$ (Fig. 4), where $c = (\Delta m_\infty - \Delta m)\Delta m_\infty$. The error in the E_a values is ±3.5%, and that in A is ±5.2%. The E_a values were calculated by the method of Gyulai and Greenhow [11].

Table 4 Kinetic parameters of thermal decomposition of Cd(II) complexes with thiourea derivatives

No.	Composition	Temperature, K	Activation energy, E_a, kJ/mol	Reaction order, n	Value of A
		Loss of one ligand molecule:			
1	$Cd(BPhTU)_3(ClO_4)_2$	373–523	210 (200)	1.2	7.8×10^9
2	$Cd(AcTU)_3(ClO_4)_2$	473–673	205 (210)	0.9	7.0×10^9
		Loss of two ligand molecules:			
3	$Cd(MeTU)_4(ClO_4)_2$	423–523	158 (165)	1.3	7.4×10^6
4	$Cd(DMeTU)_4(ClO_4)_2$	373–473	139 (135)	1.1	5.6×10^6
5	$Cd(EtTU)_4(ClO_4)_2$	373–473	152 (150)	1.0	7.0×10^6
6	$Cd(DEtTU)_4(ClO_4)_2$	373–573	149 (148)	1.2	6.9×10^6
7	$Cd(BuTU)_4(ClO_4)_2$	373–523	154 (159)	1.2	7.1×10^6
8	$Cd(DBuTU)_4(ClO_4)_2$	373–473	145 (145)	1.1	6.1×10^6
9	$Cd(PhTU)_4(ClO_4)_2$	473–573	188 (190)	1.2	1.2×10^9
10	$Cd(PhTU)_4(ClO_4)_2$	473–573	192 (195)	1.3	9.0×10^9

The obtained reaction order n might indicate a nucleus formation mechanism during thermal decomposition, but confirmation of this conclusion requires further detailed studies.

The E_a values (Table 4) indicate the influence of the ligand substituents on the thermal stabilities of the Cd(II) complexes. For an assessment of this, the effects of the substituents on the basic center of the thiourea molecule, which affects the complexation with the Cd(II) ion, were examined. The variations in the stabilities of the complexes can be explained by the differences in the electron density on the sulfur atom of the thiocarbonyl group (CS), which participates in the bonding in the complexes. The typical bond involves the donation of two electrons by the ligand to the electron system of the metal ion, resulting in a polarized electron-pair bond ("coordinate covalency"). Hence, differences in electron density in the molecules

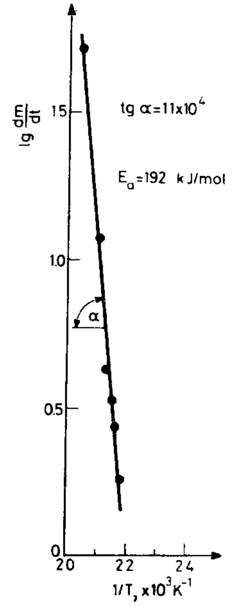

Fig. 3 Graphical determination of activation energy E_a ($E_a = 2.303 \times R \times \mathrm{tg}\,\alpha$) for reaction:

$$\mathrm{Cd(DPhTU)_4(ClO_4)_2} \xrightarrow[-2\ \mathrm{DPhTU}]{} \mathrm{Cd(DPhTU)_2(ClO_4)_2}$$

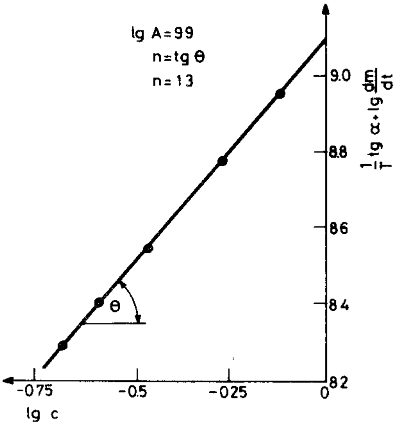

Fig. 4 Graphical determination of reaction order *n* and preexponential factor *A* for reaction:

$$\mathrm{Cd(DPhTU)_4(ClO_4)_2} \xrightarrow[-2\ \mathrm{DPhTU}]{} \mathrm{Cd(DPhTU)_2(ClO_4)_2}$$

are thought to be very important in complex formation [12]. These differences in the molecules of substituted thioureas are caused by the polar, mesomeric and steric effects of the substituents replacing the hydrogen atoms of the NH_2 groups in the thiourea molecule.

These interactions lead to the following stability sequence: alkylthioureas < phenylthioureas < acylthioureas. The lowest stability of the complexes with alkylthioureas is connected with the low electron density on the sulfur atom of the CS group and thus a reduction of the coordination capacity of the ligand.

This means that a decrease in strength of the coordinate bond between the ligand and the Cd(II) ion is accompanied by a reduction in the thermal stability of the molecule.

The highest stability of the complexes with acylthioureas can be attributed not only to the higher electron density on the sulfur, but also to the formation of a chelate ring with the Cd(II) ion, which is a very stable structure. The IR spectra confirm the existence of such a structure.

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Zusammenfassung — Die kinetischen Parameter der thermischen Zersetzung von Verbindungen der Formeln $Cd(MeTM)_4(ClO_4)_2$, $Cd(DMeTM)_4(ClO_4)_2$, $Cd(EtTM)_4(ClO_4)_2$, $Cd(DEtTM)_4(ClO_4)_2$, $Cd(BuTM)_4(ClO_4)_2$, $Cd(DBuTM)_4(ClO_4)_2$, $Cd(AcTM)_3(ClO_4)_2$, $Cd(FTM)_4(ClO_4)_2$ und $Cd(DFTM)_4(ClO_4)_2$ wurden mittels TG and DTG untersucht. Die Reaktionsordnung (n) und die Aktivierungsenergie (E_a) wurden nach der graphischen Methode ermittelt.

Резюме — На основе кривых термического разложения комплексов кадмия с замещенными производными тиомочевины (метил- и диметил, этил- и диэтил, бутил- и дибутил, фенил- и дифенил, ацетил- и бензоил-1-фенилтиомочевины), определены кинетические параметры реакции разложения и предложен механизм процесса разложения. Установлена следующая последовательность термоустойчивости этих комплексов: алкилзамещенные тиомочевины < фенилзамещенные < ацильные производные тиомочевины.